Processing at the Nanoscale

Room 133 - Session PN-MoM

Atomic/Nano-scale Manipulation

Moderator: J. Murday, Naval Research Laboratory

9:40am **PN-MoM1 The "Millipede" - More than 1000 Tips for parallel and dense AFM Data Storage**, *P. Vettiger, G. Cross, M. Despont, U. Drechsler, U. Dürig, W. Häberle, M.I. Lutwyche, H.E. Rothuizen, R. Stutz, R. Widmer, G.K. Binnig,* IBM Research, Zurich Research Laboratory, Switzerland; ***T. Albrecht,*** IBM Almaden Research Center **INVITED**

A MEMS-based AFM-array concept ("Millipede") for data storage of potentially ultrahigh density, terabit capacity, and high data rate is presented. Its storage potential has been demonstrated by a new thermomechanical local-probe technique to store, read-back and erase data in very thin polymer films. With this new technique, 30- to 40-nm-sized bit indentations of similar pitch size were made by a single cantilever/tip in a 50-nm-thin PMMA layer, resulting in a data storage density of 400-500 Gb/in.@super 2@. High data rates are achieved by parallel operation of large 2D AFM arrays batch-fabricated by silicon surface-micromachining techniques. The VLSI of micro/nanomechanical devices (cantilevers/tips) on a single chip leads to the largest and densest 2D array of 32x32 (1024) AFM cantilevers with integrated write/read storage functionality ever built. Time-multiplexed electronics control the write/read storage cycles for parallel operation of the Millipede array chip. Initial areal densities of 100-200 Gb/in.@super 2@ have been achieved with the 32x32 array chip, which has potential for further improvements.@footnote 1@ This constitutes a major step towards future ultra-dense data storage with potential capacities beyond today's storage approaches. The Millipede concept focuses on a polymer storage media, but may be expanded to other media, and not excluding magnetics, provided suitable read/write functionality can be integrated into cantilevers and tips. We also envision that Millipede may open up new perspectives in nanoscale science and technology areas such as lithography, high-speed/large-scale imaging, molecular and atomic manipulation, biotechnology and many others. @FootnoteText@ @footnote 1@P. Vettiger et al., IBM J. Res. Develop. 44, 323 (2000); M. I. Lutwyche et al., Appl. Phys. Lett. 77, 3299 (2000).

10:20am **PN-MoM3 Attractive Mode Manipulation of Fullerenes on Si(100)**, ***D.L. Keeling**, M.J. Humphry, P.H. Beton, P. Moriarty, M.A. Phillips,* University of Nottingham, UK

Room temperature STM manipulation of C60 on silicon surfaces under ultra-high vacuum has been investigated. A new intrinsic attractive mode of manipulation has been observed for gap impedances 1-3GOhm in which molecules hop towards the tip in steps of 1-3 lattice constants. These effects are observed in both polarities although a greater stability and higher probability for attractive mode manipulation is observed for negative sample bias. A similar effect can give rise to a continuous dragging of the molecule while scanning, for which the displacement is parallel to the dimer rows. For lower gap impedance, ~1GOhm, repulsive manipulation, characterised by a sawtooth response of the tip similar to that reported by Bartels et.al., is observed in which the molecule is displaced across the surface in regular steps of 1 or 3 surface lattice constants. The response of molecules to manipulation is discussed in terms of a simple model for C60-Si(100) bonding in which two out of four Si-C bonds are broken during the manipulation process and a change in molecular orientation accompanies tip induced displacement.

10:40am **PN-MoM4 Reliable Nanofabrication Method on Au Cluster Films in a Non-contact Mode with an Atomic Force Microscope**, ***K.-H. Park**, J.Y. Kim, J.S. Ha, K.-B. Song,* ETRI, Republic of Korea

Many kinds of nanofabrication methods have been studied on metal films using scanning probe microscopy so far. However, they are still far from the practical application for the data storage or lithography. Scanning tunneling microscopy(STM) is not an adequate technique because it reliably operates only at ultra high vacuum (UHV) and the throughput is very low.@footnote 1@ Contact mode fabrication methods of atomic force microscopy (AFM) also have shortcomings because the mechanical contact between the tip and the samples induces a significant damage to the tip apex causing the serious tip wear. Here, we devised a new reliable fabrication method by applying a local field on granular Au nanocluster films using conducting AFM tips in a noncontact mode. Au cluster thin films (10-50 nm) were deposited on silicons and glass substrates through the gas evaporation process under the partial Ar pressure of several mbar. The granular morphologies of the films are observed by STM at UHV in situ, and then the samples were transferred to an air ambient stage for AFM analysis. A reproducible creation of Au bits was obtained with the lateral dimension of 100 nm on granular films. The critical voltage for the fabrication is much larger than the case in a contact mode with some variation depending on the conductivity of the films. The reliability of nanofabrication is attributed to the field induced migration and current induced sintering mechanism without the contact process between the tip and samples. The near-field optical properties of fabricated structures are investigated in a view of an optical data storage. @FootnoteText@ @footnote 1@ K.-H. Park et al., Appl. Phys. Lett. v75, 139 (1999)

11:00am **PN-MoM5 Creating Nanoscale Patterns by Arranging Gold Nanocolloids with an AFM**, ***S. Hsieh**, S. Meltzer,* University of Southern California; *C.R.C. Wang,* National Chung Cheng University, Taiwan; *A.A.G. Requicha, B.E. Koel,* University of Southern California

Combining lithography methods and controlled positioning and manipulation of nanosized building blocks is a promising technique for building future nanoscale devices, e.g., SETs or near-field photonic waveguides. Gold colloids can be fabricated in well-defined shapes and sizes and are therefore ideal components for such devices. We extended the capabilities demonstrated in this field by demonstrating the manipulation of Au nanorods and spherical particles by utilizing atomic force microscopy (AFM). For anchoring of Au nanorods and subsequent manipulation, the choice of adhesive layer is crucial. 3-Mercaptopropylmethyldimeoxysilane (MPMDMS) self- assembled layers adhere to the colloid particles and still allow their lateral manipulation. The colloids can be pushed by exerting a controlled lateral force on the particles with an AFM tip. Off-center pushing results in rotation of the nanorods. The parameters for successful manipulation of nanorods and spherical particles will be compared. These techniques for arranging nanoparticles and nanorods should be useful for fabricating new nanostructures or incorporating such nanoparticles into pre-fabricated structures.

11:20am **PN-MoM6 Dynamics and Manipulation of Surface Electronic States**, ***R. Berndt,*** University of Kiel, Germany **INVITED**

We discuss two recent applications of scanning tunneling spectroscopy of surface electronic states. First, a long standing discrepancy between experimental and theoretical values for the lifetimes of holes in the surface state electron bands on noble metal surfaces is resolved with both found to have been in error. The ability of the scanning tunneling microscope to verify surface quality before taking spectroscopic measurements is exploited to remove the effects of defect scattering on experimental lifetimes. A theoretical treatment of inelastic electron-electron scattering is developed which explicitly includes intra-band transitions within the surface state band. In our model two-dimensional decay channels dominate the electron-electron interactions that contribute to the hole decay, screened by the electron states of the underlying three-dimensional electron system. Second, from a single Mn adsorbate placed within a geometrical array of adatoms on Ag(111) modification of the electronic structure is observed. The changes result from coupling between the adsorbate level and surface electronic states of the substrate. These surface states are scattered coherently within the adatom array, mediating the presence and shape of the array to the adsorbate within. The dimension and geometry of the adatom array thus provide a degree of control over the induced changes.

Surface Science

Room 120 - Session SS1-MoM

Aerosol and Related Chemistry

Moderator: T.E. Madey, Rutgers, The State University of New Jersey

9:40am **SS1-MoM1 Great Enhancements in Dissociative Electron Attachment to Chlorofluorocarbons Adsorbed on Polar Molecular Ices: A New Pathway for the Formation of the Ozone Hole**, ***Q.-B. Lu,*** University of Sherbrooke, Canada; *T.E. Madey,* Rutgers University; *L. Sanche,* University of Sherbrooke, Canada **INVITED**

Atmospheric ozone depletion is an issue of global concern. It is generally accepted that the Earth's ozone layer is depleted by chlorine atoms produced via photolysis of chlorofluorocarbons (CFCs) in the upper stratosphere, and the formation of the Antarctic / Arctic ozone hole has been attributed to heterogeneous reactions occurring on surfaces of ice particles in polar stratosphere clouds (PSCs). Based on measurements of anion yields in (~250 eV) electron stimulated desorption (ESD) from a submonolayer of CFCs coadsorbed with polar molecules, we find evidence for an unrecognized process: dissociative electron attachment (DEA) to CFCs by low energy secondary electrons is enhanced by several orders of magnitude when CFCs are adsorbed on polar molecular ices, such as water and ammonia.@footnote1,@@footnote2@ This enhancement has been identified to be due to transfer of ~ 0 eV electrons temporarily trapped in polar molecular ices to CFCs that then dissociate via DEA, based on measurements of electron trapping cross sections as a function of electron energy in the range of 0-10 eV.@footnote3@ This enhancement effect should be very efficient in the stratosphere, where low-energy electrons can be produced by cosmic-ray ionization and trapped in PSCs. In this talk, we present our laboratory measurements on anion yield enhancements in ESD and on absolute DEA cross sections of CFCs adsorbed on polar molecular ices, and discuss the physics of these processes. The implications of these observations for the formation of Antarctic / Arctic ozone holes, and correlations with data obtained by field measurements (satellite, balloon and ground station), will also be discussed. @FootnoteText@ @footnote1@ Q.-B. Lu and T.E. Madey, Phys. Rev. Lett. 82, 4122(1999); J. Chem . Phys. 111, 2861(1999). @footnote2@ Q.-B. Lu and T. E. Madey, Surf. Sci. 451, 238(2000); J. Phys. Chem. B105, 2779(2001). @footnote3@ Q.-B. Lu and L. Sanche, Phys. Rev. B63, 153403(2001).

10:20am **SS1-MoM3 Electron Stimulated Reactions of Chlorocarbons in Ice Films***, **H. Fairbrother**, A.J. Wagner,* Johns Hopkins University

Electron stimulated reactions of chlorocarbons adsorbed in ice films are of importance in atmospheric processes as well as in understanding the mechanisms of glow discharge chlorocarbon remediation. We present results on the electron -induced reactivity of carbon tetrachloride (CCl@sub 4@) adsorbed in ice films at 100K studied using a combination of reflection absorption infrared spectroscopy and mass spectrometry. Both mass spectrometry and infrared measurements indicate that CCl@sub 4@ is converted to a mixture of phosgene (COCl@sub 2@), CO@SUB 2@ and HCl as a result of electron mediated reactions within the ice/chlorocarbon film, supported by separate experiments using @super 13@CCl@sub 4@. The product branching between COCl@sub 2@ and CO@SUB 2@ was found to be sensitive to the initial H@sub 2@O:CCl@sub 4@ mixture, with H@sub2@O-rich films favoring CO@SUB 2@ production. Results will also be presented on the electron-stimulated reactions of CHCl@sub 3@, CH@sub 2@Cl@sub 2@ and CH@sub 3@Cl adsorbed in ice films.

10:40am **SS1-MoM4 Study of CO@sub 2@ Adsorption on Ice using High-pressure X-ray Photoelectron-spectroscopy***, **F. Requejo**,* Lawrence Berkeley National Laboratory*; H. Bluhm,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; D.F. Ogletree, M. Luna, Z. Hussain,* Lawrence Berkeley National Laboratory*; C.S. Fadley,* University of California, Davis*; M. Salmeron,* Lawrence Berkeley National Laboratory

Water at surfaces plays a fundamental role in atmospheric science, chemistry and biology. A new generation of experimental and theoretical tools are actually revisited this subject.@footnote 1@ Many interesting properties of water still remain unexplained at molecular level, even though it has been a capital subject of research for decades. Interaction between ice surfaces and adsorbed molecules emerges as a very attractive topic. Macroscopic studies@footnote 2@ have investigated the adsorption of CO@sub 2@ on ice, showing the existence of a quasi-liquid layer on ice. On the other hand, new studies@footnote 3@ confirm that CO@sub 2@ is the main driver in global warming and glaciation changes. Recently, by means of surface X-ray absorption spectroscopy, we have studied the premelting of ice trough to the Auger electron yield NEXAFS from its surface. This methodology has proven to be capable of detecting and measuring the thickness of the liquid layer on ice. In the present contribution, we have applied the same methodology to study the effect of atmosphere CO@sub 2@ on the premelting of ice. Samples of ice and water were condensed from vapor onto a cooled substrate, which was placed inside a cell. In equilibrium conditions between the water vapor and the sample at different temperatures, CO@sub 2@ gas was introduced into the cell at different pressures in the range of 0 to 1 Torr. Afterwards, surface-sensitive XPS measurements and Auger electron-yield NEXAFS experiments at O K-edge in the energy range of 530 to 620 eV were performed. Our results indicate unambiguously that the amount of liquid water on the surface of ice increases with the pressure of CO@sub 2@. This effect becomes more evident when the temperature is also increased. @FootnoteText@ @footnote 1@ F. Bensebaa and T.H. Ellis. Progr. in Surf. Sc., 50, 1-4 (1995) 173. @footnote 2@ J. Ocampo and J. Klinger. J. Coll. Interf. Sci. 86, 2 (1982) 377. @footnote 3@ N.J. Shackleton. Science, 298 (2000) 1897. F.G. Requejo - Postdoctotoral Fellow at MSD, LBNL. Berkeley, CA. Permanent address: Dept. Physics, FCE, UNLP and IFILP(CONICET), La Plata, Argentina.

11:00am **SS1-MoM5 Sea Salt Aerosol Reactions: Quantitative Single Particle Studies***, A.J. Laskin, M.J. Iedema, **J.P. Cowin**,* Pacific Northwest National Laboratory

Sea salt from ocean wave action is a very common aerosol. This aerosol is far from inert, with several papers in recent years looking at how it can react with HNO3 to form sodium nitrate (releasing HCl), or hydroxyl radicals to form Cl2. We present highly quantitative, time resolved studies of sea salt aerosols observed during the fall 2000 Texas Air Quality Study. We used a novel automated sampler to preserve 3000 samples (10 minute intervals) for nearly a month of continuous observation. These were preserved for automated laboratory analysis with scanning electron microscopy/energy dispersed x-ray analysis. We analyze particles down to 0.2 micron in size for elements from carbon upward. We are able to follow these reactions in detail, and relate them to the time-resolved atmospheric gases seen by other researchers there. We are able to show that nitration occurs preferentially to sulfating (until later in the daily cycle). We are able to follow the size-resolved reaction, with as expected faster reactions for the smaller particles. We used the archived samples for other techniques too. High resolution time of flight secondary ion mass spectrometry gave important molecular speciation information, on a single particle basis (0.2 micron resolution).

11:20am **SS1-MoM6 Surface Chemistry of Size-Selected, Gas-Phase Nanoparticles***, **J.T. Roberts**, K. Higgins, M.R. Zachariah, H. Jung,* University of Minnesota

A method has been developed to conduct surface chemistry and extract surface kinetic rates from size-selected aerosol nanoparticles. The measurements encompass broad ranges of particle size, phase, and composition. Results will be presented on the growth and oxidation of soot nanoparticles (particle radius between 10 and 40 nm). The particles are investigated for changes in surface area using on-line nanoparticle characterization instrumentation. Experiments emphasize two classes of reactive conditions: high temperature oxidation by O@sub 2@ and NO@sub x@, and room temperature addition of hydrocarbons. We believe these to be the first measurements of soot oxidation and condensation kinetics that have been conducted on size-selected particles. The results are important because soot emission from combustion sources is dictated by the competing surface processes of growth and oxidation. More generally, the results represent one of the first kinetic and mechanistic studies of gas-phase particle reactivity.

11:40am **SS1-MoM7 Scanning Electron Microscopy Studies of the Hydration of Mixed Alkali Halide Aerosols***, **S.A. Joyce**,* Los Alamos National Laboratory*; J.P. Cowin, J.T. Atherley,* Pacific Northwest National Laboratory

The morphologies of aerosols generated from pure NaCl, NaBr, and MgCl@sub 2@ solutions and from NaCl/NaBr and NaCl/MgCl@sub 2@ mixtures have been studied using an environmental scanning electron microscope (ESEM). For aerosols produced by nebulizing pure NaCl solutions, nearly perfect cubic crystals with widths of a few microns are normally observed. Upon raising the water vapor pressure in the specimen chamber, these pure NaCl aerosols are observed to dissolve at relative humidities consistent with previous studies. For aerosols produced by nebulizing NaCl/NaBr mixtures, ranging from 0.1 to 0.5 mole fraction NaBr, polycrystalline particles are often observed. For these polycrystalline samples, deliquescence of individual crystallites occurs at two different relative humidities. The central or core crystallite typically dissolves at relative humidities similar to that for pure NaCl, whereas the outer crystallites dissolve at humidities lower than that for either pure NaCl or NaBr. The deliquescence pressure for these crystallites is independent of the mole fraction of starting solution. The outer region, which dehydrates last, is composed of the NaCl/NaBr eutonic (0.9 mole fraction NaBr), with the inner region composed of nearly pure NaCl. For the aerosols produced by nebulizing NaCl/MgCl@sub 2@ mixtures, a crystalline core surrounded by a featureless outer region is typically observed. X-ray fluorescence measurements show that this outer region is largely magnesium-based while the inner crystallite in sodium-based. Based on available thermodynamic data, no eutonic of NaCl/MgCl@sub 2@ exists, and so phase separation into the pure components is expected. The implication of the phase-separation to surface enrichment of minority components and its potential role in heterogeneous atmospheric chemistry will be discussed. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

Surface Science
Room 121 - Session SS2-MoM

Metal Clusters

Moderator: C.F.O. Bostedt, Lawrence Livermore National Laboratory

9:40am **SS2-MoM1 Mesoscopic Strain-Induced Magic Fe Nanostructures on Cu(100)***, N. Lin, A. Dmitriev,* Max-Planck-Institut for Solid State Physics, Stuttgart, Germany*; V.S. Stepanyuk, D.I. Bazhanov,* Martin-Luther-University, Germany*; J. Weckesser,* Max-Planck-Institut for Solid State Physics, Stuttgart, Germany*; **J.V. Barth,*** EPFL, Switzerland*; K. Kern,* Max-Planck-Institut for Solid State Physics, Stuttgart, Germany and EPFL, Switzerland

We report a novel phenomenon in metal-on-metal heteroepitaxy, expressed in the arrangement of Fe islands grown at low temperature (<200K) on a Cu(100) surface. Scanning tunneling microscopy observations reveal that Fe atoms aggregate as perfectly oriented well-defined nanometer-scale arrays when Fe-Cu exchanging is inhibited. The basic unit of these nanoarrays is a tetramer of Fe atoms. More than 60 percent of the nanoarrays consist of four tetramers arranged in a square shape, aligning exactly to the high symmety directions of the Cu(100). The sharp distribution and distinct shapes of the nanoarrys can be understood in the framework of mesoscopic strain. STM and first principle calculations demonstrate that both the Fe isalnds and Cu substrate experience a large relaxation due to the mesoscopic strain: the Fe interatomic distance in the tetramers (2.0 Å) is 20% less than that in thin fcc Fe/Cu(100) films (2.5 Å), and the Cu substrate underneath the Fe nanoarrays is compressed 16.4% relative to the unrelaxed Cu surface (2.56 Å) . The giant compression and the high stress energy promote the formation of super-compressed Fe tetramers and their aggregation as magic nanoarrays with regular shape and orientation.

10:00am **SS2-MoM2 Nanostructed Growth of Metal Clusters on Ultrathin Al@sub 2@O@sub 3@ Films on Ni@sub 3@Al(111)***, **A. Rosenhahn,*** Lawrence Berkeley National Laboratory*; A. Wiltner,* Universitaet Bonn, Germany*; K. von Bergmann,* Universitaet Hamburg, Germany*; J. Schneider,* Lawrence Berkeley National Laboratory*; C. Becker,* Universitaet Bonn, Germany*; B.S. Mun,* Lawrence Berkeley National Laboratory*; F.J.G. de Abajo,* Centro Mixto CSIC-UPV/EHU*; M.A. van Hove, C.S. Fadley,* Lawrence Berkeley National Laboratory*; K. Wandelt,* Universitaet Bonn, Germany

Highly ordered, ultrathin alumina films can be grown on Ni@sub 3@Al(111) by simply exposing the alloy surface to oxygen at high temperatures.@footnote 1@ Because of the conductibility of the thin films, the properties of metal aggregates on the surface of these oxide films can easily be studied without charging of the surface. Using STM, we have investigated the nucleation properties of different types of metals reaching from very noble ones like Ag, Au, and Cu to metals which are more reactive towards oxygen like V and Mn. All clusters show preferred nucleation on distinct sites of the oxide film.@footnote 2@ As long as the oxide is not entirely covered by metal, two different mean cluster distances of 2.5 nm and 4.6 nm can be found. The distribution of the clusters on the surface reveals a hexagonal symmetry. The same periodicity can be found on the metal-free oxide film, depending on the applied bias voltage.@footnote 3@ As these superstructures reveal the same symmetry and periodicity as the cluster distribution, the nucleation is clearly determined by these sites. Because the superstructures are just at certain bias voltages visible, the prefered nucleation is not simply due to a modulation of the morphology. We will discuss, in which way the structure of the oxide film and the nucleation of the metal clusters are correlated. @FootnoteText@ @footnote 1@ A. Rosenhahn, J. Schneider, C. Becker, and K. Wandelt, J. Vac. Sci. Technol. A 18(4), 1923 (2000). @footnote 2@ C. Becker, K. v. Bergmann, A. Rosenhahn, J. Schneider, K. Wandelt, Surf. Sci. Lett., in Press. @footnote 3@ A. Rosenhahn, J. Schneider, J. Kandler, C. Becker, and K. Wandelt, Surf. Sci. 433-435, 705 (1999).

10:20am **SS2-MoM3 Nanocatalysis:Tuning Efficiency and Selectivity Atom-by-Atom***, **U. Heiz,*** University of Ulm, Germany **INVITED**

The preparation of a collection of supported metallic particles that are truly monodisperse, i.e. they all have exactly the same size, has long considered to be virtually impossible. As a consequence it has been difficult to recognize size effects for small supported clusters, as size distributions have been broad. For clusters in the gas phase, however, strong size-dependent chemical properties have been discovered during the last two decades and the obtained results lead to new concepts for understanding their chemical properties. Connections of these observations with real catalysis has often been stressed and suggestions for tuning efficiency and selectivity of a certain catalytic process by simply changing cluster size were made already in early days. Efficient and selective conversion is indeed important in catalysis, as most catalytic surfaces assist a variety of reactions. It is therefore of interest to study the factors affecting the size-dependent selective and efficient behavior of catalytic systems. We succeeded to prepare model catalysts consisting of a collection of metal particles of a single size. In these experiments metal atoms and small metal clusters are formed in the gas phase, size-selected and then deposited on thin MgO and TiO2 films grown on metal surfaces. Various chemical reactions on the obtained cluster-assembled materials are then investigated under UHV conditions by means of thermal desorption and infrared spectroscopies. Oxidation and polymerisation reactions are strongly dependent on cluster size and on the cluster-support interaction, and not only the number of product molecules per cluster is changed, but also the branching ratio of certain reactions. In many cases the measured reactivities are different from the ones obtained for the corresponding bulk systems. By combining the obtained experimental results with ab-initio calculations, a picture of the size-dependent behavior of cluster-assembled materials is now emerging.

11:00am **SS2-MoM5 Ion Beam Deposition of Size-selected Supported Metal Clusters***, **M. Aizawa**, S. Lee, S.L. Anderson,* University of Utah

We describe an experimental setup that allows us to investigate physical and chemical properties of supported metal clusters on various substrates at low impact energies(<10eV/atom). The metal cluster ions are generated by a laser ablation source, mass selected, and deposited on substrates. The performance of this instrument is illustrated with supported metal clusters (V, Ni, and Ir) on titania and graphite. Electronic structure of the supported metal clusters and chemical reactions over them will be studied by XPS and TPD, respectively, in terms of cluster size, impact energy and substrate defects.

11:20am **SS2-MoM6 Decay Characteristics of Surface Nanostructures: (100) vs (111) Surfaces@footnote 1@***, **J.F. Wendelken***, Oak Ridge National Laboratory*; M. Li, B.-G. Liu, E.G. Wang,* Chinese Academy of Sciences*; Z. Zhang,* Oak Ridge National Laboratory

The stability of nanostructures after their creation is a critical issue for nanotechnology. Here we study the fundamental mechanisms of atomic scale mass transport on surfaces with regard to the instability of surface nanostructures. Pyramidal mounds were created on Cu(100) and (111) surfaces at 297 K by molecular beam deposition of Cu atoms. The stability of the nanoscale mounds was then observed with a scanning tunneling microscope for up to 24 hours. Movies produced from sequential scans show that the mounds are unstable and the decay process is profoundly different for the (100) and (111) surfaces. Decay of the (100) mounds proceeds with removal of atoms from the base of the mounds and subsequent transport to the bottom of pyramidal holes with the result that the mound walls become steeper with time. In contrast, the (111) mound decay is characterized by loss of atoms on all terrace levels producing a constant average slope. The mechanism for the decay on both surfaces at 297 K involves the diffusion of islands or terraces by periphery diffusion@footnote 2@ to an edge where a rapid decay@footnote 3@ or avalanche process may take place. Direct observation shows that this avalanche process is site selective on the (100) surface, but is not selective on the (111) surface. Kinetic Monte Carlo simulations@footnote 4@ at 400 K show that the observed behavior is a consequence of selective vs. non-selective edge diffusion barriers and does not depend on the mechanism by which atoms are delivered to the edge. @FootnoteText@ @footnote 1@ Supported in part by the U.S. DOE through contract DE-AC05-00OR22725 with UT-Battelle, LLC, and in part by the NSF of China. @footnote 2@ W. W. Pai, A. K. Swan, Z. Zhang, and J. F Wendelken, Phys. Rev. Lett. 79, 3210 (1997). @footnote 3@ M. Giesen, G. Schulze Icking-Konert, and H. Ibach, Phys. Rev. Lett. 80, 552 (1998). @footnote 4@ Maozhi Li, J. F. Wendelken, Bang-Gui Liu, E. G. Wang, and Zhenyu Zhang, Phys. Rev. Lett. 86, 2345 (2001).

11:40am **SS2-MoM7 Reactions on Free Platinum Clusters: Adsorption of Oxygen and Hydrogen and Formation of Water***, **M. Andersson**, A. Rosén,* Chalmers University of Technology and Göteborg University, Sweden

We use a cluster beam experiment to investigate chemical reactions on the surface of small unsupported metal clusters. A pulsed beam of metal clusters is generated with a laser vaporization source, in which metal atoms are vaporized into a flow of helium gas and condense in small clusters. After expansion into vacuum, the cluster beam passes through two reaction cells. The cell pressure is varied over a range where the clusters make from less than one up to a few collisions with the reactive molecules.

The clusters are detected with laser ionization and time-of-flight mass spectrometry. By measuring the abundance of pure clusters and reaction products as a function of reaction cell pressure, the reaction probability in a cluster-molecule collision can be determined. For platinum clusters with more than 6 atoms we measure stable reaction products with both oxygen and hydrogen. The reaction probability with oxygen is for most sizes between 0.2 and 0.3, and appears lower with hydrogen though difficult to quantify since the Pt isotope distribution limits the mass resolution. If we let the clusters collide with both hydrogen and oxygen molecules, the resulting mass spectrum deviates significantly from a co-adsorption spectrum where the respective contributions are added. Instead, if, for example, the clusters first react with oxygen and then hydrogen we observe fewer oxide products and more pure clusters compared without hydrogen collisions. The only reasonable explanation for this is that water molecules are formed on the clusters and desorb. The efficiency of the reaction is high on all cluster sizes measured (8-30 atoms), with only a weak dependence on cluster size.

Surface Science
Room 120 - Session SS1-MoA

Innovations in Surface Science

Moderator: U. Heiz, University of Ulm, Germany

2:20pm **SS1-MoA2 An Accurate Paremetrization for the Extended Hückel Theory (EHT): Application to the Electronic Structure and STM Imaging of the Cu(110)+c(2x2)-Si Surface Alloy***, **J.I. Cerdá**, C. Rojas, C. Polop, J.A. Martin-Gago,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*; R. Fasel, J. Hayoz, D. Naumovic, P. Aebi,* Universite de Fribourg, Switzerland

The electronic structure of the Cu(110)+c(2x2)-Si surface alloy has been studied both experimentally and theoretically. On the experimental part, we have mainly employed Angle Resolved Ultraviolet Photoemission Spectroscopy (ARUPS) together with atom resolved images acquired with a Scanning Tunneling Microscope (STM). On the theoretical part, we have made use of a recently developed Extended Hückel Theory (EHT) parametrization scheme@footnote 1@ in order to describe the Atomic Orbital (AO) interactions, while the Cu(110)+c(2x2)-Si system has been modelled by a surface-alloy layer stacked on top of a semi-infinite Cu(110) bulk. The corresponding electronic structure and associated STM images (for different tips) have been calculated via Green's functions techniques. Despite the simplicity of the EHT approach, we find a very good agreement with the surface specific electronic features experimentally observed: Fermi surface, Surface State Bands, Atomic corrugation in the STM images, etc. This fact evidences the good transferability of the EHT parameters between different chemical and geometrical environments. @FootnoteText@ @footnote 1@J. Cerdá and F. Soria, Phys. Rev. B, Vol. 61 (2000) 7971.

2:40pm **SS1-MoA3 UV Free Electron Lasers and Their Applications in Surface Science***, **M. Marsi**,* Sincrotrone Trieste, Italy **INVITED**

Free Electron Lasers (FELs) are intense, monochromatic, tunable and coherent light sources that, thanks to their unique features, are opening new research opportunities in many different fields. For several years FEL's have been operating with success in the infrared; recently a considerable progress has been made in the UV region, where lasing wavelengths shorter than 190 nm have been able to be obtained, disclosing new opportunities for the study of the electronic properties of thin films and microstructures. UV FEL's are powerful instruments to probe the excited states of matter, especially when used in combination with synchrotron radiation in a pump-probe configuration. This kind of two-photon photoemission experiments, performed on Si surfaces and interfaces, have allowed a detailed study of the behavior of the non-equilibrium carrier distribution, making it possible to observe the role of interface states in the charge flow mechanism at photoexcited surfaces. Beside their use in combination with synchrotron radiation, UV FEL's have some unique features which make them particularly attractive also per se: in particular, being very intense and naturally tunable, they are ideal light sources for threshold photoelectron emission microscopy, and thus powerful instruments to study the electronic properties of nanostructures.

3:20pm **SS1-MoA5 An End Station for Synchroton-Based Photoelectron Spectroscopy of Actinide and Other Highly Reactive Samples***, D.A. Arena, **J.G. Tobin**,* Lawrence Livermore National Laboratory*; D. Shuh,* Lawrence Berkeley National Laboratory*; R.K. Schulze,* Los Alamos National Laboratory*; P. Boyd,* Boyd Technologies, Inc.

We have constructed a specialized UHV experimental chamber to allow for the convenient study of the electronic structure of actinide and other highly reactive samples using synchrotron radiation at the Advanced Light Source (ALS). This chamber, the Actinide Spectroscopy End Station (ASES), is currently equipped to perform high-resolution photoemission spectroscopy in both spin integrated and spin resolved modes. The system includes a novel sample introduction system where samples are brought on-site in small ion-pumped vacuum suitcases and introduced into the experimental chamber without exposure to the atmosphere. We have included a separate sample preparation chamber to provide for sample cleaning and gas dosing followed by a quick transport to the analysis position. The ASES is equipped with numerous isolation valves to allow for the removal and repair of individual components while maintaining the vacuum integrity of the overall system. The sample manipulator allows for both heating and liquid nitrogen cooling of the samples and the end station also contains a number of redundant systems such as multiple sample heating and temperature measurement stages so that experiments can continue in the event of common occurrences such as a broken heating filament or open thermocouple connection. Expansion plans include the addition of a fluorescence spectrometer and a thin film deposition system. An extensive series of experiments are planned, including resonant photoemission, spin-resolved double polarization investigations, and oxidation studies of elemental plutonium and other actinide samples. 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.

3:40pm **SS1-MoA6 Closing the Pressure Gap: Photoemission at 5 Torr and the Premelting of Ice***, **D.F. Ogletree**,* Lawrence Berkeley National Laboratory*; H. Bluhm,* Lawrence Berkeley National Lab and Fritz Haber Institute, Germany*; F. Requejo,* Lawrence Berkeley National Laboratory*; C.S. Fadley,* Lawrence Berkeley National Lab and University of California at Davis*; Z. Hussian, M. Salmeron,* Lawrence Berkeley National Laboratory

Fundamental studies of surface processes and reactions at high pressure are outside the reach of many surface science techniques - the so-called "pressure gap". Scanning probe microscopy and non-linear optical probes can be used to study surface topography and vibrational excitations, respectively, but probes of electronic structure and atomic composition are hard to come by. We have recently extended x-ray photoemission spectroscopy to pressures as high as 5 Torr using a synchrotron light source and a differentially pumped electron transfer lens. One of the first applications of this method has been a study of the pre-melting of the ice surface. The new instrument will be described, and the results on ice pre-melting will be presented. Near-edge x-ray adsorption fine structure (NEXAFS) probes the density of unoccupied molecular states. In the case of water, NEXAFS is sensitive to the effects of hydrogen bonding and can therefore distinguish between water vapor, liquid water and ice. Surface sensitivity was obtained by using the O KLL Auger electron yield as a probe of x-ray absorbtion. Electron spectroscopy allowed the Auger yield to be extracted, since total electron yield measurements were complicated by secondary electron cascades in the gas phase. Pre-melting was investigated for ice, in equilibrium with its vapor, between -40 and 0 C (the vapor pressure of ice at the melting point is 4.6 Torr). NEXAFS results showed that a liquid-like film exists at the ice surface above -20 C, reaching a thickness of ~ 2 nm near 0 C. We also found that the presence of hydrocarbon contamination strongly influenced the pre-melting of ice.

4:00pm **SS1-MoA7 Desorption/Ionization on Porous Silicon (DIOS) Mass Spectrometry: A New Methodology for Bioanalysis***, **Z. Shen**, J.E. Crowell,* University of California, San Diego*; G. Siuzdak,* The Scripps Research Institute

DIOS-MS is a new mass spectrometry strategy based on pulsed laser desorption/ionization from a porous silicon surface. DIOS-MS is similar to matrix-assisted laser-desorption ionization mass spectrometry (MALDI-MS) in that it utilizes the same instrument; however, in DIOS-MS, porous silicon is used to trap analytes deposited on the surface and laser radiation is used to vaporize and ionize these molecules, without the presence of any matrix material. We have shown that DIOS-MS can be used for a wide range of small molecules as well as biomolecules at the femtomole and attomole level with little or no fragmentation, in contrast to what is typically observed with other direct desorption/ionization approaches. DIOS-MS offers many unique advantages including good sensitivity, low background ion interference, and high salt tolerance. We will demonstrate the application of DIOS-MS to small molecule quantitative analysis, chemical reaction monitoring, enzyme-substrate reaction and inhibition characterization, and drug metabolism study. We will also demonstrate DIOS-MS as a unique scanning approach for small-molecule high throughput analysis.

4:20pm **SS1-MoA8 Enantiospecific Properties of Chiral Surfaces***, **J.D. Horvath**, A.J. Gellman,* Carnegie Mellon University

Chirality is an omnipresent feature of the biochemical and biophysical world. The handedness of the important molecules that form the basis of life creates the need for enantiomeric purity in the chemicals used for pharmaceutical and other bio-active purposes. Many of the processes used for synthesis and preparation of enantiomerically pure compounds rely on the use of chiral surfaces. This represents in interesting and important new opportunity for surface science. I will describe some of the recently discovered, enantiospecific physical and chemical properties of chiral surfaces prepared from simple high Miller Index metal surfaces. The kinked step structures of such surface are chiral. As an example, the heats of adsorption of small chiral molecules such as propylene oxide (CH@sub 3@CH(O)CH@sub 2@) and R-3-methylcyclohexanone are sensitive to the handedness of surfaces such as Cu(643). This has been observed using thermally programmed desorption measurements which reveal that the desorption kinetics of these chiral molecules are enantiospecific on chiral surfaces. They do not exhibit enantiospecificity on achiral surfaces such as Cu(111). Similarly, the orientation of chiral molecules on chiral surfaces can be shown to depend on the relative handedness of adsorbate and substrate. This has been shown by study of the infrared reflection absorption spectra of 2-butanoxy groups on the Ag(643) surface. The intensities of the absorptions by R- and S-2-butanoxy groups are dependent on the handedness of the Ag(643) substrate. Understanding and controlling these enantiospecific properties poses some extremely interesting challenges for surface chemistry and surface physics that can have broad impact in the chemical and life sciences.

4:40pm **SS1-MoA9 Can Cu-TBP Porphyrin Molecules Emit Light under an STM Excitation?***, D. Fujita, H. Nejo, S. Yokohama, S. Mashiko,* ***Z.-C. Dong,*** National Institute for Materials Science, Japan

Photon emission on metal surfaces induced by tunneling electrons is thought to arise from the radiative decay of localized surface plasmons. While this theory is still not yet complete due to the negligence of non-local effects, the situation becomes more complicated and difficult to study when molecules are sandwiched between the tip and surface. It remains unclear how molecules couple with the electrodes and electromagntic field to give out light. We demonstrate here a technique to produce tunneling-electron induced photon emission from Cu-TBP porphyrins on Cu(100). The emission intensity and optical spectra show not only the enhancement effects, but also new features revealing the molecular origin of light emission. The quantum efficiency is estimated to be 10@super -4@ photons per electron. The observation of a broad peak around 630 nm associated with molecules is particularly exciting but puzzling, since Cu-centered porphyrin molecules are known not to fluoresce under photoexcitation. This broad peak appears dramatically enhanced when the bias voltage is above 3 V, in good agreement with the high B-band absorption via optical excitation. These observations suggest that while energy absorption behavior by electrons appears in parallel with that by photons, the excitation or decay mechanism might be different in the two processes, and may thus bring up new physics. Tunneling electrons can excite surface plasmons in metal substrates, which causes the enhancement of local electromagnetic field. Excitation of molecules occurs via the resonant coupling of molecular electronic states with the localized electromagnetic modes between the tip and substrate. Light is emitted when excited molecules decay to the ground state. The decoupling of luminescent porphyrin cores from the substrate, a means to suppress the fast nonradiative energy dissipation, is found to be important for efficient light emission.

5:00pm **SS1-MoA10 A Fourier Transform-Based TOF HREELS Spectrometer***, R.H. Jackson, L.J. LeGore, Y. Yang, P. Kleban,* ***B.G. Frederick,*** University of Maine

A major limitation of the conventional, dispersive sector, electron energy analyzer is that it is inherently a serial device, leading to long data acquisition times in high resolution electron energy loss spectroscopy (HREELS). A throughput advantage of order 500-1000 can be achieved by combining time-of-flight (TOF) methods with pseudo-random (PRBS) modulation of the back-scattered electron beam. We present the first results of this new approach to HREELS and compare with simulations of the TOF spectrometer. Although PRBS modulation techniques have been applied to a number of other areas,@footnote 1,2@ the Poisson noise distribution arising from pulse-counting detection and the sub-nanosecond time resolution required for meV resolution in HREELS place several demands upon the chopper, detection electronics and digital signal processing software. We will discuss how the chopper, based upon the "interleaved comb" device,@footnote 3@ limits the minimum gating time and the nominal time resolution of the spectrometer. Traditional cross correlation methods, utilized to recover the signal in PRBS modulation, obtain a throughput advantage over single pulse TOF at the expense of resolution; however, the methods are not strictly valid when the noise correlates with signal power. To overcome these limitations, we have developed maximum likelihood methods which account for the Poisson noise distribution and achieve a resolution enhancement of up to a factor of 8, relative to the nominal TOF time resolution, depending upon the signal to noise ratio. @FootnoteText@ @footnote 1@ Y. Uehara, T. Ushiroku, S. Ushioda, Y. Murata, Jap. J. App. Phys., 29 (1990) 2858-2863. @footnote 2@ J. L. Buevoz, G. Roult, Rev. de Phys. Appl., 12 (1977) 59 7. @footnote 3@ P. R. Vlasak, D. J. Beussman, M. R. Davenport, C. G. Enke, Rev. Sci. Instrum., 67 (1996) 68-72.

Surface Science
Room 121 - Session SS2-MoA

Molecular Interactions with Oxide Surfaces

Moderator: U. Diebold, Tulane University

2:00pm **SS2-MoA1 Probe Molecules on Hydroxylated @gamma@-Al@sub 2@O@sub 3@/NiAl(100): Characterization of Surface OH Acidity***,* ***K.A. Layman****, J.C. Hemminger,* University of California, Irvine

Hydroxylated thin films of @gamma@-Al@sub 2@O@sub 3@ are grown by exposing a NiAl(100) single crystal to 100 L H@sub 2@O at 1000 K. In HREELS analysis, these films exhibit the phonon modes in agreement with @gamma@-Al@sub 2@O@sub 3@ films grown on the NiA l(100) substrate using 2400 L O@sub 2@ at 1000 K. In addition to the observed phonon modes, a single OH stretch is observed at 3270 cm@super -1@ (FWHM approximately 100 cm@super -1@). This frequency is indicative of non-interacting OH groups bonded to 2 or 3 Al atoms. To characterize the acidity of the surface OH groups, we have studied the adsorption of probe molecules, such as pyridine, benzene, and toluene, on the hydroxylated @gamma@-Al@sub 2@O@sub 3@ surface at 150 K. The probe molecules, acting as bases, form acid-base complexes with the surface OH groups. HREELS spectra were recorded as a function of probe molecule coverage. Complex formation causes the OH bond strength to decrease and the OH stretch to shift to lower frequency. The adsorption and complex formation is observed to be reversible. The OH frequency shift is dependent on the probe molecule basicity and the OH acidity. Our results indicate that two types of isolated OH with different acidity exist on the surface. The correlation between OH frequency shift and probe molecule basicity allows us to determine the acid strength of the surface OH groups quantitatively.

2:20pm **SS2-MoA2 Evidence for a Radical-Radical Reaction between O@sub 2@ and OH on TiO@sub 2@(110)***,* ***M.A. Henderson****, C.L. Perkins,* Pacific Northwest National Laboratory

Water readily dissociates at oxygen vacancy sites on TiO@sub 2@(110) to form bridging OH groups.@footnote 1-3@ These OH groups exhibit properties that are more consistent with what one would expect from OH radicals rather than from OH@super -@ ions. A surface consisting solely of these OH groups is easily prepared by adsorption of a multilayer water exposure at 130 K followed by heating to 300 K to desorb all molecular water. Recombination of the bridging OH groups occurs in a TPD peak at about 500 K. ELS spectra of the 10% vacancy-covered surface before and after exposure to water both possess the 0.8 eV loss feature attributable to Ti@super 3+@ cations. The inability of water/OH to oxidize Ti@super 3+@ cations at vacancy sites is consistent with earlier photoemission studies.@footnote 4@ In contrast, this ELS feature is absent after O@sub 2@ exposure at RT due to oxidation of the vacancies. Surprisingly, exposure of O@sub 2@ to bridging OH groups results in replacement of the 500 K recombinative desorption state of water with a sharp H@sub 2@O TPD state at 300 K. Concurrent with this change, the Ti@super 3+@ cations are oxidized and O adatoms are deposited on the surface. We speculate that the most likely explanation for this behavior is a radical-radical reaction between O@sub 2@ and OH. Such a reaction does not occur between OH groups and diamagnetic molecules like CO@sub 2@.@footnote 5@ These findings suggest that bridging OH groups on TiO@sub 2@(110) formed from the dissociative adsorption of H@sub 2@O at vacancy sites might be useful in exploring the thermal chemistry OH radicals believed to be formed on TiO@sub 2@ photocatalysts. @FootnoteText@ @footnote 1@. M.B. Hugenschmidt, et al., Surf. Sci. 302 (1994) 329. @footnote 2@. M.A. Henderson, Langmuir 12 (1996) 5093. @footnote 3@. W.S. Epling, et al., Surf. Sci. 412/413 (1998) 333. @footnote 4@. R.L. Kurtz, et al., Surf. Sci. 218 (1989) 178. @footnote 5@. M.A. Henderson, Surf. Sci. 400 (1998) 203. R.

2:40pm **SS2-MoA3 Sulfur Adsorption and Reaction with a TiO@sub 2@(110) Surface: O - S Exchange and Sulfide Formation***,* ***J. Hrbek****, J.A. Rodriguez, J. Dvorak, T. Jirsak,* Brookhaven National Laboratory

Upon sulfur adsorption on TiO@sub 2@(110) at 600 K all surface oxygen is replaced by S. High-resolution photoemission data show a complete loss of oxygen from the surface layer, a large binding energy shift and attenuation of Ti core levels, and the presence of three different S species. The bonding of sulfur is examined using first-principles density-functional calculations and the periodic supercell approach. At saturation the top layer of the oxide surface is converted to sulfide, with the majority of sulfur buckled above the Ti lattice plane and the remaining sulfur bonded in bridging sites. A mechanism for this self-limiting thermodynamically unlikely surface reaction is proposed. This research was carried out at Brookhaven National

Laboratory under contract DE-AC02-98CH10086 with the US Department of Energy (Division of Chemical Sciences).

3:00pm **SS2-MoA4 Molecular Adsorbate Geometries and Bondlengths on NiO(100); A Failure of Current DFT Theories***,* ***M. Kittel,*** *J.-T. Hoeft, M. Polcik,* Fritz-Haber-Institut der MPG, Germany*; R.L. Toomes, J.-H. Kang,* University of Warwick, UK*; M. Pascal, C.L.A. Lamont,* University of Huddersfield, UK*; D.P. Woodruff,* University of Warwick, UK

Current density-functional theory has been shown to be extremely successful in reproducing the local geometries and bondlengths of adsorbates on metal surfaces, for which there is a significant body of experimental data. In the case of oxide surfaces, however, there is a dearth of experimental structural data to compare with the results of such theory. Here we present the results of quantitative structure determinations for new studies of CO and NH@sub3@ on NiO(100) epitaxial films using photoelectron diffraction in the scanned-energy mode (PhD) combined with full multiple scattering simulations. Both species, like NO which we studied previously, occupy sites atop surface Ni atoms, with bondlengths which are slightly longer than we have found for the same species on metallic Ni surfaces, but much shorter (by up to 0.79 Å) than predicted by theory. The results highlight a major failure of current theory to provide an adequate description of molecule/oxide bonding, which was previously only evident through a comparison of experimental thermal desorption data with theoretical bonding energies. A comparison of the molecule-Ni nearest neighbour bondlengths for these singly-coordinated sites on NiO(100) with those found on metallic Ni(111) shows that while the bondlengths on the oxide surface are systematically longer than on the metal surface, these effects are far more subtle than those reflected by current theoretical treatments.

3:20pm **SS2-MoA5 The Stability of Polar Oxide Surfaces and Their Interaction with Deposits***,* ***C. Noguera,*** CNRS, France*; J. Goniakowski,* CRMC2, France*; F. Finocchi,* Laboratoire de Physique des Solides, France **INVITED**

It has long been recognized that the most interesting or active surfaces for the applications are not necessarily the most perfect ones. In insulating oxides, geometric defects, nanofacets, or stoichiometric defects are usually associated to specific electronic states located in the forbidden gap region, which confer a higher reactivity to the surfaces. From this view point, polar oxide surfaces are of prominent interest: their intrinsic instability, due to the existence of a non-zero dipole moment in the repeat unit perpendicular to the surface, may be overcome by a deep modification of the surface electronic structure --- total or partial filling of surface states, sometimes leading to surface metallization --- or by strong changes in the surface stoichiometry --- spontaneous desorption of atoms, faceting, large-cell reconstructions, etc. We will examine several of these issues, through the results of first principles simulations of the MgO(111) surface, based on the density functional method. We will discuss the relative stability of various surface reconstructions, in relation with recent grazing incidence X Ray diffraction and atomic force microscopy experiments. The mechanism by which is achieved the charge compensation necessary to heal the polarity when transition metal atoms are deposited on the surface will be described and the trends in the adhesion energy along the transition series will be discussed. Finally we will present recent results on the dissociation of water on MgO(111).

4:00pm **SS2-MoA7 Small Molecule Adsorption on SrTiO@sub 3@ and CaTiO@sub 3@ Surfaces***,* ***K.F. Ferris,*** Pacific Northwest National Laboratory, us*; L.-Q. Wang,* Pacific Northwest National Laboratory

Interactions of water and formate with stoichiometric and defective on (001) MTiO3 surfaces (M=Ca, Sr) have been studied using semiempirical and first principles electronic structure calculations. Preliminary results for water interaction with (001) CaTiO 3 indicate weaker adsorption than TiO2 surfaces, consistent with experimental results. Though energetically similar, water adsorption on TiO2- and CaO-terminated CaTiO3 surfaces result in a distinctly different geometric arrangements due to the surface ox ygen atoms and the charge distribution of these acceptor sites. Stepped (001) CaTiO3 surfaces have oxygen sites with greater accessibility and lower coordination, and are predicted to have increased reactivity for H2O and HCOOH. Preliminary results for fo rmate interaction with (100) SrTiO3 indicate strong adsorption consistent with experimental results, but in a distinctly different geometric arrangement from the TiO2 surfaces due to absence of bridging oxygen sites. Further results will be discussed in terms of potential reaction mechanisms and correlations with ongoing experimental studies. This work was supported by the U.S. Department of Energy, Office of Science, Material Sciences Division, under contract DE-AC06-76RLO 1830.

4:20pm **SS2-MoA8 Dramatic Cooperative Effects in Chemisorption of NO@sub x@ on Oxide Surfaces***,* ***W.F. Schneider,*** Ford Research Laboratory*; M. Miletic,* University of Michigan*; K.C. Hass,* Ford Research Laboratory*; J.L. Gland,* University of Michigan

NO@sub x@ adsorption by base metal oxide sorbents is central to numerous NO@sub x@ aftertreatment technologies, including those essential to enabling fuel-efficient "lean burn" combustion for transportation applications. While the ability of base metal oxide surfaces to form surface nitrites and nitrates is well established by TPD, XPS, and IR experiments, the identity and mechanisms of formation of the adsorbates are not well understood, inhibiting attempts to design oxides with more useful adsorption properties. In this work, first-principles DFT calculations are used to study NO@sub x@ adsorbates on alkaline earth oxide surfaces. We show that isolated NO or NO@sub 2@ are weakly physisorbed to these surfaces, but that adsorption is strongly enhanced by the formation of adsorbate pairs. This remarkable and unprecedented cooperative chemisorption phenomenon is a consequence of the amphoteric character of NO and NO@sub 2@ and the acidity and basicity enhancements possible when charge is transferred between two adsorbates. These results provide a novel and consistent picture of oxide surface nitrition and nitration and are a key step along the path of rationally designed NO@sub x@ adsorbants.

4:40pm **SS2-MoA9 CO@sub 2@ and BF@sub 3@ Adsorption on Cr@sub 2@O@sub 3@ (1012): Probing Surface Basicity and Oxygen Anions***, M.W. Abee,* ***D.F. Cox,*** Virginia Polytechnic Institute & State University

The basic properties of oxide surfaces are often associated with surface lattice oxygen anions. CO@sub 2@ is the standard probe molecule for investigating surface basicity, but little information is available in the surface science literature concerning its interaction with well-defined (single crystal) oxide surfaces. On Cr@sub 2@O@sub 3@ (1012), CO@sub 2@ interacts primarily with cation/anion site pairs to form bidentate carbonates that are stable at room temperature. These sites are associated with five-coordinate Cr@super 3+@ cations on the stoichiometric, non-polar (1012) surface. Terminating the surface cations with chromyl oxygen (Cr=O) via dissociative O@sub 2@ chemisorption breaks the interaction and gives rise to a weakly-bound CO@sub 2@ moiety. BF@sub 3@, a strong Lewis acid, interacts directly with anions on the stoichiometric surface, giving a surface/adsorbate complex stable to above room temperature. However, unlike CO@sub 2@, BF@sub 3@ forms a more stable complex with chromyl oxygen on the oxide-terminated surface. The results demonstrate that thermal desorption experiments with BF@sub 3@ provide a means for probing the Lewis basicity of surface oxygen anions of different coordination.

5:00pm **SS2-MoA10 Synchrotron X-ray Photoelectron Studies of the CCl@sub 4@ Chemistry on Fe@sub 3@O@sub 4@ (111)- 2x2 Surfaces***,* ***K. Adib****, N. Camillone III, J.P. Fitts, Z. Zhu, R.M. Osgood, Jr.,* Columbia University*; S.A. Joyce,* Pacific Northwest National Laboratory*; D.R. Mullins,* Oak Ridge National Laboratory

We have used synchrotron x-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) to investigate the reactions of CCl@sub 4@ with Fe@sub 3@O@sub 4@ (111) surfaces. Natural single crystals of @alpha@-Fe@sub 2@O@sub 3@ were cut and polished in the (0001) orientation. They were processed in ultrahigh vacuum to produce a surface selvedge of Fe@sub 3@O@sub 4@ (111)- 2x2 and exposed at ~100 K to CCl@sub 4@. TPD results indicate a highly reactive surface in which the dissociation of CCl@sub 4@ into Cl and CCl@sub 2@ plays an important role. XPS results confirm the presence of three Cl-containing species immediately upon dosing. The data is consistent with presence of unreacted CCl@sub 4@, and chemisorbed CCl@sub 2@ and Cl on the surface. We propose that upon subsequent heating of the surface, the chemisorbed species can (1) abstract an oxygen and desorb as OCCl@sub 2@, (2) associatively desorb as C@sub 2@Cl@sub 4@ or (3) recombinatively desorb as CCl@sub 4@. We have observed differences in the TPD spectra following the initial dosing of the surface as compared to those following subsequent dosings. These marked changes in the surface are explained in terms of incomplete desorption of iron chloride and carbon species upon heating as verified by XPS. At sufficiently high dosages of CCl@sub 4@, the iron chlorides formed on the surface consisted of multiple species, possibly FeCl@sub 2@ and FeCl@sub 3@.

Surface Science
Room 134/135 - Session SS1-MoP
Electronic Structure Poster Session

SS1-MoP1 The Surface Sensitivity of the Unoccupied Bands of Mo(112)*, **H.-K. Jeong**, T. Komesu,* University of Nebraska-Lincoln*; I.N. Yakovkin,* National Academy of Sciences of Ukraine*; P.A. Dowben,* University of Nebraska-Lincoln

We present results of unoccupied states of Inverse photoemission on Mo (112). The data are compared with the calculated band structure. The comparison between the calculated and experimental bands along the of the surface Brillouin zone is key to the elucidation of the important features of the electronic structure of Mo (112) surface. Because the Brillouin zone does not change along for these two surfaces, the angle -resolved inverse photoemission spectra can be compared to determine surface sensitivity all along this symmetry direction from zone center to zone edge. Enhanced surface sensitivity of inverse photoemission from the comparison of spectra for clean and the p(1x2) oxygen covered surfaces has been investigated. In particular, different sensitivity of the surface states 0.5 eV and 2.2 eV to oxygen adsorption can be attributed to different symmetry of the states at the surface Brillouin zone center. Thus, the 0.5 eV state found to have a1 symmetry in theory, while the 2.2 eV band is found to be odd with respect to the mirror plane in theory.

SS1-MoP3 High Spatial Resolution Soft X-ray Photoemission Study of WO3 Thin Films*, **L. Lozzi**, M. Passacantando, S. Santucci,* University of L'Aquila, Italy*; S. La Rosa, N. Yu Svetchnikov,* Sincrotrone Trieste SCpa, Italy

Tungsten trioxide (WO3) is a wide gap n-type semiconductor and it is the subject of an intense both theoretical and experimental studies because of its interesting applications, such as gas sensors towards different gases, like NO2 and H2S, and as electrochromic film. Many of these possible applications are mainly due to the oxygen vacancies. For example, in the sensing mechanism, the gas species are adsorbed on the surface changing the concentration of the free electrons on the surface. These electrons are present on the surface because of the oxygen vacancies. The variation of this concentration modifies the electrical conductivity of the film. Similarly, the presence of substoichiometric WO3-x compounds, determines the optical properties of these films. An important parameter in the preparation of WO3 thin films is the thermal treatment following the sample growth. For example it has been shown that the gas sensitivity and response time are strongly influenced by the annealing procedure, because of the phase transitions induced by the annealing. In this work the WO3 surface chemical composition has been studied by means of high resolution soft X-ray photoemission spectroscopy. We have studied the surface properties of both as deposited samples and samples after annealing in air at high temperatures. Valence band and W 4f core levels have been analysed on different samples positions and high resolution maps have been acquired. The valence band spectra have shown W 5d density of state at the Fermi level, indicating the presence of metallic tungsten on the surface. This has been confirmed by the W 4f signal, which present both metallic and oxidized phases. The high resolution maps, obtained following both valence and core states, have clearly evidenced the presence non stoichiometric areas and of some metallic islands.

SS1-MoP4 Femtosecond Dynamics of Electrons in Image-potential States on Stepped Cu(001)*, **M. Roth**, M. Pickel, J. Wang, M. Weinelt, Th. Fauster,* Universität Erlangen-Nürnberg, Germany

The Rydberg-like series of image-potential states (|n>, n = 1, 2, ...) is a prototype system for loosely bound electrons at a metal surface. The electronic structure and the femtosecond dynamic of these states is studied by energy- and time-resolved two-photon photoemission spectroscopy. The electron trapped in the image-potential moves virtually free lateral to the surface exhibiting a parabolic dispersion with effective mass close to the free-electron mass. In this intermediate state the electron is subject to inelastic and quasielastic scattering processes which cause decay of the population and phase relaxation. The influence of surface corrugation on these processes has been investigated for stepped Cu(117) and Cu(119) surfaces which are vicinal to Cu(001). The dynamics depend on both the distance of the electron in front of the surface (~ n@super 2@) and the parallel momentum perpendicular to the step edge. Only for the lowest image-potential state |1> we can identify umklapp processes. An electron in this state which moves upstairs apparently has a longer lifetime than an electron moving downstairs. In the second image-potential state |2> the decay rate decreases linearly with kinetic energy but independent of direction. While quasielastic scattering with small momentum transfer is mainly observed for the first image-potential state, the population of state |2> decays in addition via resonant scattering from the band bottom to states of band |1> with finite momentum. Compared to the Cu(001) surface the latter process is considerably enhanced on the stepped surfaces.

Surface Science
Room 134/135 - Session SS2-MoP
Surfaces and Interfaces Poster Session

SS2-MoP1 Effects of Na and Se Annealing on CuInSe2 Single Crystals*, V. Lyakhovitskaya, K. Gartsman, **Y. Feldman**, H. Cohen, D. Cahen,* Weizmann Institute of Science, Israel

We report on X-ray photoelectron spectroscopic, secondary ion mass spectroscopy, scanning electron microscopy, electron-beam induced current and energy dispersive X-ray fluorescence studies of high quality, travelling heater-grown single crystals of CuInse2, that were subjected to controlled heat treatments from 300 C upwards for varying times, in Se atmosphere, in Na atmosphere and in a mixture thereof. We find that with Na the surface of the crystals is gradually destroyed, while with Se a gradual topotactic type conversion takes place, controlled by Cu diffusion towards the surface, rather than by Se diffusion into the bulk. This is accompanied by formation of a separate Cu-Se phase on the surface. The implications of these findings for the effects of Na on the performance of CuInse2-based solar cells will be considered, in terms of both possible surface and bulk effects.

SS2-MoP2 Two-dimensional and Three-dimensional Growth of Ag Islands on a Ge(001) Surface Studied by Photoemission Spectroscopy*, **M. Yamada**, K. Nakatsuji, T. Iimori, S. Ohno,* ISSP, The University of Tokyo, Japan*; Y. Naitoh,* CREST, Japan Science and Technology Corp.*; T. Okuda, A. Harasawa, T. Kinoshita, F. Komori,* ISSP, The University of Tokyo, Japan

Growth mode of Ag thin films on a Ge(001) surface depends on the substrate temperature: two-dimensional (2D) growth is predominant at low temperatures and three-dimensional (3D) growth becomes dominant at room temperature.@footnote 1@ According to the recipe found by the STM study, we prepared samples composed of 2D (monolayer-thick) or 3D (several-monolayer-thick) Ag islands, and investigated their electronic structure by synchrotron radiation photoemission spectroscopy. A clean Ge(001) surface gives a Ge3d spectrum with a shoulder at the low binding energy side, which is due to surface core-level shift (SCLS) of topmost, 2x1 reconstructed Ge atoms. After Ag deposition at 95K, the shoulder disappeared and the LEED pattern changed to 1x1. These facts indicate that the interaction between Ag and Ge atoms is strong enough to destroy the 2x1 reconstruction in the 2D Ag islands. The Ag4d peak was narrow until Ag thickness of 1.3Å, indicating that the Ag-Ag interaction is weak in the 2D Ag islands. Above 1.3Å a new broad component was observed in the Ag4d spectrum, which suggested the presence of 3D Ag islands. The breadth of the new component indicates the strong Ag-Ag interaction in the 3D Ag islands. When Ag was deposited on a Ge(001) surface at room temperature, the LEED pattern remained to be 2x1 and the shoulder due to the SCLS did not disappear in the Ge3d spectrum. The Ag4d band was broad and bulk-like. These facts indicate that Ag grows three-dimensionally and leaves intact most of the clean Ge(001)-(2x1) surface at room temperature. @FootnoteText@ @footnote 1@ F. Komori et al., Surf. Sci., 438 (1999) 123.

SS2-MoP3 Initial Growth of Ag Islands on Ge(001) Surface at Low Temperature*, **Y. Naitoh**, K. Nakatsuji, F. Komori,* ISSP, University of Tokyo, Japan*; K. Seino, A. Ishii,* Tottori University, Japan

The Ag on Ge(001) surface has been an interesting issue for the last decade since suddenly increase of the surface electronic conductivity at 2K was reported.@footnote 1@ It is suggested the interface between Ag and Ge has peculiar electronic state because neither Ag nor Ge bulk have superconductivity. In the latest STM observation@footnote 2@ showed that mono-atomic-layer (ML) thick Ag islands parallel to the dimer-row of the Ge(001) surface and Ag chains along the dimmer direction are formed at the initial stage of the Ag deposition on a 90 K substrate followed by annealing to room temperature (RT). In the present paper, we show the Ag adsorbed sites on Ge(001) surface by STM without annealing to RT. The STM experiments were performed in an ultra high vacuum (below 1x10@super -8@Pa) system. The surface of a Ge(001) crystal, which was cut from n-type Ge(001), was cleaned by several cycles of Ar@super +@ bombardment and annealing. Ag was deposited onto the clean Ge surface at 90K with the rate of 1 ML/min, and then the substrate was moved to the STM unit as keeping the low temperature. Bright dots, which indicate Ag atoms, were observed between the Ge dimer rows. It was found some dots were arranged to form chains along both the dimer row and the dimer direction having intervals of 2a@sub Ge@ (a@sub Ge@=0.4nm) and islands with 2a@sub Ge@ width elongating along the dimer row. As annealing the substrate to RT bright dots disappeared and the conventional Ag chains and islands were found to be formed. This shows Ag sites on Ge(001) surface without annealing to RT are quasi-stable. These were compared with the stable site of Ag on the surface given by the first-principles calculation. @FootnoteText@ @footnote 1@ M. J. Burns et al., Solid State Comm. 51, 865 (1984) @footnote 2@ F. Komori et al., Surf. Sci. 438, 1234 (1999).

SS2-MoP4 In-Situ X-Ray Reflectometry of the Martensitic Transformation of AuCd Alloys*, H. Shimazu,* *S. Shibata, S. Doi, I. Takahashi,* Kwansei Gakuin University, Japan*; T. Ohba,* Shimane University, Japan

Numerous works have been dedicated to the study of meaning of surfaces for bulk phase transitions. For second order transitions, importance of the dimensionality has been understood thoroughly. Thus, an answer for this issue might have been obtained. Compared to such a situation, we must admit that many phenomena at the surfaces for first order phase transitions have not fully been understood. Especially, peculiarity of nucleation and evolution of domains at the surface triggered by the first order bulk transition remain unveiled, although those in bulk have been investigated. The martensitic transformation is a first order phase transition, responsible for shape-memory effects. In a low temperature phase, bulk domains called "variants" appear. On the other hand, the surface exhibits a morphological change (surface relief). Many people consider that the surface relief is a mere termination of the bulk variants. If they are correct, the evolution of the surface relief may start simultaneously as the variants start to evolve. However, as far as the authors' knowledge, there is no accepted study on the relationship between nucleation of the surface relief and that of the bulk variants. In the present paper, we focus on in-situ observations about the surface relief and the micro-variants in the vicinity of martensitic transformations of AuCd alloys: We observed the surface relief by X-ray reflectivity, whereas Bragg reflection gave information on bulk variants.@footnote 1@ An image plate detector was adopted with an X-ray camera.@footnote 2@ Our study revealed peculiar properties on the evolution of the surface relief. They indicated that the surface plays an intrinsic role at the first stage of the martensitic transformation. An aging effect was also detected in the surface diffraction. @FootnoteText@ @footnote 1@ S. Doi and I. Takahashi; Philosophical Magazine A, 80(2000) 1889-1899. @footnote 2@ S. Shibata, S. Doi and I. Takahashi; to be published in Surface Science (2001).

SS2-MoP6 Metastable Crossed Row Structure and Nano-structural Change on TiO@sub 2@(001) Studied by STM*, R. Tero,* *K. Fukui, Y. Iwasawa,* The University of Tokyo, Japan

Atom-resolved structures on a rutile TiO@sub 2@(001) surface were visualized by scanning tunneling microscopy (STM). We have found that a flat ordered structure, which consists of crossed rows along the [110] and the [11-0] directions, can be prepared by annealing an Ar ion-sputtered TiO@sub 2@(001) surface at 850-1050 K under UHV with heating and cooling rates at 7-10 K s@super -1@. Its LEED pattern was identical to that for a {114}-faceted structure proposed in previous studies. The rows had a bleacher-like structure, which formed stairs at both sides with an average slope identical to the {114} face. An atom-resolved STM image showed that units of three bright spots, which were lined perpendicular to the steps, were arranged by 0.65 nm on each narrow step. The crossed row structure was metastable and its stability depended on the degree of the bulk reduction. Structural transformation occurred at much lower temperatures than that for preparing the crossed row structure. Particles with nm scale appeared on the crossed row structure by reannealing the surface under UHV at 400-490 K. The surface was covered up with the particles of 0.9-6 nm in diameter. Adsorption of formic acid on the crossed row structure before reannealing drastically modified the structural transformation. The particle size was distributed to 2-8 nm in diameter after the formic acid-covered crossed row structure was reannealed at 710 K. The stability of the crossed row structures and the mechanism of the particle growth, which depended on the degree of bulk reduction and reaction of adsorbates, will be discussed.

SS2-MoP7 Theoretical Analysis of Short Range Order of Au/Si(100) 5x3.2 Structure*, Y. Yagi,* *K. Kakitani, H. Kaji, A. Yoshimori,* Okayama University of Science, Japan

It is known that the metal adsorbed semiconductor surfaces show various characteristic structures. One of them is the Au adsorbed on Si(100) surface. According to the recent experimental results by STM and LEED, this system shows the 5x3.2 structure.@footnote 1-4@ Au adsorbates and Si substrate atoms form the 5x3 structure. This structure is made up with the "band" structure along the direction of 3 times and the "band" structures arrange with 5 times period in the perpendicular direction. The STM results indicate that the 5x3.2 structure seems to be formed by protrusions called "wall" in the topmost layer on the 5x3 structure. We describe this system by the lattice gas model for adsorbates (adatoms) in the topmost layer on the 5x3 structure with semi-long ranged repulsive interaction and short ranged attractive interactions, assuming that the protrusion is formed by the adsorbate (adatom), and perform Monte Carlo simulation. We obtain the two adsorbate positional correlation functions and the structure factor of this surface system. The obtained theoretical results are compared with experimental ones, in particular, the correlation function obtained from the STM images. Our results reproduce experimental features semi-quantitatively. The degree of ordering in the 3.2 times period does not seem perfect in the STM images and it may be a structure with short range order. The ratio of interactions with temperature and the most probable interaction ratios are determined by the comparison. @FootnoteText@ @footnote 1@X. F. Lin, K. J. Wan, J. C. Glueckstein and J. Nogami, Phys. Rev. B47, (1993) 3671. @footnote 2@G. Jayaram and L. D. Marks, Surf. Rev and Lett., 2 (1995) 731. @footnote 3@H. Minoda, K. Yagi, F.-J. Meyer zu Heringdorf, A. Meier, D. Kahler, and M. Horn von Hoegen, Phys. Rev. B59, (1999) 2363. @footnote 4@R. Hild, F.-J. Meyer zu Heringdorf, P. Zahl and M. Horn-von Hoegen, Surf. Sci. 454-456 (2000) 851. .

SS2-MoP9 Experimental and Theoretical Investigation of Multi-layer Films with Ultra-thin Intermediate Layers*, I.G. Levchenko,* Kharkov Aerospace University, Ukraine

The multi-layer films were applied by the ion deposition method. The three-layered and four-layered films consisting of titanium carbide, titanium nitride, chromium nitride, zirconium nitride, carbonitrides, and aluminum oxide with ultra-thin copper and silver intermediate layers were investigated. The total film thickness was ten to twenty five micrometers. The ultra-thin layers were applied between the main layers, the ultra-thin layer thickness being of ten to hundred atomic layers. The main layers were applied at a voltage of one or two hundred volts and the intermediate layers were applied at five to eight hundred volts. The conditions of intermediate layer application ensured creation of the continuous layers. The aim of ultra-thin layers was to provide relaxation in the main layers, to remove the residual stresses, to ensure the high level of adhesion force between the main layers, and to reduce the porosity due to the penetration of ultra-thin layer metal into the main layers. The measurements of the porosity coefficient were performed by electrolytic method using the hydrogen penetration. The porosity factor was found to decrease twice for copper intermediate layers and thrice for the silver intermediate layers. The micro-stress levels were found to be five times less than those for the film of the equal thickness applied without the intermediate layers. The abrasion test had shown the improved wear resistance due to the absence of microchipping as a result of low micro-stress level and high enough film thickness. The main layer application voltage - intermediate layer application voltage ratio was found to be the significant value in reducing a porosity factor.

SS2-MoP10 About the Interface between a Quasicrystal and its Oxide Overlayer*, V. Fournèe,* *J.W. Anderegg, A.R. Ross, T.A. Lograsso, P.A. Thiel,* Iowa State University

When the surface of an Al-Pd-Mn icosahedral quasicrystal (QC) is exposed to air at room temperature, an almost pure alumina overlayer develops across it. The thickness of this oxide is rather small and is similar to the passivating layer on fcc-Al. This is of course an attractive characteristic which, combined with other surface properties like low friction coefficients or low adhesion, makes QC surfaces relevant for technological applications.@footnote 1@ In particular, the low adhesion property, related to a low surface energy, is believed to be influenced by the gradient, through the surface, of the electronic density of states at the Fermi level (N(EF)). This assume that the low N(EF) characteristic of the bulk electronic structure of QC is effectively maintained up to the surface. However, in a practical situation where an aluminium oxide overlayer is formed, the interface just under the oxide may be depleted in Al and enriched in Pd and Mn. The concentration may be shifted out of the stability range of the QC phase and structural transformation may occur. This also should affect the electronic properties at the interface. In an effort to clarify this point, we will present our recent experimental results on this subject. Experiments were performed on a five-fold surface of a single grain Al-Pd-Mn icosahedral QC. The clean surface was prepared in UHV and later oxidized in-situ. A depth profile of the chemical composition across the oxidized surface is acquired both by Auger and photoelectron spectroscopies. Informations on the morphology of this surface are derived from both scanning electron and scanning tunneling microscopies. Finally, an analysis of the photoelectron core-level lineshape, as a function of the escape depth of the photoelectrons, provides insight into the variations of the metallic character through the surface. @FootnoteText@ @footnote 1@ P.A. Thiel, C. J. Jenks, A. I. Goldman, in Physical properties of Quasicrystals, ed. Z. Stadnik (Springer Verlag, Berlin, 1999).

SS2-MoP11 Temperature Effect of Well-ordered Al@sub2@O@sub3@ Film on NiAl(110), ***T.T. Lay***, *M. Yoshitake, B. Mebarki,* National Institute for Material Science, Japan

It is known that the oxidation of the (110) surface of intermetallic compound NiAl leads to the formation of a well-ordered Al@sub2@O@sub3@ film.@footnote 1@ It has the potential of application in metal-insulator-metal(M-I-M) electron emitter which needs wide gap insulator. In our previous work epitaxial ultra-thin Al@sub2@O@sub3@ film was grown on NiAl(110) by introducing 1200L oxygen at 570K and subsequent annealing at 1070K. The crystalinity of the epitaxial film varied from pressure 5 x 10@super-7@ to 5 x 10@super-8@ Torr. The best crystalinity was obtained when oxygen was introduced at pressure of 5 x 10@super-8@ Torr. However, to get 1200L oxygen at 5 x 10@super-8@ Torr, the time needed is 400minutes. For thick epitaxial Al@sub2@O@sub3@ film, multi-oxidation is required and time needed to growth desire film thickness is too long. To get well-ordered thick expitaxial Al@sub2@O@sub3@ film in higher growth rate, we have carried out the temperature control in oxidation. Oxidation temperature varied from 570K to 720K at constant pressure of 5 x 10@super-7@ Torr for 1200L. After oxidation subsequent annealing is performed at 1070K in a vacuum chamber equipped with LEED/AES. From the LEED pattern, the crystalinity of epitaxial Al@sub2@O@sub3@ film become distinct as temperature increases and shows optimum at temperature around 670K. AES measurement also has good correlation with the results of LEED patterns. The ratio of O/Ni peak intensity is directly related to film thickness.@footnote 2@ The optimum ratio of O/Ni was obtained at temperature around 670K and approximately equal to several multi-oxidations at pressure 5 x 10@super-8@ Torr at 570K. The result shows crystalinity and thickness can be control by oxidation temperature. @FootnoteText@ @footnote 1@ R.M. Jaeger, H.Kuhlenbech, H.J.Freund, M.Wuttig, W. Hoffmann, R. Franchy and H. Ibach, Surf. Sci., 259,235(1991) @footnote 2@ M. Yoshitake and B. Mebarki, 6th. Int.Symposium on Advanced Physical Fields, Tsukuba, Japan, March 6-9, 183(2001)

SS2-MoP12 Initial Growth and Alloy Formation of Ni Ultrathin Films on Pt(111), ***C.W. Su,*** National Taiwan Normal University, Taiwan, R.O.C.*; Y.E. Wu, C.S. Shern,* National Taiwan Normal University

Low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and Ultraviolet photoelectron spectroscopy (UPS) were used to study of the initial growth of Ni ultrathin films on Pt(111) at room temperature. As the coverage of Ni between 0.3 ML to 1.0 ML , a (@sr@(3)*@sr@(3))R30° commensurate structure was observed. As the coverage increases from 1 ML to 1.2 ML, the superposition of Pt(1x1) and epitaxial Ni(1x1) LEED pattern is formed. When the coverage of Ni increases from 1.3 ML to 6 ML, the structure is changed to the incommensurate epitaxy with fine satellites around the (1x1) hexagonal LEED pattern. Deposition of Ni films more than 7 ML up to 12 ML, the p(2x2) LEED pattern is appeared gradually. After high temperature annealing, the formation of Ni-Pt alloy with different coverages of Ni was confirmed by AES and UPS. The starting temperature of alloy formation increases as the coverage of Ni increases. The density of state also shows some interesting changes during the thermal annealing process.

SS2-MoP14 Photoemission from Graphite Overlayers on SiC(0001), ***T. Balasubramanian,*** Lund University, Sweden*; T. Kihlgren, L. Walldén,* Chalmers University of Technology, Sweden*; R. Yakimova,* Linköping University, Sweden

For lack of large graphite crystals with well defined termination overlayers of the material prepared by heating SiC can provide an attractive alternative to natural crystals or to samples of highly oriented pyrographite, which is often used as substrate for adsorption and absorption studies. Using LEED, STM and UPS (20 to 140 eV photon energy) for sample characterization we find that heating (2200 K, 1/2 h) an off axes (8 degrees) 4H-SiC(0001) produces a well ordered, multilayer thick overlayer, which shows a 3-fold LEED pattern and gives quite well resolved photoemission spectra. We use the latter to monitor the dispersion of valence electrons, photoemission line widths and cross sections. Particularly narrow emission lines are observed for the Fermi level electrons near K-H in the Brillouin zone and for the upper @sigma@ state at the zone center. Of interest for adsorption studies is that the latter gives a line width on par with that of the C 1s core level.For an on axes 6H-SiC(0001) crystal a similar preparation procedure yields a 6@sr@3x6@sr@3 LEED pattern and photoemission spectra with no dispersion along the c-axes for the @pi@ state, which indicates that the overlayer in this case is a single graphene layer. Such a layer in vacuum should be a zero gap semiconductor with a band crossing at K defining the Fermi level. For the adsorbed monolayer we find that the bands do not cross but form a 0.2 eV gap centered 0.35 eV below the Fermi energy. The gap splits of a thin electron gas with a filled band width of 0.25 eV and an estimated surface density corresponding to 0.06 electrons per C atom.For both mono- and multilayers the photoemission cross sections are oscillatory with nearly out of phase variations for the @pi@ and @sigma@ states when plotted versus the kinetic electron energy and the curves shifted to around 5 eV higher energy for the monolayer.

SS2-MoP15 Local Tunneling Barrier Height Measurement of Cs Monolayer on a Pt(111) Surface, ***Y. Yamada,*** *A. Sinsarp, M. Sasaki, S. Yamamoto,* University of Tsukuba, Japan

The local tunneling barrier height (LBH) image of the Cs monolayer on a Pt(111) surface is measured in atomic resolution by means of an STM technique. The Cs atoms form three different superstructures, (2x2), (@sr@3x@sr@3) and (@sr@3x@sr@3)R30, depending on its surface coverage on the Pt(111) surface. We find that the (2x2) structure is thermally stable at room temperature in contrast to other structures which disappear in few hours. Only for the (2x2) structure, we could obtain a clear atom-resolved STM/LBH image at room temperature. We find the atomic LBH distribution in the image corresponding to atomic geometry of this structure. This distribution, however, cannot be considered to be identical to the distribution of the classically defined work function. The average barrier height of this structure is, however, about 2.2eV smaller than that of a clean Pt(111) surface, suggesting the work function reduction of about 4.4eV from the clean Pt(111) value. This agrees well with our macroscopical work function results measured by means of the Kelvin contact potential method. The (2x2) surface corrugation amplitude obtained from the STM image is as large as 0.6Å, suggesting that the spatial distribution in the electron density of this structure is strongly localized, in contrast to the case of other 'metallic' superstructures, where no atomic image is observed by STM. It is speculated that the charge localization with some charge transfer causes the lowest work function of the (2x2) structure and its high thermal stability.

SS2-MoP16 Dynamics and Thermal Stability of Cs Super-structures on a Pt(111) Surface, ***T. Kondo,*** *H. Kozakai, T. Sasaki, S. Yamamoto,* University of Tsukuba, Japan

Understanding the dynamics and the thermal stability of alkali-metal atoms adsorbed on a metal surface is essentially important for controlling the monolayer growth and unveiling the origin of the work function reduction due to adsorption. We have made clear the dynamics from formation to destruction and the thermal stability of the Cs super-structures on a Pt(111) surface by means of Helium atom scattering (HAS) which enables us to study at high sensitivity the dynamics of the ultra-thin delicate layer of Cs atoms. Among three structures previously identified by LEED, both the (@sr@3x@sr@3) and the (@sr@3x@sr@3)R30° structures are found unstable and destructed at around 350K, transforming into the more stable (2x2)structure. The (2x2) structure which is stable up to about 450K exhibits a large corrugation of the potential energy surface seen by He atoms. This suggests a strong bond between Cs and Pt atoms and the localization of electron cloud density for the (2x2) structure as a result of the charge transfer from Cs atoms to the substrate Pt(111) surface. It is also suggested that the work function minimum, attained at the Cs coverage 0.25 forming the (2x2) structure, is closely related to this charge transfer. On the contrary, the small corrugation for the (@sr@3x@sr@3) structure at a full coverage indicates that a bond among adsorbed Cs atoms is metallic, the electrostatic potential being delocalized along the direction parallel to the surface.

**SS2-MoP17 ARPES Study of 2x2 Mn-Pt(111) Surface Alloys*, F.J. Palomares,* *P.P. Martin, H. Isern, M. Alonso, F. Soria,* Instituto de Ciencia de Materiales de Madrid (CSIC), Spain

The annealing of metallic layers grown on single crystal substrates has enabled the synthesis of ordered surface alloys and metastable phases non existing in the bulk diagram. This behavior has been reported for the Mn-Pt(111) interface, for which two apparently different 2x2 surface ordered alloys are identified as temperature increases. Angle-resolved photoelectron spectroscopy with synchrotron radiation has been used to study the electronic structure of thin films of these two alloys. Normal and off-normal emission geometries are investigated, for photon energies in the range of 12 to 70 eV. The corresponding results are analyzed in comparison with those from the starting Pt(111)-1x1 surface. Our data confirm that such alloy phases exhibit distinct electronic features, which are discussed taking into account the properties calculated for related systems.

SS2-MoP18 Kinematic Analysis of a Dispersion Region Probed in High-resolution Electron Energy-loss Spectroscopy*, T. Inaoka,* Iwate University, Japan

In high-resolution electron energy-loss spectroscopy (HREELS) with the specular-reflection geometry, a probed dispersion region determined kinematically depends upon the incident angle @alpha@ and the incident energy E@sub 0@. With change in @alpha@ and E@sub 0@, we make a kinematic analysis of the probed dispersion region with special attention to its width. Simultaneously, we evaluate the effect of the image force and the analyzer aperture on the probed region. Our analysis shows that, with a grazing angle @alpha@ fixed and with E@sub 0@ varied in a broad range, we can scan a sharply narrowed probed region on the wavenumber-energy (Q-@omega@) plane to make a close observation of the dispersion relation of surface-excitation modes. Even at grazing incidence, the image force has no substantial influence on the probed region, though it operates to reduce the energy-loss intensity remarkably at low E@sub 0@. When the parameter h@omega@/2E@sub 0@ becomes appreciable compared with the aperture angle, presence of the aperture causes a certain decrease in the width of the probed Q region. In the HREELS with the off-specular geometry, the incident energy E@sub 0@ is restricted to a lower range to insure sufficient intensity, and the probed dispersion region depends upon @alpha@ and an off-specular angle @theta@. With change in @alpha@ and @theta@, we make the same analysis of the probed dispersion region with close attention to its width as in the specular-reflection geometry. The results of this analysis for the off-specular geometry will also be reported at the conference.

SS2-MoP19 Spectroscopic Ellipsometry in the Infrared Range Applied on HF-cleaning*, J.-C. Cigal, G.M.W. Kroesen,* Eindhoven University of Technology, The Netherlands

Spectroscopic ellipsometry is a powerful non-destructive diagnostic tool for the study of interfaces and layered systems. By combining this method with Fourier transform infrared spectroscopy one can obtain information on the physical parameters of a complex surface like the complex refractive index, and the thickness of the different layers of the system, and on its chemical composition. We report the design of an ellipsometer running on the principle of rotating compensator ellipsometry. This technique offers many advantages compared to other photometric methods. Among them are the non-ambiguous determination of the ellipsometric parameters and the self-calibration of the apparatus. The imperfect components of the different optical elements are taken into account in the calculation algorithms. To illustrate the performance of such an ellipsometer we will clean a silicon wafer with hydrogen fluoride. The surface will be H-passivated. The wafer will be then exposed to open air. The goal of this experiment is to demonstrate the sensitivity of the instrument by analyzing the first steps of the oxidation of the silicon surface.

SS2-MoP20 Surface Structure Influence on Reactivity of Small Molecules on SrTiO@sub 3@(100) Surfaces*, L. Wang,* Pacific Northwest National Laboratory, usa*; K.F. Ferris,* Pacific Northwest National Laboratory, us*; M.H. Engelhard,* Pacific Northwest National Laboratory

Interactions of water, methanol and HCOOH with stoichiometric, stepped, and reduced SrTiO3(100) surfaces have been studied using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and electronic structural calculations. Comparison of TPD spectra and equilibrium adsorption geometries for H2O on SrTiO3(100) with unreconstructed TiO2 (110) and (100) surfaces reveals the structural influence on the water adsorption and desorption behavior. A unique geometric arrangement of surface atoms on stoichiometric (TiO2-terminated) SrTiO3(100) surfaces due to the lack of surface bridging oxygen atoms results in very different adsorption and desorption properties of H2O on SrTiO3(100) compared to TiO2 (110) and (100) surfaces. Electronic structure calculations show that stepped SrTiO3(100) surfaces enhance the localized interaction between the adsorbed molecule and the oxide surface. No reaction products were observed at above 400 K for methanol on annealed stepped SrTiO3(100). However, reactivity of methanol on SrTiO3(100) surfaces are enhanced for the reducing SrTiO3(100) surfaces prepared by Ar+ sputtering. Reaction products of H2, CH4 and CO were observed at above 400 K on the reduced SrTiO3(100) surface. Formic acid was dissociated to form formate and a surface proton below 250 K on SrTiO3(100) surfaces. Formate was decomposed primarily through dehydration to produce CO and H2O, instead of through dehydrogenation to produce CO2 and H2. Different reaction pathways were observed for formaldehyde formation from formic acid on SrTiO3(100) surfaces. On stoichiometric and stepped surfaces, formaldehyde was produced through bimolecular coupling of two formates. However, on reduced surfaces, formaldehyde formation involves the reduction of surface formate by the oxidation of reduced Ti cations.

SS2-MoP21 Anomalous Growth of Ba on Ag(111)*, O.M.N.D. Teodoro,* New University of Lisbon, Portugal*; J. Los,* FOM- Institute for Atomic and Molecular Physics, NL*; A.M.C. Moutinho,* New University of Lisbon, Portugal

The deposition of alkalis or earth alkali elements on other metals often produce a well-known decrease of the surface's work function. Such films make possible to achieve work function values lower than 2 eV. These surfaces found applications, for example, in long life cathodes or in negative ion converters. When these electropositive elements are adsorbed the work function drops steeply and reaches a minimum at coverage lower than 1 monolayer. Then, it increases slightly and the work function converges to the value of the deposited element. In this work, we report an anomalous behavior found during the deposition of barium on an Ag(111) surface. After the minimum of about 2.4 eV the work function did not increase up to 2.7 eV, the bulk barium work function, no matter the amount of barium deposited. These results were corroborated by Auger Electron Spectroscopy where we measured a permanent and constant intensity of the Ag MNN peak for high coverages of barium. To explain this anomalous growth of barium on Ag(111) we propose a model based in the diffusion of silver atoms to the barium film. Details of this model will be presented. Further experiments, showed that co-adsorption of oxygen before a second deposition of barium blocked the diffusion allowing the work function to reach the value of 2.7 eV.

Surface Science
Room 134/135 - Session SS3-MoP
Clusters and Aerosols Poster Session

SS3-MoP3 A Study on the High Rate Deposition of MgO Films Synthesized by Pulsed DC Magnetron Sputtering Process*, Y.M. Chung,* Sungkyunkwan University, South Korea

Magnesium Oxide (MgO) with a NaCl structure is known to exhibit high secondary electron emission, excellent high temperature chemical stability, high thermal conductance and electrical insulating properties. MgO films are very useful as a buffer layer for the deposition of high Tc superconducting and perovskite-type ferroelectric films, and as a protective layer for AC-plasma display panels to improve discharge characteristics and panel lifetime. For these purposes, the deposition and characteristics of the MgO films have been intensively studied by means of E-beam evaporation, Molecular Beam Epitaxy (MBE) and Metalorganic Chemical Vapor Deposition (MOCVD). However, there have been some limitations such as low deposition rate, micro-cracks during deposition process, and high erosion rate caused by ion bombardment in the glow discharge of AC-PDP. To improve these drawbacks MgO films were deposited on the dielectric substrates by pulsed DC magnetron sputtering with Mg and MgO targets. We have investigated the plasma states with various pulsed DC conditions, partial oxygen pressure and the deposition temperatures by Langmuir probe and Optical Emission Spectroscopy (OES). In order to confirm the relationships between plasma states and film properties deposition rate, microstructure, surface morphology, and composition were analyzed by Î±-step profilometer, XRD, TEM, AFM, and XPS.

SS3-MoP4 The Surface Modification of PZT by Ion Bombardment*, J.M. Choi,* Samsung Advanced Institute of Technology, Korea*; H.I. Lee,* Korea Research Institute of Standards and Science (KRISS)*; J.C. Lee,* Samsung Advanced Institute of Technology, Korea, R. of Korea*; D.W. Moon,* Korea Research Institute of Standards and Science (KRISS), Korea

The surface of PZT (Pb@sub 1.0@Zr@sub 0.4@Ti@sub 0.6@O@sub 3.0@) film is modified by ion bombardment or reactive ion etching (RIE) process.@footnote 1,2,3@ In this work, Auger electron spectroscopy (AES),X-ray photoelectron spectroscopy (XPS), medium energy ion scattering spectroscopy (MEIS) and transmission electron microscope (TEM) were adapted to quantitatively analyze the modified surface layer. The AES and XPS depth profiles always show a rapid decrease of Pb intensity in the initial stage of sputter depth profiling, which has been known as the results of surface segregation of Pb@footnote 3@. But MEIS and TEM clearly showed that it is due to the formation of Pb depleted layer due to Pb preferential sputtering. The reduction of Pb concentration in the modified surface layer was about 30% and the thickness of Pb depleted layer was about 13nm by MEIS, in agreement with a 13.2nm thick amorphic layer observed by TEM. XPS spectra showed that Pb 4f shifted to the metallic phase, whereas Zr 3d and Ti 2p shifted to the ZrO@sub 2@ and TiO@sub 2@ phase. Preliminary results on recovery of the Pb depletion by electron beam bombardment and thermal treatment will be reported. @FootnoteText@ @footnote 1@Sharmila M. Mukhopadhyay and Tim C.S. Chen. J. Appl.Phys. 74(2),872(1993).@footnote 2@June Key Lee et al. Appl. Phys. Lett.75,No.3,334(1999).@footnote 3@Yin-yin Lin,Qin Liu,Ting-ao Tang and Xi Yao. Appl. Surf. Sci.165,34(2000).

SS3-MoP5 Formation of Boron-carbon Binary Clusters by Reactive Molecular Ion Irradiation*, H. Yamamoto,* Japan Atomic Energy Research Institute, Japan*; T. Saito,* Japan Atomic Energy Research Institute, JAPAN*; H. Asaoka,* Japan Atomic Energy Research Institute

We have observed boron-carbon clusters (B@sub n@C@sub m@) emitted from a boron surface under irradiation of reactive molecular ions, such as C@sub 6@F@sub 5@@super +@, at 2-8 keV, 1µmA/cm@super 2@. In our previous work, enhanced silicon (Si@sub n@@super +@, n@<=@8) and carbon (C@sub n@@super -@, n@<=@12) cluster formation have been observed emitted from an Si(100) and graphite surface under irradiation of molecular SF@sub 5@@super +@ ions at 4 keV, 1µmA/cm@super 2@.@footnote 1@ In both clusters, the intensities of n=4 and 6 are relatively higher than those of the neighboring clusters. Silicon-carbon binary cluster was also observed by the irradiation of C@sub 6@F@sub 5@@super +@ to Si(100) surface. However, Si@sub n@C@sub m@ binary clusters which contain more than two carbon atoms (m@>=@2) were scarcely observed.@footnote 2@ In the present study, B@sub n@C@sub m@ binary clusters are formed through the reaction between the irradiated ion and target atoms. The observed clusters show a yield alternation between odd and even number of constituent atoms. The intensities of n+m=4 and 6 clusters are relatively higher than those of the neighboring clusters even at the present condition. The intensities of the B@sub n@C@sub m@ clusters (m@>=@2) are also higher than those of Si@sub n@C@sub m@ (m@>=@2). It can be considered that the B@sub n@C@sub m@ (m@>=@2) clusters are more stable than Si@sub n@C@sub m@ (m@>=@2) since the diameter of the boron and carbon atoms are not so different.. @FootnoteText@ @footnote 1@ H. Yamamoto and Y. Baba, Surf. Sci., 433-435 (1999) 890. @footnote 2@ H. Yamamoto and H. Asaoka, Appl. Surf. Sci., 169-170 (2001) 305.

SS3-MoP8 Controlled Surface Charging in XPS as a Tool for Fine Structural Analysis*, H. Cohen,* The Weizmann Institute of Science, Israel

Surface charging in XPS can seriously smear chemical information. On the other hand, it frequently provides valuable structural and electrical information. Can the controlled surface charging (CSC)@footnote 1@ become a quantitative tool? What are the limits of this probe in terms of spatial resolution, reliability and applicability? These questions and others are discussed in view of supporting experimental results. Enhanced capabilities for structural analysis, down to nm resolution, are demonstrated. @FootnoteText@ @footnote 1@ Nature 406, 382 (2000); JACS 122, 4959 (2000).

Biomaterials

Room 102 - Session BI+MM-TuM

Biomems & Microdevices

Moderator: W. Knoll, Max-Planck-Institut für Polymerforschung, Germany

8:20am **BI+MM-TuM1 Amplification of Biomolecular Interactions into Optical Signals using Liquid Crystals on Nanostructured Surfaces***, **N.L. Abbott**, J. Brake,* University of Wisconsin **INVITED**

Anisotropic interactions between thermotropic liquid crystals and surfaces typically cause liquid crystals to be "anchored" in one or more orientations near surfaces. In this talk, we report the use of surface anchoring phenomena involving liquid crystals for the imaging of biomolecular recognition events on surfaces. The approach is based on the observation that anisotropic forces acting between a liquid crystal and an appropriately designed surface can be perturbed by the formation of biological complexes on the surface. The change in structure of the liquid crystal near the surface is communicated deep into the bulk liquid crystal because the orientational correlation lengths of liquid crystals are typically large (micrometers). We report the design of surfaces with nanometer-scale topography and patterned surface chemistry such that protein molecules, upon binding to ligands hosted on these surfaces, trigger changes in the orientations of 1-20 micrometer-thick films of supported liquid crystals, thus corresponding to a reorientation of ~100,000-1,000,000 mesogens per protein. Binding-induced changes in the intensity of light transmitted through the liquid crystal are easily seen with the naked eye and can be further amplified by using surfaces designed so that protein-ligand recognition causes twisted nematic liquid crystals to untwist. We also use the average gray-scale brightness of the optical appearance of the supported liquid crystal to construct an optical response curve as a function of the amount of bound protein. This approach to detection of ligand-receptor binding does not require labeling of the analyte, does not require the use of a complex apparatus, provides a spatial resolution of micrometers, and is sufficiently simple that it may find use in rapid, direct-read assays performed away from centralized laboratories.

9:00am **BI+MM-TuM3 Micropatterns of Biomolecules on Silicon Hydride Surfaces***, J. Pipper, U. Fritz, R. Dahint, **M. Grunze**,* University of Heidelberg, Germany

Biochips yield a high potential for technological progress in the fields of diagnostics, drug discovery and nanotechnology. They are usually fabricated by photo- and softlithographic methods, various printing techniques or the use of micro electrodes. Common substrate materials are glass-, silicon oxide- and gold surfaces. A powerful alternative to these approaches is the photochemically initiated attachment of terminally functionalized 1-alkenes onto silicon hydride surfaces accompanied by Si-C single bond formation. Although the high potential use of silicon microstructures for biosensing applications has been postulated for years, it has not been exploited yet due to a lack of functional groups suitable for the coupling of biological species. Problems in surface derivatization occur as a result of unwanted parallel chemical reactions and a possible fragmentation of the organic compounds during illumination. This dilemma has now been overcome by temporarily masking the chemical functionalities with non-photolabile protective groups. The paper reports on the spatially resolved, photochemical modification of planar and porous silicon hydride surfaces for the immobilization of DNA, proteins and cells. In combination with photoactive compounds, the method of light induced surface derivatization can also be transferred to organic materials.

9:40am **BI+MM-TuM5 Nano-Scale Effects on the Interfacial Fluidity of Organic Films***, **R.C. Bell**, M.J. Iedema, K. Wu, J.P. Cowin,* Pacific Northwest National Laboratory

Interfaces cause fluids in nano-scale spaces to behave very differently than in bulk. We are able to spatially resolve this fluidity with 0.1 nm resolution and show how nanometer films of glassy 3-methylpentane (3MP) are much less viscous at the vacuum-interface than at the 3MP-metal interface using ion mobility to probe the spatially varying flow properties. The amorphous 3MP films are constructed using molecular beam epitaxy on a Pt(111) substrate at low temperatures (<30 K). A 1 eV hydronium (D@sub 3@O @super +@) ion beam gently deposits ions on or into the films (the latter by depositing more 3MP on top of the ions). The ion motion is monitored electrostatically as the film is heated at a rate of 0.2 K/s above the bulk glass transition temperature of 3 MP (77 K). However, the ions begin to move at temperatures as low as 40 K near the vacuum interface, well below the bulk glass transition temperature. The viscosity near the vacuum-interface at 80 K is found to be 12 orders of magnitude lower than that expected of a bulk film. Furthermore, the fluidity perturbations were found to persist over 2.5 nm, which was determined by precisely placing the ions at increasing distances from the interfaces and monitoring the effect on the ion's mobility. Computer modeling is employed to further extract information about the nature of these films.

10:00am **BI+MM-TuM6 Interfacial BioMEMS: Bridging the Micro to the Macro***, **T. Desai**,* University of Illinois at Chicago **INVITED**

A great deal of consideration has been given in recent years to the biological uses of micro-electro-mechanical systems (MEMS). However, such devices are not yet found in many clinical settings due to lack of appropriate interfacing between these devices and the biological world. This talk will describe approaches to engineer interfaces that enhance the biocompatibility and functionality of implantable MEMS based devices. First, the surface modification of silicon-based devices on the nanometer and micron scale to ensure device functionality and integration will be described. Such chemical modifications must be incorporated onto silicon substrates to modulate the interfacial response, while at the same time ensuring compatibility with microfabrication and micromachining processing. Secondly, microfabrication techniques that can be used to selectively attach and spatially localize chemical species in order to control interfacial reactions with the body will be discussed. By integrating surface modification protocols with MEMS processing, one can create device surfaces that interact appropriately with multiple populations of cells and the surrounding tissue. The identification of principles for engineering microdevice surfaces will aid in developing therapeutic bioMEMS, lab on a chip platforms, and drug delivery systems that can more effectively interface with the biological world.

10:40am **BI+MM-TuM8 Dynamics of Biomolecular Recognition on Calibrated Beads in Microfluidic Channels***, **G.P. Lopez**, T. Buranda, J. Huang,* The University of New Mexico*; V.H. Perez-Luna,* Illinois Institute of Technology*; L.S. Sklar,* The University of New Mexico

We have developed a new approach for the analysis of biomolecular recognition in microfluidic systems. The method is based on real-time detection of biomolecular binding to receptor-bearing microspheres comprising affinity microcolumns. The microcolumn format ensures efficient analyte contact with receptors and rapid mixing. Molecular assemblies on microspheres can be characterized and calibrated using flow cytometric techniques prior to packing. Model assays demonstrated include direct fluorescence methods of quantitatively detecting recognition of model analytes by protein receptors and ligands displayed in well-characterized affinity matrices. We establish a model system for detection of recognition between a monoclonal antibody and the FLAG@super TM@ epitope tag. The assay can detect sub-femtomole quantities of antibody with good signal-to-noise ratio and a large dynamic range spanning nearly four orders of magnitude in analyte concentration. Kinetic and equilibrium constants for the reaction of this receptor-ligand pair are obtained through modeling of kinetic responses of the microcolumn and are consistent with those obtained by flow cytometry. Because of the correlation between kinetic and equilibrium data obtained for the microcolumns, quantitative analysis can be done in minutes, prior to the steady state endpoint of the recognition reaction. The approach has the potential to be generalized to a host of bioaffinity assay methods including analysis of small molecule analytes, protein and nucleic acid complexes, and microsystem-based multi-analyte determinations.

11:00am **BI+MM-TuM9 Microfluidic Patterning of Biopolymer Matrices for Cellular Pattern Integrity***, **W. Tan**, T. Desai,* University of Illinois at Chicago

The ability to design and create biologically relevant patterns via microfluidic patterning on surfaces provides new capabilities for cell biology, the production of biosensors and tissue engineering. However, cellular patterns, defined by microfluidic methods, often lose integrity over time due to cell growth and migration immediately upon removal of the PDMS stamp. In this study, biopolymer matrices were used in conjunction with cellular micropatterning to control cell attachment, growth, and long-term maintenance of these patterns. The incorporation of appropriate matrix materials with microfluidic cell patterning methods results in highly compliant patterns of adherent human endothelial cells (HUVECs) and fibroblasts after several day in vitro. Furthermore, cell type and chemical components in these biopolymer matrices influence the ability of the biopolymer matrices to control cell growth, proliferation and compliance to the patterns. Cell growth and migration in micropatterned biopolymers such as agarose, collagen, collagen-GAG mimics, and collagen-fibronectin are quantitatively measured and compared, and cell-matrix interactions are also examined over time. Results suggest that the use of an appropriate biopolymer matrix helps to control cell growth and maintain pattern integrity for long periods of time. This is essential for conducting stable biological experiments, as well as achieving control over tissue engineering constructs with multiple cell types.

11:20am **BI+MM-TuM10 High Throughput Techniques for Non Invasive Cancer Cell Detection***, W.C. Wilson, L.F. Pardo, X.Z. Yu,* ***T. Boland,*** Clemson University

The usefulness of patterned surfaces, which specifically bind antagonists has been recognized for a wide variety of biomedical applications ranging from drug screening to tissue engineering. Current technologies for creating patterned surfaces suffer from many drawbacks. For optimized results, technologies that are flexible, use a large number of different proteins, high-throughput and inexpensive are warranted. Ink jet technology has shown promise in meeting these criteria and commercial systems are being developed. High throughput and quantitative assaying of the patterns is equally challenging. For example, in early cancer detection, it is desirable to detect a few abnormal cells within millions of normal cells. It is unlikely that PCR based techniques or gene chips will be economically feasible tools for early detection since most of the cost will be associated with analyzing normal DNA. Economical high-throughput screening and concentration technologies may be able to discriminate and select abnormal cells for further analysis. We developed a piezo driven protein and cell printer in our laboratory, able to simultaneously deposit picoliter drops of cell or protein solutions out of nine nozzles. The printer can deliver a single cell per drop to a surface with submicron resolution. Furthermore, it is equipped with a robotic arm and conveyer belt allowing for truly high-throughput printing. Examples of its use including for anti angiogenesis drug screening will be presented. Quantitative assaying is done using a cell scanner. The cell scanner has a resolution of less than 2 Âµ, is fully computer controlled, high-throughput and an economically attractive when compared to epifluorescent microscopes. Results will be presented with fluorescently labeled cells demonstrating the potential of the cell scanner for high-throughput discrimination and selection of prostate cancer cells.

11:40am **BI+MM-TuM11 Electrochemically-Activated Switching of Surface Chemistry Using Tethered Molecular Machines***,* ***B.C. Bunker,*** *D.L. Huber, J.G. Kushmerick, M. Kelly, C.M. Matzke,* Sandia National Laboratories*; J.F. Stoddart, J. Cao, J.O. Jeppesen, J. Perkins,* University of California, Los Angeles

Sandia National Laboratories is integrating "smart" coatings into microanalytical systems for transporting, separating, and detecting species such as proteins. This paper describes the first demonstration of the use of electrochemically-activated molecular machines to switch surface chemistries. The "motor" for the machines being studied consists of an open aromatic ring system (cyclobis(paraquat-p-phenylene)) referred to as the "blue-box" due to its strong optical absorption properties. Reversible oxidation or reduction of the blue box makes it attract or repel aromatic threads such as functionalized naphthalenes or tetrathiafulvalene (TTF). Researchers at UCLA have succeeded in attaching a disulfide-terminated tail to the blue box which is used to tether the blue box to gold surfaces. Ellipsometry and atomic force microscopy measurements indicate that monolayer films of the blue box are produced. Electrochemical measurements indicate that while the voltages required to reduce the blue box are similar to voltages known to induce switching of the box in solution, adsorption of naphthalene threads is irreversible. Reversible switching is only seen for TTF threads that can themselves be oxidized. Contact angle measurements show that reversible changes in surface chemistry can be induced using appropriate threads. A simple microelectronic device has been constructed to demonstrate how the molecular machines can be used to move liquids or dissolved species within microfluidic systems.

Semiconductors
Room 124 - Session SC-TuM
Semiconductor Interfaces and Thin Films

Moderator: L.J. Brillson, The Ohio State University

8:20am **SC-TuM1 Nanometer-scale Studies of Possible Dislocation Charging at GaN Interfaces***,* ***J.P. Pelz,*** *H.-J. Im, Y. Ding, E.R. Heller,* The Ohio State University*; B. Heying, J.S. Speck,* University of California, Santa Barbara*; W.J. Choyke,* University of Pittsburgh **INVITED**

Threading dislocations (TDs) in III-Nitride films are thought to be electrically active and of major concern for device applications. Several recent studies of GaN and AlGaN/GaN films suggested that TDs might develop significant fixed negative charge (up to 1 e- every c-axis lattice spacing) at or near the TD core. We have quantified possible dislocation charging near metal/GaN interfaces using ultra high vacuum Ballistic Electron Emission Microscopy (BEEM) measurements of identifiable TDs, which were compared with electrostatic modeling of conduction band (CB) bending due to fixed local negative charge. Surprisingly, measurements of TDs in GaN films (grown by molecular beam epitaxy (MBE) under Ga droplet conditions) do not indicate any negative charge at TDs close to the metal-GaN interface, with an estimated upper limit of ~0.25 (e-)/c along the TDs. In contrast, we generally observe a mild decrease in the local CB at TDs as well as at step edges, which may be due to piezoelectric surface charge induced by local stress variations. We will discuss on-going measurements of near-interface dislocation charging of III-Nitride films grown under different conditions (MBE Ga-poor, MOCVD, etc.) to investigate how growth conditions affect local dislocation charging and local transport behavior. Time permitting, we will also discuss on-going measurements of how the Schottky Barrier height on metal/SiC contacts depends on SiC polytype, interface orientation, and deposited metal. This work was supported by the Office of Naval Research.

9:00am **SC-TuM3 Nanometer-scale Studies of Phase Separation in Compound Semiconductor Alloys***,* ***B. Shin,*** *A. Lin, K. Lappo, R.S. Goldman,* University of Michigan*; M.C. Hanna, S. Francoeur, A.G. Norman, A. Mascarenhas,* National Renewable Energy Laboratory

Thin films of compound semiconductor alloys can be grown with a wide range of band gap energies and lattice constants, useful for the development of novel electronic and optoelectronic devices. In most of these systems, growth conditions have been reported for which phase separation occurs. Yet, the thermodynamic versus kinetic origin of phase separation, as well as the experimental conditions for determining the presence of phase separation has been the subject of debate for nearly 20 years.@footnote 1,2@ In thin films of compound semiconductor alloys, both the difference in binary bond lengths and the film/substrate misfit are expected to play a significant role in the initiation of alloy phase separation. In this work, we have examined phase separation in the misfit-free InAlAs/InP system using ultra-high vacuum cross-sectional scanning tunneling microscopy (XSTM) and x-ray reciprocal space mapping. For p-doped thin InAlAs layers, XSTM reveals the presence of isotropic non-uniformities which consist of nanometer-sized clusters. For thicker, undoped InAlAs layers, longer wavelength quasi-periodic modulations perpendicular to the growth direction are apparent. These lateral modulations are observed in both topographic and conductance XSTM images, suggesting that they are due to a combination of compositional and strain variations. A signature of these modulations is also apparent in x-ray reciprocal space maps. Interestingly, the modulation wavelengths increase with film thickness and are notably lower than those reported for similar films grown at higher temperatures.@footnote 3@ Together, these results suggest that phase separation is a thermally activated kinetic process which may be significantly affected by the presence of impurities such as dopants. @FootnoteText@@footnote 1@G. B. Stringfellow, J. Cryst. Growth 65, 454 (1983). @footnote 2@A. Zunger and S. Mahajan, in Handbook on Semiconductors (North-Holland, Amsterdam, 1994), Vol. 3, p. 1399. @footnote 3@H. K. Cho et al, Mat. Sci. Eng. B 64, 174 (1999).

9:20am **SC-TuM4 Scanning Tunneling Spectroscopy on Adsorbate Induced Two Dimensional Electron Systems on InAs(110)***,* ***J. Klijn,*** *M. Morgenstern, Chr. Meyer, D. Haude, R. Wiesendanger,* Hamburg University, Germany

Two dimensional electron systems (2DES) are usually prepared in heterostructures and thus buried below the surface. Scanning probe methods are consequently restricted to resolutions above 100 nm.@footnote 1@ To increase the spatial resolution, we have prepared an adsorbate induced 2DES close to the surface on n-type InAs(110).@footnote 2@ We measured the local density of states of this 2DES in zero and in finite magnetic field (T=6K, B<=6T). The data at zero field reflect the scattered wave functions at the residual dopants. The corresponding Fourier transformation identifies the k-vector of the undisturbed 2DES as the strongest contribution. However, mixing with other k-vectors due to the potential scattering leads to broadening of the k-space features. The magnetic field data show Landau quantization of the 2DES and exhibit distinct changes in the local density of states. @FootnoteText@ @footnote 1@ S.H. Tessmer et al., Nature 392(1998)51; N.B. Zhitenev et al., Nature 404(2000)473; P. Weitz et al., appl.Surf.Sci. 157(2000)349 @footnote 2@ M. Morgenstern et al., Phys. Rev.B 61(2000)13805.

9:40am **SC-TuM5 InAs Surface Passivation for Electronics and Biosensors*,* *D.Y. Petrovykh,*** University of Maryland, College Park*; M.J. Yang, L.J. Whitman,* Naval Research Laboratory

Many semiconductor-based chemical and biological sensors operate by detecting changes in the device conductivity caused by adsorption of organic or inorganic molecules on the sensor surface. The conductivity is affected by the surface charge induced by adsorbates, so sensors based on very thin films or nanostructures should be inherently more sensitive. InAs is a natural material for these applications, because the charge accumulation layer, naturally formed on its surface, provides intrinsic conductivity down to nm-scales. To be used in chemical/biological sensors, InAs films and nanostructures must be properly passivated and functionalized. Ammonium sulfide treatment, commonly used in GaAs processing, is known to effectively remove the oxide and other surface contaminants. We show that it also offers sub-5 nm etching, and the resulting S-passivated surface resists oxidation during short-term exposure to ambient air, or immersion in water (with a range of pH) or organic solvents. We will discuss the possibility of using alkanethiol films for longer-term stability and surface functionalization, including the use of selective deposition by dip-pen nanolithography. For sensor applications, it is also important to control the surface Fermi level pinning. We use conductivity measurements and electron spectroscopy to examine band bending in InAs films and the effects on the conductivity of different capping layers, passivation treatments and other common device processing steps. @FootnoteText@ This work was carried out at the Naval Research Laboratory and supported by the Office of Naval Research, National Nanotechnology Initiative Program on the Nanoscience Basis for Miniaturized, Intelligent Sensors.

10:00am **SC-TuM6 Formation of Co Silicides on Si@sub 0.7@Ge@sub 0.3@ Layer in the Presence of Thin Interposing Au Layer and Capping Ti Layer*, W.W. Wu,*** *T.F. Chiang, S.L. Cheng, H.H. Lin, L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.*; H.H. Cheng, Y.H. Peng,* National Taiwan University, Taiwan, R.O.C.

Strained SiGe alloys offer the possibility of bandgap engineering for silicon-base devices. Due to their high mobility, SiGe/Si heterostructures have been investigated for use as SiGe channels in MOSFET@super '@s as well as high speed and high transconductance MODFET@super '@s, elevated source-drain contacts and gate material in CMOS technologies. Silicide/Si@sub 1-x@Ge@sub x@/Si(001) heterostructures are promising structures for use in devices such as the heterojunction bipolar transistor and infrared detectors with high cutoff wavelength. Due to its low resistivity, low Schottky barrier, good thermal stability, and possibility of self-aligned formation at relatively low temperatures, CoSi@sub 2@ is an attractive contact material for submicron Si devices. However, in the Co/Si@sub 0.7@Ge@sub 0.3@ system, the CoSi@sub 2@ tended to agglomerate at relatively low temperatures. The formation of Co silicides on Si@sub 0.7@Ge@sub 0.3@ alloys with a thin interposing Au layer and capping Ti layer has been investigated. CoSi@sub 2@ was observed to be the only silicide phase in Si@sub 0.7@Ge@sub 0.3@ samples annealed at 650-950 °C with a thin interposing Au layer and capping Ti layer. The sequence of phase formation is the same as the reaction of Co with single-crystal Si. The presence of Au was found to decrease the formation temperature of CoSi@sub 2@ by about 300 °C compared to that of Co(30nm)/Si@sub 0.7@Ge@sub 0.3@ samples. In addition, a thin capping Ti layer improves the uniformity and thermal stability of CoSi@sub 2@ layer. For Ti(5nm)/Co(30nm)/Au(1nm)/Si@sub 0.7@Ge@sub 0.3@ system, the process window of CoSi@sub 2@ was extended to 650-950 °C. SIMS analysis indicated that a large amount of Au diffused from the Co/Si@sub 0.7@Ge@sub 0.3@ interface to disperse in CoSi@sub 2@ layer during annealing.

10:20am **SC-TuM7 Intrinsic Defects of Cl-doped ZnSe Epitaxial Layers Examined by Photothermal Spectroscopy*, K. Yoshino,*** Miyazaki University, Japan*; M. Yoneta, K. Ohimori, H. Saito, M. Ohishi,* Okayama University of Science, Japan

Photothermal (PT) measurements have recently been carried out as one of the new methods to study the physical properties of semiconductors. One of the great advantages of the PT measurements is that the nonradiative carrier recombination processes are measured directly. Therefore, the PT may complement a photoluminescence (PL) and PL excitation (PLE). Furthermore, the PT also is much easier than deep-level transient-capacitance spectroscopy (DLTS) since no electrodes are needed in the PT system. In our previous paper,@footnote 1@ the PT measurements were carried out for nondoped and N-doped ZnSe epitaxial layers grown by molecular beam epitaxy (MBE), and we obtained the nonradiative carrier recombination centers in those samples. In this paper, we carried out the PT and PL measurements on Cl-doped ZnSe epitaxial layers from 80 to 300 K. The net carrier concentration is from 5.8 ´ 10 @super 17@ to 2 ´ 10@super 18 cm@super 3@. Three distinct peaks correspond to bandgap energy of ZnSe and two kinds of Cl related centers are observed. The activation energies of the Cl defects are estimated to be about 25 and 250 meV. The energy of 25 meV is known to be an activation energy of Cl atom in the Se site and the energy of 250 meV is not unknown. The emission due to the deep defect is not observed in the PL spectrum. Therefore, it indicates the defect with an activation energy of 250 meV acts the nonradiative carrier recombination center. @FootnoteText@ @footnote 1@ K. Yoshino et al., J. Crystal Growth 214&215 (2000) 572.

10:40am **SC-TuM8 Metal-Induced States and Polytype Transformations at SiC Interfaces*, S.P. Tumakha,*** *L.J. Brillson, G.H. Jessen,* Ohio State University*; R.S. Okojie, D. Lukco,* NASA-Glenn Research Center

We have used low energy electron-excited nanoluminescence (LEEN) spectroscopy to probe electronic structure at chemically-treated and metallized 4H and 6H-SiC interfaces. SiC high temperature electronics requires metal contacts with controllable barriers and minimal deep level electronic states. LEEN spectra over incident electron beam energies E from 0.5 to 5 keV identify the presence of localized states and their spatial distribution on a nanometer scale. With increasing E, the electron cascade and resultant generation of free electron-hole pairs peak at increasing depth ranging from 10 nm at 0.5 keV to 200 nm at 5 keV. The resultant band-to-band and band-to-defect luminescence is detected selectively at the intimate metal-SiC interface, the near-interface region extending tens of nanometers into the SiC, or the bulk SiC up to 0.2 microns into the solid. Pt/Ti/SiC junctions were prepared by standard cleaning, oxidation, and etching methods. 6H-SiC exhibits optical emission that varies with depth from the intimate interface and with surface chemical preparation. The depth-dependent spectra exhibit 2.9 eV near band edge (NBE) features of 6H-SiC for bulk excitation vs. a disordered and/or defected region within a few nm of the metal contact. Spectra from the near interface region indicate the existence of a SiC polytype with a higher band gap of ca 3.4 eV - resembling 4H-SiC as well as a discrete deep level, i.e., emission energy = 1.9 eV, for a specific surface treatment. Metal-induced features on 4H-SiC are similar. In addition, oxidation before or after metallization produces 2.5 eV emission extending hundreds of nm into the 4H bulk, characteristic of polytype conversion to 3C-SiC and confirmed by TEM. A strong impurity doping dependence suggests that oxidation or metallization-induced strain drives this transformation. The structural as well as electronic changes at SiC interfaces have significant device and processing implications.

11:00am **SC-TuM9 Growth and Electrical Characterization of Ultra-Dense Phosphorous Delta-Doping Layers in Silicon*, T.-C. Shen,*** *J.-Y. Ji,* Utah State University*; M. Zudov, R.-R. Du,* University of Utah*; J.S. Kline, J.R. Tucker,* University of Illinois

If dopant atoms substitute a substantial fraction of a monolayer of the Si atoms within a crystal, the resulting 2D dopant sheet may provide unique electrical properties for novel nano-scale devices. We have demonstrated that depositing phosphine molecules onto Si(100) surfaces in ultrahigh vacuum, followed by 35-50ML of Si epitaxy at T<500K, can yield a conducting layer that does not freeze out even at 0.3K. At 1/4ML saturation coverage at room temperature, the positive phosphorous ions create very large electric fields in the growth direction, producing a tightly confined 2D electron system. Within the plane, however, wavefunctions for these bound electrons are expected to couple across relatively large distances of a few Bohr radii (~2.5nm for P-atom donors), opening up new possibilities for lateral tunnel junctions. Initial magnetotransport measurements reveal an electron density of ~ 2.6x10@super 14@cm@super -2@ (~1/4ML) at 0.3K indicating complete electrical activation of the donor layer. From 60 to 0.3K the sheet resistance grows logarithmically with decreasing T, yielding a resistance of 1.16 k@ohm@/sq and a mobility of 21cm@super 2@/Vs at 0.3K. Studies of the correlation between electrical characteristics and phosphine deposition parameters will be presented. In addition, a new paradigm for devices based on selectively patterned 2D electron/hole systems will be discussed.

Surface Science
Room 120 - Session SS+BI-TuM
Poirier Memorial Session: Self-Assembled Monolayers I

Moderator: N.D. Shinn, Sandia National Laboratories

8:20am **SS+BI-TuM1 Greg Poirier's STM Landscapes of Alkanethiol Monolayers on Gold: A Retrospective*, M.J. Tarlov,*** National Institute of Standards and Technology **INVITED**

The surface science community lost one of its bright young stars, Gregory E. Poirier, who passed away in September at the age of 39. During Greg's brief career at NIST he made many noteworthy contributions in the areas of surface science and chemical sensing, however, it was his STM studies of alkanethiol self-assembled monolayers (SAMs) on gold that earned him the greatest recognition. Greg's STM images were some of the first to reveal the structural complexity and phase behavior that governs the 2-D world of alkanethiols on gold. Through meticulous and rigorous interpretation of these images he unlocked many structural details of SAMs and gained an understanding of the molecular forces that govern the assembly of SAMs. This talk will review some of the highlights of Greg's STM studies including the rich variety of molecular-scale crystal structures of alkanethiol SAMs, their associated defect structures, and the development of a general mechanism for SAM formation.

9:00am **SS+BI-TuM3 Imaging and Diffraction: Two Complementary Probes of Self-Assembled Monolayer Structure and Properties*, G. Scoles,*** Princeton University **INVITED**

Using Self-Assembled Monolayers (SAMs) as test systems, a few introductory examples of the well known complementarity between imaging (local SAM structure and defects) and diffraction (precise determination of overall SAM structure) will be given. Starting from the pioneering detection, by Poirier, of the c(4x2) superlattice superimposed to the basic hexagonal structure of alkylthiol SAMs on Au(111), we will review the present status of the question concerning the presence of at least two inequivalent sulfur atoms in the equilibrated monolayers. After reviewing the overwhelming experimental evidence that points in that direction, we will present recent Density Functional Theory calculations that may finally provide a way out of this ten year old controversy. Returning to the complementarity between imaging and diffraction, we will point out a few less known features of both methods. In particular, the sensitivity of atomic beam diffraction to very small vertical displacements (not detectable with either X-rays or STM) will be discussed along with the possibility, offered by X-rays, to provide information on buried SAM interfaces. We will conclude showing how the synthetic flexibility afforded by SAMs coupled with the local sensitivity of STM provides unique opportunities to understand electron transfer processes at the organic/metal interface.

9:40am **SS+BI-TuM5 Characterization of Self-assembled Monolayers Using Near-edge X-ray Absorption Spectroscopy*, T.M. Willey,*** Univ. of California at Davis and Lawrence Livermore National Lab*; A.L. Vance, A.W. vanBuuren,* Lawrence Livermore National Lab*; C.F.O. Bostedt,* Univ. of Hamburg, Germany, and Lawrence Livermore National Lab*; G.A. Fox, A.J. Nelson, L.J. Terminello,* Lawrence Livermore National Lab*; C.S. Fadley,* Unive. of California at Davis and Lawrence Berkeley National Lab

We have investigated methyl and carboxyl terminated alkanethiols (hexadecanethiol and mercaptohexadecanoic acid) and other more complex self-assembled monolayers (SAMs) on Au(111). We characterize these SAMs using x-ray absorption at the Carbon K-edge, Sulfur L-edge, ans well as Oxygen and Nitrogen K-edges where applicable. Near-edge X-ray Absorption Spectroscopy (NEXAFS) gives information about chemical state, and polarization effects in these spectra probe the orientation of chemical bonds. Simple, carboxyl-terminated alkanethiols supposedly do not form well-ordered films. We currently investigate attachment, uniformity, and order of these films as a function of solvent, chemical state of the carboxyl group, and by intermixing with well-ordering methyl-terminated alkanethiols. We have also investigated attachment and order of more complex, disulfide containing thioctic acid derivatives. Preliminary results indicate that we have been successful in chemisorbing both sulfur-functionalized ends of a number of these molecules to the gold surface. T. Willey acknowledges a Student-Employee Graduate Research Fellowship through LLNL. This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL.

10:00am **SS+BI-TuM6 Structure of Alkyl Thiol and Dialkyl Disulfide on Au(111)*, H. Nozoye,*** Nanotechnology Research Institute, AIST, Japan*; T Hayashi, C. Kodama,* University of Tsukuba, Japan*; Y. Morikawa,* JRCAT, AIST, Japan

The structure and formation process of self-assembled monolayers on Au(111) have been a long-standing unsolved problem. We determined the adsorption state of alkane thiol and dialkyl disulfide with different alkyl chain length on Au(111), which are prototypical self-assembled monolayer systems, by using temperature programmed desorption (TPD), high sensitivity low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS) and density functional theory (DFT) calculation. We concluded that the SH bond of alkane thiol and the SS bond of dialkyl disulfide break below room temperature, spontaneously desorbing hydrogen and resulting in the formation of highly ordered adsorption state of thiolate on the surface. The spectra above 500cm@super-1@ contain the information of the orientation of the alkyl moiety, however, those of low energy region contain the information of the bonding between S and Au. HREELS spectra of low energy region were almost the same for all the thiolate species, irrespective of the difference of the coverage of the thiolate and of the chain length of alkyl moiety, although the spectra above 500cm@super-1@ were changed depending on the coverage of the thiolate species. The change of the HREELS spectra above 500cm@super-1@ agreed with the conclusion obtained from STM measurements, that is the lying-down configuration in the low coverage region and standing-up configuration at the saturation coverage. The HREELS spectra of the low energy region were analyzed with the DFT calculation; The location of S of the thiolate on Au(111) is the bridge site and the SC bond is inclined about 50 degree from the surface normal. From these results we concluded that the structure of the root part of the thiolate species is common, at least for alkyl thiolate with relatively short chain, notwithstanding the difference of the orientation of the alkyl moiety, that is the lying-down and standing-up structures.

10:20am **SS+BI-TuM7 Two-dimensional Phase Diagram of Decanethiol on Au (111)*, J.M. White,*** *W.P. Fitts,* The University of Texas at Austin **INVITED**

Based on variable temperature ultrahigh vacuum scanning tunneling microscopy data, we propose a two-dimensional phase diagram of monolayer decanethiol on Au(111). Four triple point temperatures were determined: T@sub1@ at ~ 27 @degree@C, T@sub 2@ at ~ 33 @degree@C, T@sub3@ at ~ 35 @degree@C and T@sub 4@ ~ 56@degree C. T@sub 1@ defines the lowest temperature melting point and T@sub 4@ defines the temperature above which striped phases are metastable. These data provide a fundamental framework to understand and control meso-scale monolayer structure; moreover, they provide fundamental insight into two dimensional phase behavior of molecules with many degrees-of-freedom.

11:00am **SS+BI-TuM9 Odd-Even Effects in the Electron-induced Damage of Biphenyl-substituted Alkanethiol Self-assembled Monolayers*, M. Zharnikov,*** *S. Frey, H.-T. Rong,* Universität Heidelberg, Germany*; M. Buck,* University of St Andrews, U.K., Scotland*; K. Heister, M. Grunze,* Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) formed on Au(111) from biphenyl-substituted alkanethiols CH@sub 3@(C@sub 6@H@sub 4@)@sub2@(CH@sub 2@)@sub n@SH (BPn) exhibit odd-even changes in the packing density and the tilt angle of the biphenyl moieties with varying length of the aliphatic part. We have applied X-ray photoelectron spectroscopy, near-edge X-ray absorption fine structure spectroscopy, infrared absorption spectroscopy, and advancing contact angle measurements to study electron beam induced damage in these systems as well as in pure aromatic biphenylthiol (BP0) SAMs on Au substrates. Although the character of the electron-induced damage in all investigated SAMs was found to be similar, the extent and rate of the observed changes exhibited a clear correlation with the packing density and orientation of the biphenyl moieties in the BPn SAMs: The densely packed BPn films are noticeably more insensitive (in terms of the orientational order, irradiation-induced desorption, and anchoring to the substrate) towards electron irradiation than the loosely packed BPn layers. The extent of the irradiation-induced damage in pure aromatic BP0 SAMs was observed to be very close to that in the loosely packed BPn films, which indicates that the former films are in some sense also "loosely packed". Considering the potential applications of the aromatic SAMs as lithographic resist or template, the introduction of the short aliphatic chain in the respective molecules provides a simple and efficient way to manipulate their reaction toward ionizing irradiation in a desirable way. This work has been supported by the German BMBF (05 SF8VHA 1).

11:20am **SS+BI-TuM10 Highly Ordered Organic Monolayers with Reduced Antiphase Domain Walls Due to Growth from Two-dimensional Gas- and Fluid- Phases***, **L. Gross**, C. Seidel, H. Fuchs,* University of Münster, Germany

The growth process of monolayers of perylene and coronene on the metal surfaces Ag(110), Au(110) 1x2 and Au(111) 23x@sr@3 was investigated by means of low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). The preparation was done by molecular beam epitaxy (MBE), with the possibility of LEED or STM measurements during evaporation. Both molecules show (restricted on Au(110) 1x2) an evolution from isotropic disordered structures in the submonolayer regime to a highly (substrate-dependent) ordered monolayer. In all presented systems the adsobate begins to form highly ordered structures just before the coverage of a complete monolayer is reached. The final monolayer structures are coincident, except coronene on Au(111) which is commensurate, furthermore perylene on Au(110) and coronene on Au(111) show uniform domain orientation. The lateral ordering process of these molecules allows epitaxial growth with a reduced density of antiphase domain boundaries, because crystallization does not start from islands in the submonolayer regime, but from two-dimensional gas- and fluid- phases.

Surface Science
Room 121 - Session SS1-TuM
Adsorption on Oxide Surfaces

Moderator: J.A. Rodriguez, Brookhaven National Laboratory

8:20am **SS1-TuM1 Microstructure of the Al@sub 2@O@sub 3@(11-20) Surface and Ultrathin Nb Films***, **G. Witte**, Th. Becker, A. Birkner, Ch. Woöll,* Ruhr-Universität Bochum, Germany

Despite the technological importance of sapphire such as a support for devices or catalysts the microstructure of its surfaces have yet not been investigated in great detail. Here we report on a combined AFM, LEED, HAS and XPS study of the microstructure of the Al@sub 2@O@sub 3@(11-20) surface and the initial growth of ultrathin (110) oriented Nb-films. The samples were first heated in air which leads to atomically flat but carbon coated surfaces as indicated by the AFM and XPS measurements and requires a further preparation by sputtering and annealing to produce clean and well ordered surfaces. The resulting surface structure was found to depend sensitively on the annealing temperature. Heating above 1300K causes a substantial oxygen reduction at the surface which is accompanied by a long ranging highly periodic surface reconstruction without facetting. The subsequent growth of ultrathin Nb-films reveals the well known epitaxial relation between Nb and sapphire but also indicates that the films are not continuos. Instead flat islands are formed in a growth mode similar to that obtained for Ni on diamond.@footnote 1@ @FootnoteText@ @footnote 1@J.Braun, J.P.Toennies and Ch.Wöll, Phys. Rev. B60, 11707 (1999).

8:40am **SS1-TuM2 Growth and Structure of Ultrathin Silver and Silver Oxide Films on Sapphire Surfaces***, F.X. Bock,* University of Maine*; S.B. Rivers,* Rhode Island College*; **R.J. Lad**,* University of Maine

Silver oxide is a p-type semiconductor that has potential applications as a sensing film or optical recording element. Silver is relatively inert towards oxygen and silver oxide is rather unstable. We studied the interactions of Ag with r-cut sapphire (@alpha@-Al@sub 2@O@sub 3@) surfaces at ambient temperature resulting from (i) thermal evaporation of Ag in UHV, (ii) evaporation of Ag in molecular O@sub 2@, and (iii) evaporation of Ag in the presence of an electron cyclotron resonance (ECR) oxygen plasma source. Pure Ag deposited in UHV grows with a random polycrystalline structure. However, when Ag is evaporated in a 10@super -4@ Torr molecular O@sub 2@ background, epitaxial Ag growth with (110) orientation is observed as determined by RHEED and XRD. No oxygen is incorporated in the film as measured by XPS and only a slight lattice mismatch at the Ag/sapphire interface is found suggesting that the adsorbed oxygen acts as a surfactant in influencing the Ag nucleation and surface transport. Using an ECR oxygen plasma, Ag@sub 2@O is formed with a structure being dependent on deposition rate; below 0.2 Å/s, (111) orientation is formed while at faster rates the oxide is amorphous. The Ag@sub 2@O films are unstable above ~180@super o@C. AFM observations of the evaporation process following vacuum annealing treatments indicate that the decomposition occurs through a nucleation process leaving behind metallic Ag clusters on the bare sapphire.

9:00am **SS1-TuM3 STM Study of Metal Growth on ZnO Surfaces***, **O. Dulub**,* Tulane University*; L.A. Boatner,* Oak Ridge National Laboratory*; U. Diebold,* Tulane University

Metals on ZnO surfaces are widely applied in catalysis, gas sensing, and microelectronic fabrication. The morphology of the polar zinc-terminated (0001) and oxygen-terminated (000-1), as well as the non-polar (10-10) and (11-20) prism faces of ZnO was investigated with STM. Images of polar surfaces, prepared by sputtering and annealing at 500-750°C, show two types of terraces rotated by 60° with respect to each other. Mono-atomic steps alternate between straight and saw-toothed profiles. Increasing the annealing temperature to 800°C smoothes the surfaces but creates a higher density of small holes on the stepped terraces. A (1x3) reconstruction was observed on the ZnO (000-1) surface after annealing at 750°C. After sputtering and annealing the ZnO (10-10) surface at 550â€“700°C, the terraces are separated by steps running along either [000-1] (type A) or [11-20] (type B) directions. The same treatment of the ZnO (11-20) surface leads to a â€œwavyâ€� surface morphology, i.e., hills (consisting of small terraces) with an average height of 80Å and a separation of 55Å. Near-atomic resolution was achieved on both non-polar faces. Cu nucleation is strongly correlated with surface defects. Cu deposited on a "freshly-annealed" ZnO (10-10) surface shows preferential nucleation of exclusively 3D islands oriented perpendicular to the atomic row direction at the step edges. When the density of impurity atoms on the terraces is high, both 2D and 3D islands are randomly distributed across the terraces. These results are compared with those obtained for growth of Cu and Pt on the other faces of ZnO. Work performed at Tulane was supported by a NSF-CAREER grant. ORNL is supported by the U.S. DOE-BES under contract No. DE-AC05-96OR22464.

9:20am **SS1-TuM4 Metal - Support Interactions between Pt and Thin Film Cerium Oxide@footnote 1@***, **D.R. Mullins**, K. Zhang,* Oak Ridge National Laboratory

We have examined the interaction between Pt and reduced or oxidized cerium oxide (CeO@sub X@). Reduced CeO@sub X@ strongly modifies the chemisorption of CO on the supported Pt. Two different modifications are evident depending on how the sample is annealed. If the sample is annealed to greater than 800 K, the amount of CO that adsorbs on the Pt at 150 K is dramatically reduced. In addition, annealing at elevated temperatures decreases the Pt XPS intensity significantly. These results suggest that, similar to Pt on reduced TiO@sub X@, the Pt is covered by the reduced CeO@sub X@ at elevated temperatures. If the sample is annealed to 700 K or less before CO is adsorbed at 150 K, there is no decrease in the amount of CO that adsorbs. However, the CO desorption temperature is shifted to a much lower temperature compared to CO adsorbed on a Pt single crystal. This shift in the CO desorption temperature is ascribed to a weakening of the CO - Pt bond that results from an electronic interaction between the Pt and the reduced ceria. The behavior of Pt on CeO@sub X@ is very different from Rh on CeO@sub X@. The CO - Rh bond is strengthened on CeO@sub X@ compared to Rh single crystals and there is an increase in the CO dissociation activity. Rh also shows no evidence of encapsulation when annealed to higher temperatures. CO desorption from Pt on oxidized CeO@sub 2@ resembles that observed from Pt on Al@sub 2@O@sub 3@ and from Pt single crystals and therefore indicates no significant modifications of the Pt chemisorption properties by the CeO@sub 2@. @FootnoteText@ @footnote 1@Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

9:40am **SS1-TuM5 Electronic Structure of Epitaxial Thin NiO(100) Films Grown on Ag(100): Towards a Firm Experimental Basis***, L. Duò, M. Portalupi, G. Isella, R. Bertacco, **M. Marcon**, F. Ciccacci,* Politecnico di Milano, Italy

In the field of electron correlations in solids NiO definitely plays a key role. A large amount of work on the electronic and magnetic properties of NiO has been done, but the longstanding problem of the full description and understanding of its electron states is still open. While for photoemission (PE) results on NiO a large set of data is available in literature, with a general consensus on the lineshapes, concerning inverse PE (IPE) only few pioneering works have been carried out in the early eighties. They gave rise to significant discrepancies, due both to the quality of the sample and to charging problems. This has relevant consequences concerning the application of model systems in terms, e.g., of the magnitude of the correlation energy and the charge transfer energy . On the other hand, very recently the possibility of growing well characterized NiO(100) monocrystalline thin films has shown up. This is achieved by evaporation of Ni in an O@sub 2@ atmosphere onto Ag(100), whose lattice parameter agrees with that of NiO. We have therefore measured IPE spectra of NiO(100) thin films (up to about 50 monolayers) grown by such a method. By studying the dispersion behavior of the various IPE features we were able to classify them as d- or sp-derived states and a d-like ligand hole structure at high energy is clearly shown. By combining these results to X-ray photoemission spectroscopy taken on the same surfaces we find that the magnitude of the gap is similar to what previously found. A new aspect is instead related to the position of the Fermi level (E@sub F@) which is near the middle of the gap. This is at variance with previous results which showed a strong pinning of E@sub F@ at the top of the valence band and were interpreted in detail as an intrinsic effect of "pure" NiO.

10:00am **SS1-TuM6 Surface Structures of Ultrathin Vanadium Oxide Films on Pd(111)@footnote *@***, **S. Surnev,*** Karl-Franzens-Universität Graz, Austria*; G. Kresse,* Universität Wien, Austria*; M.G. Ramsey, F.P. Netzer,* Karl-Franzens-Universität Graz, Austria

The growth and the atomic structure of epitaxial vanadium oxide thin films on Pd(111) have been investigated by scanning tunnelling microscopy (STM) and low-energy electron diffraction (LEED), combined with ab-initio density-functional theory (DFT) calculations. At submonolayer coverage a well ordered (4x4) oxide overlayer forms which transforms into a porous oxide network with an internal (2x2) periodicity upon exposure with H@sub 2@ at room temperature. The reactivity of the (4x4) phase towards H@sub 2@ is very high, so that small amounts of H@sub 2@ from the residual atmosphere are often sufficient to promote this transformation. The (2x2) phase represents an interface-stabilised surface-V@sub 2@O@sub 3@ layer, which becomes compact upon mild annealing in vacuum exhibiting a (2x2) honeycomb structure. Between 0.5 and 1.0 monolayer equivalents (MLE) the growth of oxide islands with a zigzag stripe structure is observed along with the (2x2) layer. At 1 MLE several VO@sub 2@-like phases are coexistent at the surface in the form of islands with rectangular and hexagonal structures, which are distinguished from the known bulk-type rutile VO@sub 2@ lattice. The detailed atomic structure and energetic stability of these monolayer V-oxide phases have been revealed by the DFT calculations. Above 2 MLE three-dimensional crystallites grow epitaxially on Pd(111) with the corundum structure, which is typical of the bulk-type V@sub 2@O@sub 3@. Two stable V@sub 2@O@sub 3@(0001) terminations have been found in the STM images, which are due to bulk-type oxygen planes and terminal vanadyl species, as suggested by the DFT calculations and confirmed by HREELS. @FootnoteText@ @footnote *@ Supported by the Austrian Science Foundation.

11:00am **SS1-TuM9 Dissociative Adsorption of NO on TiO@sub 2@ (110) Surfaces***, **J. Abad**, O. Böhme, E. Roman,* Institute of Materials Science of Madrid, Spain

The interaction of NO with stoichiometric and defective TiO@sub2@ (110) surfaces has been studied by x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and low energy electron diffraction (LEED). Surfaces with different degree of defects have been characterized monitoring the evolution of the electronic surface structure, with the aim to study the influence of the surface defects on the interaction with NO. The interaction was studied for exposures up to 500L. However, the main effects occur already in the first 2L. The exposure of the surfaces to NO resulted in healing of defect sites without nitrogen adsorption.

11:40am **SS1-TuM11 Investigation of Internal Interfaces: Characterization of Structure, Chemistry, and Relative Adhesion at Metal-Ceramic Interfaces***, **E.A.A. Jarvis**[1], E.A. Carter,* University of California, Los Angeles

Reliable, detailed characterization of internal interfaces has become a topic of increasing interest over the past decade. Naturally, both fundamental scientific interest and a wide variety of applications may benefit from improved understanding of heterogeneous interfaces. We employ pseudopotential, planewave density functional theory to investigate local structure and chemistry at several metal-ceramic interfaces. The particular systems under investigation may hold implications for technological advancement of thermal barrier coatings for jet engine turbines. Specifically, we study interfaces between nickel "alloys" and zirconia as well as the nickel-silica interface. By selectively varying the composition of the metal alloy we compare relative adhesion at these interfaces. Our results indicate that inclusion of early transition metals (Group III and IV) at the nickel-zirconia interface may dramatically increase the interface adhesion strength. The potential application of silicon additions designed to form protective oxides on nickel alloys is discussed in light of our predicted behavior of such interfaces under high temperature conditions similar to those anticipated in jet engine turbine applications. For all systems studied, we analyze the geometric structure and the behavior of the valence electron density to provide insight into the bonding character as well as the trends in adhesion at these interfaces.

Surface Science
Room 122 - Session SS2-TuM
Water at Surfaces

Moderator: E.M. Stuve, University of Washington

8:20am **SS2-TuM1 A Molecular Beam Study of Water Adsorption, Desorption, and Clustering on Pt(111)***, **J.L. Daschbach**, B.M. Peden, G. Teeter, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

Adsorption, desorption, and clustering are investigated by molecular beam techniques. Specular He atom scattering is used to probe the sub-monolayer H2O surface coverage on Pt(111) over the temperature range 22K to 185K. Structural rearrangements of H2O adsorbed at 22K are studied as a function of initial coverage and temperature in the coverage range from 0.01 ML to 1.0 ML by measuring the specular He intensity using linear temperature ramps in the range 0.1 K/s to 10 K/s. Either or both of two transitions are observed depending on coverage, with the first corresponding to the onset of surface diffusion and trapping of mobile H2O by step edges or defects, and the second corresponding to Oswald ripening of 2-D condensed phase islands. Adsorption and desorption kinectics are interrogated isothermally by measuring the H2O coverage in time as a function of H2O beam flux and temperature. At temperatures between 150 K and 165 K the adsorption and desorption spectra are linear in time and therefore independent of coverage. In this region the desorption kinetics are strictly zero-order and can be measured with high precision. The zero order kinetics are a consequence of the existence of a 2-D two phase H2O system present on the Pt surface. At temperatures above 172 K, depending on flux, a transition to non-zero order kinetics is observed with the kinetics consistent with first order. This transition occurs when the system has moved from a two-phase coexistence region to a single phase 2-D gas.

8:40am **SS2-TuM2 Water/MgO Interactions after High Temperature Annealing***, **C.J. Hirschmugl**, M. Harland,* University of Wisconsin-Milwaukee*; R. Plass,* Sandia National Laboratories*; K. Rewolinski, M. Gadjardziska-Josifovska,* University of Wisconsin-Milwaukee

Infrared transmission measurements of MgO(100) and MgO(111) samples as a function of annealing (between 900-1500K) and exposure to air, reveal strikingly different absorption signatures. The measurements are taken 30 degrees from normal incidence to couple to vibrations of adsobates perpendicular and parallel to the surface. Previously, it has previously been surmised that MgO(111) samples annealed to 1500 K undergo a reconstruction at the surface, while MgO(100) does not undergo any similar reconstruction. Notably, the infrared absorption observed for both terminations of MgO(100) and (111) were similar. Samples annealed to 900 K show broad water absorption bands between 3400-3600 cm@super -1@, corresponding to a layer of hydrogen bonded water at the surface. However, this prominent feature disappeared for samples annealed to 1500 K, and a series of weak, sharper bands appeared over the same frequency range. An examination with D@sub 2@O will be used to identify the nature of the bands due to interaction between MgO and water.

9:00am **SS2-TuM3 Morphology of Vapor-Deposited Ice at Low Temperatures by Atomic Force Microscopy***, **S.C. Fain**,* University of Washington*; J.M.K. Donev,* University of Washington and Pacific Northwest National Laboratory*; S.A. Joyce,* Pacific Northwest National Laboratory

Atomic force microscopy (AFM) is being used to study the morphology of multilayer films of vapor-deposited water ice on various substrates as a function of deposition and annealing temperatures below 150K. These experimental studies are coordinated with theoretical studies by other investigators to provide improved understanding of ice growth and

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

properties of ice for use in other fields. For example, nucleation and growth of crystalline ice particles in the upper atmosphere is of central importance for cloud formation, global energy balance, and dynamics of ozone depletion. For these experiments the films are deposited in-situ in ultra-high vacuum from an effusive doser at an angle of 67 degrees from the surface normal. The first measurements were made for ice films deposited on Au(111) on mica. These films were profiled by a probe tip attached to a quartz crystal (Omicron needle sensor) which provides nanometer resolution of surface features. Films deposited below 100K appear relatively flat, adopting the surface texture of the Au(111) substrate. Three-dimensional clusters typically 30 nm high form after annealing these films up to 130K. The lateral dimensions of the clusters depend on the initial coverage. These changes are produced by surface diffusion producing a non-wetting film. The rearrangement happened even if the annealing was done without imaging. Previous thermal desorption measurements by Kay and coworkers [J. Chem. Phys. 91, 5120-5121 (1989) and Surface Science 367, L13-L18 (1996)] have inferred amorphous ice clusters surrounded by bare substrate for films deposited on Au(111) at low-temperatures. Further measurements are in progress using non-contact AFM (Omicron beam-deflection) with the same deposition geometry and different substrates. Supported by Department of Energy's Office of Biological and Environmental Research, a U. W. Nanotechnology Fellowship Award to J.M.K.D., and NSF KDI 99-80125.

9:20am **SS2-TuM4 Initial Growth of Water on Ru(001) and Cage Formation of CD@sub 3@Cl***, **Y. Lilach**, V. Buch, M. Asscher,* The Hebrew University, Israel

The adsorption of H@sub 2@O on Ru(001) and the coadsorption system H@sub 2@O+CD@sub 3@Cl/Ru(001) were studied using Temperature Programmed Desorption (TPD) and work function change (@DELTA@@PHI@) measurements. We developed a kinetic model that fits the measured @DELTA@@PHI@ upon water adsorption at 80K. The model indicates that at very low coverages water monomers dominate, while as coverage increases di- tri- and tetramers are formed. Water tetramers were observed recently by IR measurements to be the dominant species in similar adsorption conditions. The effective @DELTA@@PHI@ contribution of these species suggests an adsorbed cyclic tetramer, with inclined water dipoles. Molecular Dynamics (MD) simulations using the TIP4P potential energy surface for the water-water interaction, were performed as a means for gaining deeper insight into the experimental results. The effective dipoles of the small clusters obtained from the MD simulations were in good agreement with the dipoles predicted by the kinetic model. Adsorbed CD@sub 3@Cl molecules were found to be compressed and then caged under H@sub 2@O layers, as indicated by complex @DELTA@@PHI@ curves monitored upon adsorption. These are explained by the following sequence (a) H@sub 2@O molecules initially compress CD@sub 3@Cl into separate islands. Desorption from this stage suggests that the structure of methyl chloride resembles that of multilayer CD@sub 3@Cl, namely chlorine down in the first layer, while in the second layer it flips up. (b) Hydrophobic displacement of CD@sub 3@Cl from surface sites to become trapped within the water layer. Further increase of the water coverage produces a tight cage of the CD@sub 3@Cl molecules inside the ice structure, as indicated by a sharp, explosive desorption at 165 K.

9:40am **SS2-TuM5 Using Nanoscale Amorphous Films to Study Mixing, Transport and Phase Separation in Deeply Supercooled, Metastable Binary Solutions of Methanol, Ethanol, and Water***, **P. Ayotte**, Z. Dohnalek, G.A. Kimmel, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

The relatively large diffusivities exhibited by amorphous deposits of water, methanol, and ethanol at cryogenic temperature (<160K) opens up the possibility to investigate liquid-phase kinetics in the deeply-supercooled, metastable thin film regime. Compositonally tailored, multilayer films grown by molecular beam dosing techniques are particularly well suited for the characterization of diffusion and desorption kinetics as shown previously for thin film water. While it is well-known that liquid mixtures of alcohol and water exhibit non-ideal solution behavior due to hydrophobic solvation, the complexity of their liquid-solid phase diagrams has been interpreted in terms of formation and decomposition of different crystalline hydrates (stochiometric and/or clathrates). We use molecular beam scattering and programmed desorption (both TPD and isothermal) to study the desorption and mixing kinetics as well as the crystallization of mixed multilayer ices of water, ethanol, and methanol. The desorption spectra exhibit complex features that depend strongly on both the film's composition and thickness. Analysis of the desorption spectra using a kinetic model that describes liquid solution evaporation reveals both the extent of mixing and the details of the solvation kinetics in the metastable liquids. We compare these results with existing liquid-solid phase diagrams for these binary mixtures. While thin binary films of methanol and ethanol exhibit ideal behavior, binary mixtures of water and either alcohol display strongly non-ideal behavior presumably caused by precipitation of solid crystalline hydrates from the deeply-supercooled, metastable liquid solutions. @FootnoteText@ P. Ayotte is an NSERC Postdoctoral Fellow. Pacific Northwest Laboratory is a multiprogram National Laboratory operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

10:00am **SS2-TuM6 Crystallization Kinetics of Amorphous Solid Water on Hydrophobic and Hydrophilic Substrates***, **G. Teeter**, Z. Dohnalek, R.S. Smith, G.A. Kimmel, B.D. Kay,* Pacific Northwest National Laboratory

The crystallization kinetics of thin film (5-200 BL) Amorphous Solid Water (ASW) has been studied using Temperature Programmed Desorption (TPD) and Fourier Transform Infrared Spectroscopy (FTIR). ASW thin films were deposited by molecular beam on clean, well-ordered Pt(111) and decane (C@sub 10@H@sub 22@) thin film substrates in order to probe the dependence of H@sub 2@O crystallization kinetics on substrate-H@sub 2@O interactions. H@sub 2@O wets the Pt(111) surface and is non-wetting on the decane substrate. In both cases crystallization of the ASW thin film proceeds via nucleation and 3D growth of the crystalline phase. As-deposited ASW kinetically wets the decane substrate at low temperature, but TPD and FTIR results indicate that crystallization is accompanied by de-wetting the H@sub 2@O film from the decane substrate. Details of the experimental techniques, results, and implications will be presented.t. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830. a.

10:20am **SS2-TuM7 A Two Step Dissociative Ionization and Desorption Mechanism for Water Ion Cluster Emission from a Pt Field Emitter Tip***, **C.J. Rothfuss**, V.K. Medvedev, E.M. Stuve,* University of Washington

Our recent work on the behavior of water molecules adsorbed on a Pt emitter tip in high fields (~1 V/ Å) has provided an understanding of the behavior of water dissociation and ion cluster [H@super +@(H@sub 2@O)@sub n@] emission. Water ion emission from an emitter tip has traditionally been treated as a single step event. While differing n cluster types have been observed, typically ranging to 10 or above, no detailed explanation of the mechanism for cluster formation has been suggested. Mass resolved ramped field desorption experiments from field adsorbed water layers (T>170K) have given field dependencies for specific ion cluster masses. As the field was ramped, each cluster type was observed, in turn, beginning with high n clusters and transitioning to lower n clusters. The emission of high n clusters was energetically favored, while low n clusters were favored kinetically. However, at low temperatures (T

10:40am **SS2-TuM8 Bonding of Water to Metal Surfaces Studied with Core-level Spectroscopies***, **H. Ogasawara**, D. Nordlund,* Uppsala University, Sweden*; B. Brena,* University of Stockholm, Sweden*; L.-Å. Näslund, M. Nagasono,* Uppsala University, Sweden*; L.G.M. Petterson,* University of Stockholm, Sweden*; A. Nilsson,* Uppsala University, Sweden and Stanford University, Sweden

The chemical interaction between water and a metal surface is important in many practical fields, including corrosion, electrochemistry, molecular environmental science and heterogeneous catalysis. On smooth metal surfaces, (e.g. fcc(111) or hcp(0001)), water molecules adsorb intact with strong intermolecular forces between the water molecules. This leads to the formation of a hexagonal two-dimensional ice lattice proposed as a "bilayer structure".@footnote 1@ The unit cell contains two water molecules, which are different in the interaction with respect to the metal surface. We have studied the water "bilayer structure" on Pt(111) with X-ray absorption and X-ray emission spectroscopies. These two techniques provide atom specific information about electronic structure. We have identified two different water-metal chemical bonds in the "bilayer structure". @FootnoteText@ @footnote 1@ P.A. Thiel and T.E. Madey, Surface Science Reports 7, 211 (1987).

11:00am **SS2-TuM9 The Interaction of Carbon Monoxide with Hydrogen-bonding Molecular Ice Surfaces***, J.W. Dever, M.P. Collings, **M.R.S. McCoustra**,* University of Nottingham, UK

Carbon monoxide (CO) is the second most abundant molecule in the Universe after hydrogen. It's interaction with solid grain surfaces is key therefore to understanding gas-grain interactions in the interstellar medium, whether those interactions relate to the freezing out of molecules on grains in cold, dark molecular clouds or their eventual reappearance in the gas phase and their role in radiative cooling of warm, collapsing protostellar objects. Using a combination of temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS), we have conducted state-of-the-art surface physicochemical studies of the interaction of CO with hydrogen-bonded molecular ice (water, ammonia and methanol) surfaces that represent a model of the surfaces of some types of interstellar grains. We will present the results of these first detailed ultrahigh vacuum studies of realistic gas-grain interactions and their interpretation in terms of simple models of the CO-ice interaction.

11:20am **SS2-TuM10 Water Reactivity with MgO(100)Thin Film Surfaces Studied by Electron Stimulated Desorption***, D. Cáceres, I. Colera, I. Vergara, R. González,* Universidad Carlos III de Madrid, Spain*; E.L. Román,* ***J.L. de Segovia,*** CSIC, Spain

The adsorption of two isotopic forms of water, D@sub 2@ @super 16@O and H@sub 2@ @super 18@O, with well characterised MgO(100) thin film surfaces at 300 K was studied by Electron Stimulated Desorption, ESD. Oriented MgO(100) thin films were grown on Si(100) at 940 K by rf-sputtering with a Mg target and at a total pressure of 7 x 10@super -3@ mbar (10% O@sub 2@ and 90% Ar). These films were characterized by X-Ray diffraction, Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS), and Electron Energy Loss Spectroscopy (EELS). Previous ESD results@footnote 1,2@ of O@super +@ desorbed species from clean surfaces of bulk MgO(100) showed a bimodal energy distribution structure with peaks at 6 and 9 eV. Their origin was assigned to O@super +@ desorption from surface defects and to desorption from the oxide, respectively. The aim of the present ESD study of MgO(100) thin films is twofold: (i) to compare the previous results on bulk defective surfaces (stepped or with oxygen vacancies) with a thin film surface with no steps, and (ii) to study the reactivity of water with these thin films, and the influence of surface defects on the hydrolisis processes. D and @super 18@O isotopes were used to distinguish them from the H contamitation and from the @super 16@O of the oxide, respectively. Ion yield experiments using H@sub 2@ @super 18@O show @super 18@O@super +@ and @super 18@OH@super +@ desorbed ions in addition to the usual H@super +@ and @super 16@O@super +@ ions. The adsorption of @super 18@O is related to the @super 16@O defective sites on the MgO(100) thin films. Preliminary results indicate that the Feibelman-Knotek mechanism is responsible for the desorption processes. Ion kinetic distribution curves at different electron energies are also discussed. @FootnoteText@@footnote 1@ I. Colera, E. Soria, E. Rom@aa a@n and R. Gonz@aa a@lez, Vacuum 48 nº 7-9 pag 647 to 649 (1997) @footnote 2@ I. Colera, R. González, E. Soria, J.L. de Segovia, E.L. Román and Y. Chen, J. Vac. Sci. Technol. A 15(3) pag 1698-1703 (1997).

11:40am **SS2-TuM11 The Influence of Calcium Carbonate Coatings on Contamination Reactivity***,* ***T. Droubay****, S.A. Chambers,* Pacific Northwest National Laboratory

High energy-resolution x-ray photoemission spectroscopy (XPS) is used in conjunction with scanning probe microscopy to investigate the influence of calcium carbonate coatings on the adsorption of aqueous CrO@sub 4@@super 2-@ on epitaxial Fe@sub 3@O@sub 4@/MgO(001) surfaces prepared by oxygen plasma assisted molecular beam epitaxy (OPA-MBE). Deposition of calcium carbonate films was accomplished with the use of a polymer-induced liquid-precursor (PILP) process, which utilizes polyaspartate to suppress growth of crystal aggregates and results in the formation of flat films. Of the three polymorphs of CaCO@sub 3@, the films primarily consist of a combination of vaterite and calcite with undetectable amounts of aragonite. X-ray photoemission analysis and atomic force microscopy reveal a thin polymer interfacial layer between the underlying Fe@sub 3@O@sub 4@ and carbonate overlayer which acts as a template for vaterite growth. An increase of the intensity in the low binding energy shoulder of the Fe 2p@super 3/2@ core-level and a decrease in the Fe(III) non-charge transfer satellite is evidence of an increase in Fe(II) at the magnetite surface as a result of the aqueous growth environment. This result is consistent with surface reduction found during the interaction of Fe@sub 3@O@sub 4@/MgO(001) with liquid water. The effects of carbonate coating on substrate reactivity, emphasizing electron transfer reactions responsible for the reductive immobilization of Cr(VI)O@sub 4@@super 2-@ will be discussed. These results have application in chromate remediation efforts centered on the reduction of chromate contamination by Fe(II).

Surface Science
Room 120 - Session SS+BI-TuA
Poirier Memorial Session: Self-Assembled Monolayers II
Moderator: M.J. Tarlov, NIST

2:00pm **SS+BI-TuA1 Self-Assembling Monolayers and Thin-Film Templates - Driven Assembly of Functional Organic Structures*, R.G. Nuzzo,*** University of Illinois at Urbana-Champaign **INVITED**

The properties of complex matter and assemblies follow from structural elements embedded at a variety of length scales. These influences begin at the most microscopic level--that is at sizes associated with the atomic or molecular constituents--and extend upwards through increasingly more complex hierarchies of organization. While it is common in research to focus on organizations that arise via a thermodynamically directed assembly, it is now possible to design and study assemblies that form solely as a result of the temporal evolution of the underlying dynamics of the system. In this talk I will explore these ideas, focusing on the important role played by dynamics in prototypical complex organic thin-film assembly systems. Specific attention will be given to thin film systems that develop interesting mesoscopic organizations as a result of driven processes occurring at a substrate surface.

2:40pm **SS+BI-TuA3 Adsorption and Photoinitiated Chemistry on Organic-functionalized Semiconductor Surfaces*, N. Camillone III,*** *K. Adib, R.M. Osgood, Jr.,* Columbia University

Greg Poirier's pioneering imaging work had a specific and important role in the scientific and intellectual development of one of the authors (N.C.), and played an instrumental part in the growth of our understanding of the structure and dynamics of self-assembled monolayers. Many experiments have been conceived based upon this understanding. We report results of one such experiment, which characterizes the growth and photoinitiated chemistry of methyl bromide monolayers adsorbed at the surface of short-chain thiolate monolayers on GaAs(110) surfaces. The thiolate monolayers are grown in UHV by exposure of the GaAs to alkyl disulfides. Temperature programmed desorption reveals that the CH@sub 3@Br-surface interactions are strongly modified by the presence of the thiolate spacer layer. With increasing chain length, the CH@sub 3@Br becomes progressively less tightly-bound. The simple layer-by-layer growth behavior observed on bare GaAs(110) is lost, and CH@sub 3@Br appears to form clusters at critical coverages. Exposure to 248 nm light results in the dissociation of the CH@sub 3@Br, most likely due to the dissociative attachment of excited substrate electrons. The cross section for the reaction is strongly enhanced in the case of the ethyl disulfide spacer layer. The implications of the results will be discussed within the context of electron transport through molecular spacers, adsorbate affinity level shifts, and deexcitation mechanisms.

3:00pm **SS+BI-TuA4 Photoinduced Processes in Self-Assembled Monolayers on Semiconductor Surfaces*, T. Ye,*** *E. McArthur, E. Borguet,* University of Pittsburgh

The photoreactivity of ODS(Octadecylsiloxane) SAMs on semiconductor surfaces under UV illumination in air, has been investigated by a combination of contact angle, FTIR and AFM. This work provides strong evidence that SAM degradation does not result from ozone alone. A combination of UV and oxygen is necessary for monolayer degradation to proceed. AFM measurements on submonolayer coverage SAMs provide direct evidence of the degradation of ODS SAMs and reveal the role of defects in the degradation process. FT-IR and AFM results suggest that the hydrocarbon chain is the reactive site of the monolayers. A microscopic mechanism of the degradation involving hydrogen abstraction is suggested based on the mechanism of gas-phase oxidation of alkanes. These results have implications for photoresist micropatterning and nanotechnology applications that require high spatial resolution.

3:20pm **SS+BI-TuA5 Organic Monolayers on Silicon and Silica Surfaces Via Covalent Linkages*, X.-Y. Zhu,*** University of Minnesota **INVITED**

Monolayer assemblies on silicon and silica surfaces are of interest for a number of technological reasons, such as substrates in micro-arrays, surface passivation in MEMS, and monolayer mask in soft-lithography. I present novel approaches for the formation of molecular monolayers on silicon and silica surfaces. These approaches rely on a two-step strategy: in the first step, a silicon or silica surface is activated to give reactive functional groups; in the second step, the activated surface reacts with simple organic molecules for monolayer assembly. Examples of alkyl, aromatic, and PEG monolayer assemblies will be presented and their applications in MEMS and micro-arrays will be demonstrated.

4:00pm **SS+BI-TuA7 Study of Alkylsilane Monolayers Islands on Mica in the Presence of Water*, M. Luna,*** Lawrence Berkeley National Laboratory*; I. Diez, F. Teran, F. Sanz,* Universitat de Barcelona, Spain*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The increasing interest in the study of self-assembled monolayers for the last two decades is related to their potential in different fields of science and technology such as biological sensors, @footnote 1@ optoelectronics,@footnote 2@ tribology@footnote 3@ and corrosion inhibition. @footnote 4@ The knowledge of the stability of the packing, the electrostatic and dielectric properties, and the understanding of the formation process of SAMs constitute crucial phenomena to be investigated in the presence of a changing relative humidity atmosphere. Thus we have performed several series of experiments on alkylsilane monolayer islands vs. relative humidity by means of Polarization Force Microscopy and Dynamic Force Microscopy. The results show that the autoorganizacion is achieved starting from a layer where the molecules are lying down. Also, due to the hydrophilic properties of the alkylsilane monolayer islands, water adsorbs only on mica. This produces an important increase of the dielectric constant on the mica which, in polarization force microscopy, reverses the topographic contrast at around 30% and reaches a maximum at 80%. In addition, by measuring the relative topographic distance between the mica and the islands we are able to quantify the amount of water adsorbed on mica at high relative humidity. . @FootnoteText@ @footnote 1@ K. Shierbaum, T. Weiss, E. T. van Velzen, J. Engbersen, D. Reinhoudt and W. Göpel, Science 265, 1413 (1994). @footnote 2@ A. Ulman, Thin Films: Self-Assembled Monolayers of Thiols, Academic Press, New York, 1998. @footnote 3@ J. I. Siepmann and I. R. McDonald, Phys. Rev. Lett. 70, 453 (1993). @foornote 4@ F. Zamborini and R. Crooks, Langmuir 14, 3279 (1998).

4:20pm **SS+BI-TuA8 "Interphase" Liquid Structure and Interfacial Forces*, H.I. Kim,*** *J.E. Houston,* Sandia National Laboratories

There is growing evidence that liquids behave differently within nanometer-proximity to surfaces due to the formation of quasi-ordered "interphase." Understanding the correlation between the surface chemistry, the interphase structure and the resulting in terfacial forces between neighboring surfaces is of fundamental importance to various aspects of nano-scale materials research, including biomaterials, nanotribology and microelectromechanical (MEMs) devices. We use interfacial force microscopy (IFM) to q uantitatively measure interfacial bonding and frictional forces in order to identify the correlation between surface chemistry and interphase sturcture. We outline the results from two systems. In the first, we measure forces between a gold tip and sample, both coated with oligo(ethylene glycol)-terminated SAMs, in water. We observe anomalous interfacial forces due to the interphase water layer, which dominates the interfacial properties. It has been suggested that the interphase water is responsible for the protein-resistant nature of this SAM surface. In the second, we use a long-chain hydrocarbon liquid, hexadecane, which is known to form an ordered layer on a flat metal surface (e.g., gold). We find that this ordered layer passivates the interfacial i nteraction of a tungsten tip with a gold surface even under high stresses. The structure of this layer can be perturbed by applying an electric field and results in extended frictional forces without significant changes in the behavior of the normal-force. These results will be discussed in terms of the interfacial chemistry and the structure of the interphase liquid. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under a Contract DE-AC04-94AL85000.H. H.

4:40pm **SS+BI-TuA9 Alkanethiols on Copper Single Crystal Surfaces*, S. Vollmer,*** *G. Witte, C. Wöll,* Ruhr-Universität Bochum, Germany

Ultrathin organic films of self-assembled molecules (SAMs) have attracted considerable interest because of their promising technical applications. Whereas the vast majority of related studies have been focused on alkanethiolate (C@sub n@) films on gold surfaces, which are considered as prototype systems, the structure and properties of SAMs on transition metal surfaces are by far less intense studied. Here we present the results of a comprehensive study of the formation and structure of alkanethiol monolayers of various chain length (n @<=@ 12) on the low indexed copper surfaces [i.e. (111), (100) and (110)]. The films which have been prepared by gas phase adsorption under UHV conditions were characterized by means of XPS, TDS, LEED and HAS. At low temperatures alkanethiol molecules are physisorbed with their molecular axis parallel to the surface without any long range ordering. With increasing temperature (110-250K) a conversion into a copper thiolate species takes place depending on the alkyl chain length which is accompanied by an upright tilting of the molecules. Upon adsorption at room temperature highly ordered thiolate monolayers are observed of which structures depend only on the substrate orientation but not on the chain length. Heating the films above 380K causes a S-C bond cleaving and desorption of the entire alkyl chains leaving the S-atoms on the surface. Surprisingly, the saturation structures are metastable and decompose already at about 250K upon partial desorption of the alkyl chains into a thermodynamically stable mixture of thiolate and sulfide species. The presently observed differences to the case of SAMs on gold surfaces are attributed to the much stronger S-Cu interaction.

5:00pm **SS+BI-TuA10 Electro-Rheology of Liquid Hexadecane Near a Au Surface***, **J.E. Houston**, H.I. Kim,* Sandia National Laboratories

In an earlier study we showed that C10 and C12 alkanethiol self-assembled monolayers on Au surfaces conduct only with significant applied stress and that the friction increases along with the increasing current, indicating significant changes in both structural and electronic properties of the film. In this presentation we outline results from a similar interfacial force microscope (IFM) study of hexadecane films near a Au(111) surface immersed in liquid. At room temperature, hexadecane forms mechanically stable surface multi-layers, which also inhibit conduction. However, under an applied electric field, the film structure is perturbed causing friction forces at extended separations but with no significant repulsion. We discuss these findings in terms of both the molecular and dielectric properties of the films as well as the effect of liquid temperature. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

Surface Science

Room 121 - Session SS-TuA

Metal Oxides: Structure and Photocatalysis

Moderator: C. Noguera, Universite Paris Sud

2:00pm **SS-TuA1 Scanning Tunneling Microscopy Study of the Reduced Fe@sub 3@O@sub 4@(111) Terminated Selvedge on a Natural Single Crystal @alpha@-Fe@sub 2@O@sub 3@(0001) Surface: Termination and Surface Reaction with Carbon Tetrachloride***, **K.T. Rim**, J.P. Fitts, T. Muller, K. Adib, N. Camillone, R.M. Osgood,* Columbia University*; S.A. Joyce,* Pacific Northwest National Laboratory*; G.W. Flynn,* Columbia University

Scanning Tunneling Microscopy(STM) and Low Energy Electron Diffraction(LEED) have been used to study the degradation of CCl@sub 4@ on the reduced surface of a natural @alpha@-Fe@sub 2@O@sub 3@(0001) surface. STM and LEED results indicate that repeated cycles of Ar@super +@ sputtering at 2kV and annealing in vacuum and in 10@super -6@Torr of O@sub 2@ partial pressure at 850K reduces the @alpha@-Fe@sub 2@O@sub 3@(0001) surface. Based on STM images approximately 90 % of the reduced surface is terminated by Fe@sub 3@O@sub 4@(111), while the remaining 10 % is terminated by FeO(111) and an unidentified phase. CCl@sub 4@ vapor was dosed on the reduced surface at room temperature. STM images were obtained at room temperature before and after the surface was exposed to CCl@sub 4@. STM images before dosing CCl@sub 4@ reveal a lateral distance of 6.0Â±0.5Å between atoms and a step height of 4.8Â±0.5Å between terraces. A related Temperature Programmed Desorption(TPD) study on the same surface concludes that CC l@sub 4@ is adsorbed dissociatively on the Fe@sub 3@O@sub 4@(111) terminated surface and that only Cl atoms remain on the surface when the dosed surface is flashed up to 590K. STM images after dosing and flashing up to 590K show bright features on the Fe @sub 3@O@sub 4@(111) terminated surface that are identified as individual Cl atoms. These atoms are bound atop Fe atoms, which occupy tetrahedral Fe sites on the Fe@sub 3@O@sub 4@(111) surface, located in three-fold hollow sites of the underlying close-pa cked O plane. STM images before dosing and the chemical reactivity of a Fe@sub 3@O@sub 4@(111) terminated surface with Cl atoms suggest that this Fe@sub 3@O@sub 4@(111) surface is iron-terminated. In contrast, no changes indicating reactivity of the FeO(111) terminated surface were observed. To further clarify the nature of bright features, STM studies are performed where the surface is exposed to Cl@sub 2@ at room temperature.

2:20pm **SS-TuA2 Photo-catalytic Reactions of Organic Molecules Over TiO@sub2@(001) Single Crystal - Effect of Surface Structure***, H. Idriss, **J. Wilson**,* The University of Auckland, New Zealand

No work has addressed so far the effect of surface reconstruction on the photochemical reactions of wide band-gap oxide semiconductors. Rutile, TiO@sub2@(001) single crystal a n-type semiconductor, band-gap 3.0 eV, is unique in that it possess two stable surface structures that can be obtained by thermal treatment. They are the (011)-faceted (750 K) and the (114)-faceted (> 950 K) surface. We have investigated the steady state reaction of acetic acid (as a prototype organic molecule) under photo-excitation (365 nm) over the two thermodynamically stable surfaces under ultra high vacuum conditions. Acetic acid was readily decomposed at room temperature into CO@sub2@ and CO. Moreover the formation of ethane, by the so-called "Photo-Kolbe" mechanism was clearly observed. On the (011)-faceted and at an acetic pressure of 2.4 x 10@super-7@ Torr the CO@sub2@, CO and, ethane production was 1.02 x 10@super-8@, 1.7 x 10@super-8@, and 4.51 x 10@super-9@ Torr, respectively. The product distribution on the (114)-faceted surface was found similar. However, it appears that this latter surface, the one containing Ti@super4+@ cations in 4, 5 and 6-fold coordination to oxygen anions is less active than the (011)faceted surface (all Ti@super4+@ cations are 5-fold coordinated to oxygen anions), under similar conditions.

2:40pm **SS-TuA3 Semiconductor Photocatalysis over Titanium Dioxide***, **D.F. Ollis**,* North Carolina State University **INVITED**

Near-UV illuminated titania surfaces allow for total oxidation of trace organic contaminants in water or air, at room temperatures and with molecular oxygen as the ultimate oxygen source. We examine the origins, progress, and prospects for photocatalysis in four key areas: air purification and remediation, air sterilization, self-cleaning surfaces, and photo-initiated polymeric coatings.

3:20pm **SS-TuA5 Valence Band Photoemission from Pure and Sr Diffused Single Crystal Anatase TiO@sub 2@(001) Surfaces***, **S. Thevuthasan**, V. Shutthanandan, M.A. Henderson, G.S. Herman, S.A. Chambers, Y. Liang, C.H.F. Peden,* Pacific Northwest National Laboratory*; S. Mun, N.M. Hamdan, D. Shuh, C.S. Fadley,* Lawrence Berkeley National Laboratory

Single crystal rutile titanium dioxide has been extensively studied as a model oxide surface because of its commercial availability and its wide use in a variety of technological applications. In contrast, investigations of high-quality anatase titanium dioxide are limited in the literature due primarily to the lack of availability of single crystals. Recently, we have successfully grown epitaxial single crystal anatase TiO@sub 2@(001) thin films with high quality surfaces on SrTiO@sub 3@(001) substrates at the Environmental Molecular Sciences Laboratory's (EMSL) MBE facility.@footnote 1@ We have carried out valence band photoemission experiments on pure anatase TiO@sub 2@(001) thin films, and those with outdiffused Sr at the Advanced Light Source. During these experiments, we investigated the valence band region that includes the band gap and O 2p band as a function of photon energy ranging from 35 eV to 80 eV. The results were compared with those for rutile TiO@sub 2@ surfaces. Valence band spectra from sputtered and annealed (in vacuum and oxygen environments) anatase show differences compared to the valence band spectra from rutile surfaces. However, outdiffused Sr results in no visible changes to the valence band spectra. This result suggests that Sr may occupy the cation sites in a strontium titanate-like structure that exhibiting the band gap similar to the band gap of anatase titanium oxide. These results will be discussed along with the ion channeling measurements of Sr outdiffusion and substitution for cation sites. @FootnoteText@ @foontote 1@G.S. Herman, M.R. Sievers, Y. Gao, Phys. Rev. Lett. 84, 3354 (2000). Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research, the Environmental Management Science Program, and the laboratory directed research and development (LDRD) program.

3:40pm **SS-TuA6 Surface Investigations of TiO@sub 2@ Anatase (101)***, **N. Ruzycki**, D.L. Ederer,* Tulane University*; G.S. Herman, M.A. Henderson,* Pacific Northwest National Laboratory*; U. Diebold,* Tulane University

Titanium dioxide exists in three cyrstallographic structures, rutile, anatase, and brookite. The surfaces of rutile, especially the most stable (110) face, are very well investigated, but far less is know about the technologically much more relevant anatase phase. We report a study of the lowest-energy face, the (101) surface of an anatase mineral sample. After sputtering and annealing to a temperature of 650°C, a sharp (1x1)LEED pattern is observed. In STM the surface morphology is dominated by small triangularly-shaped terraces separated by monoatomic steps.@footnote

1@ The step directions are consistent with the ones expected from simple bond-counting rules. Surprisingly, very few point defects are observed with atomic-resolution STM images and HREELS. This is consistent with the low surface free energy predicted in first-principles calculations.@footnote 2@ It is in contrast to rutile (110), however, where a similar surface treatment creates a few percent of oxygen vacancies. These surface defects play a major role in the surface chemistry of rutile (110), for example, they promote the dissociation of water.@footnote 2@ Adsorption of water is used to probe the surface reactivity of anatase (101). Predominantly molecular adsorption is found, consistent with the picture that po int defects do not play a major role. @FootnoteText@@footnote 1@W. Hebenstreit, N. Ruzycki, G. S. Herman, and U. Diebold, Phys. Rev. B 64 (24) (2000) R16334. @footnote 2@A. Vittadini, A. Selloni, and M. Gratzel, Phys.Rev.Lett.. 81 (14) 2954. 3. M. A. Henderson, Surf. Sci. 335 (1996) 151.

4:00pm **SS-TuA7 Characterization of Surface Defects on Flat and Porous MgO Surfaces***, **Z. Dohnálek**, D. McCready, J.S. Young, A. Dohnálková, G.A. Kimmel, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

We use the physisorption of gases such as N@sub 2@, Ar, and CO and standard surface analytical techniques to characterize the surface defects on thin films of dense and porous MgO. Different types of defects are prepared on the MgO films by careful adjustment of the deposition conditions. Significant changes are observed on the surfaces of films grown on the Mo(100) substrate at various substrate temperatures, O@sub 2@ pressures, deposition rates, and film thicknesses. Temperature programmed desorption (TPD) of physisorbed molecules reveals distinct desorption features associated with different binding sites on the defective films. The analysis of TPD spectra yields the binding energies and concentrations of these defect sites. The information from flat MgO(100) surfaces is utilized in the characterization of porous, crystalline MgO films. Details of the experimental techniques, results, and implications of the results will be presented. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

4:20pm **SS-TuA8 A Study of the Surface Reconstruction of Fe@sub 3@O@sub 4@ (100) Using Antiferromagnetic Tips***, **G. Mariotto**, S. Murphy, I. Shvets,* Trinity College Dublin, Ireland

We have studied the surface structure and chemical composition of an artificially grown single crystal of Fe@sub 3@O@sub 4@ (100) using scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The crystal has been also characterized by electrical resistivity measurements as a function of temperature. Two different preparation procedures are discussed. The first one consists of mechanically polishing the sample with diamond paste and then annealing it in situ at a temperature of 990 ± 50 K. It has been found that this procedure gives rise to a surface characterized by the presence of square terraces with the edges aligned along the [110] and [1-10] directions. A p(1x1) LEED pattern has been associated with this type of images and sample preparation. The steps separating adjacent terraces are 2 ± 0.2 Å high, which corresponds to the distance between like sites of iron atoms. A longer annealing induced the onset of a different type of structure: the square terraces split into rows that become sharper and narrower as the annealing time is increased. The separation between these rows ranges from 24 to 40 Å. This type of surface structures manifests itself in the LEED pattern with the presence of satellite spots around the primary spots. Surface contamination by impurities segregating from the bulk are discussed. The second preparation procedure consists of argon ion etching followed by annealing. This method produces a c(2x2) reconstruction that is clearly visible in the LEED pattern. AES spectra indicate a clean surface of magnetite. Terraces separated by 2 ± 0.2 Å are routinely observed. Atomically resolved pictures have been obtained on a sample prepared according to this procedure using an antiferromagnetic MnNi tip. The differences between the two preparation procedures are discussed.

4:40pm **SS-TuA9 Characterization of Copper Oxides Formed by Thermal and Plasma Oxidation Using Linear Sweep Voltammetry, Galvanostatic Reduction and XPS***, **M.A. Hossain**,* Lamar University*; J.R. Parga,* Instituto Tec. de Saltillo*; H. McWhinney,* Prairie View A&M University*; R. Schennach,* Technical University of Graz*; D.L. Cocke,* Lamar University

The growing importance of copper in the semiconductor industry has led to a renewed interest in the properties and growth modes of copper oxides under a variety of conditions. While thermal oxidation of copper has been studied extensively over the last decades, recent surface studies seem to ignore the possible formation of Cu@sub 3@O@sub 2@. It has been shown that thermal oxidation of copper leads to multilayer structures, which consist of Cu@sub x@O, Cu@sub 2@O, Cu@sub 3@O@sub 2@ and CuO, depending on the oxidation conditions. These oxides have been analyzed by electrochemical methods, which probe the buried interfaces in an electrical potential controlled order. XPS combined with depth profiling has been used to obtain information which applied with controlled growth complements the electrochemical methods. Linear sweep voltammetry (LSV) and galvanostatic reduction (GR) have been used to characterize the oxides formed by thermal and plasma oxidation. LSV and GR show that plasma oxidation at room temperature leads to the formation of a pure CuO film, which cannot be formed using thermal oxidation and provides insight into the formation of the other oxides and about their subsurface interfaces.

5:00pm **SS-TuA10 The Surface Kinetics of the Initial Stages of Metal Oxidation Visualized by In situ UHV-TEM***, **J.C. Yang**, G.W. Zhou, M.D. Bharadwaj, D. Evans,* University of Pittsburgh

Copper has played a significant role in the development of oxidation theories, ranging from the classic oxidation studies of the epitaxial growth of the thermodynamically stable oxide scale to the surface science investigations of the dynamics of oxygen interaction with the bare metal surface. We are visualizing the initial oxidation stage of Cu thin films by in situ ultra-high vacuum (UHV) transmission electron microscopy (TEM) where we have varied temperature, oxidation pressures and oxidizing environment. In situ UHV-TEM provides unique information, such as real-time structural changes and information on buried interfaces, where extremely clean surface conditions are obtained inside the microscope. Based on our data, we have developed a semi-quantitative model of the initial oxidation stage where the dominant mechanism for transport, nucleation and growth of oxide islands is oxygen surface diffusion. We are presently examining other metallic systems, such as Aluminum.

Surface Science

Room 134/135 - Session SS+SC-TuP

Semiconductor Deposition Poster Session

SS+SC-TuP1 Fabrication of a-Si:H Films by Plasma CVD*, T. Nishimiya,* Mitsubishi Heavy Industries Ltd., Japan

We have succeeded in getting high-deposition rate and high quality for preparing hydrogenated amorphous silicon (a-Si:H) films, as well as micro-crystalline siliconï¼ˆmc-Siï¼‰films, by Very-high-frequency (VHF) plasma CVD using a ladder-shaped electrode. Recently, VHF plasma CVD technique has become one of the topics in the field of the fabrication of solar cell and thin film transistors, because its high plasma density enables high-speed deposition. However, in the large area deposition, which is needed in the application of commercial production, the effective gas flow rate fed into the plasma region limits the deposition rate and the film qualities because the gas depletion condition leads to the degradation of the film quality. We developed the ladder shaped electrode, which has an advantage over a conventional parallel-plate electrode in the controllability of the gas flow. The experiments are performed using a ladder-shaped electrode consisted of 9 stainless-steel rods 160 mmÃ-160 mm in external dimension. The material gases are introduced into the plasma region between each rod of the electrode. Using the VHF-SiH4 plasma at the frequency of 60MHz, we got a-Si:H film at the deposition rate of 1.2 nm/s with the ratio of photo conductivity/dark conductivity of 106. We also applied this electrode to fabricate the mc-Si film and succeed very high-speed of 3.4 nm/s using the plasma of SiH4 diluted with H2 at the frequency of 100 MHz. These were demonstrated that this electrode is highly suitable for the production technique.

SS+SC-TuP2 Growth Characteristics of Si@sub 1-x-y@Ge@subx@C@sub y@ on Si(100) and SiO@sub 2@ in Ultraclean Low-Temperature LPCVD*, **Y. Hashiba**, M. Sakuraba, T. Matsuura, J. Murota,* Tohoku University, Japan

The growth characteristics of Si@sub 1-x-y@Ge@subx@C@sub y@ films on Si(100) and SiO@sub 2@ were investigated. The films were deposited at 550°C in a SiH@sub 4@-GeH@sub 4@-CH@sub 3@SiH@sub 3@-H@sub 2@ gas mixture using ultraclean hot-wall low pressure chemical vapor deposition (LPCVD) system. The total deposition pressure was 30Pa, and the partial pressures of SiH@sub 4@, GeH@sub 4@ and CH@sub 3@SiH@sub 3@ were in the range of 6.0Pa, 0-2.0Pa (Ge fraction x=0-0.57) and 0-0.2Pa (C fraction y=0-0.05), respectively. Si films are epitaxial on Si(100) and amorphous on SiO@sub 2@. The deposition rate of Si on SiO@sub 2@ (1.2-1.4nm/min) is 10-20% larger than that on Si(100), however, with the addition of CH@sub 3@SiH@sub 3@, the deposition rate on SiO@sub 2@ decreases to that on Si(100). It is considered that CH@sub 3@SiH@sub 3@ molecules are scarcely adsorbed at Si-Si pair site on Si(100) but not at the other sites on amorphous Si surface. With the addition of GeH@sub 4@, the deposition rate increases and that on Si(100) becomes larger than that on SiO@sub 2@. Si@sub 1-x@Ge@sub x@ films are epitaxial on Si(100) and or random oriented polycrystalline on SiO@sub 2@. This is explained by the modified Langmuir-type adsorption and reaction with the assumption that SiH@sub 4@ and GeH@sub 4@ are adsorbed more preferentially on the Si-Ge pair site than Si-Si, Ge-Ge pair site, single Si and Ge bond sites. With the addition of CH@sub 3@SiH@sub 3@, the deposition rates decreases and that on Si(100) tends to become the same as that on SiO@sub 2@. It is suggested that the adsorption and reaction of SiH@sub 4@ and GeH@sub 4@ are suppressed by the adsorption of CH@sub 3@SiH@sub 3@ molecule at the Si-Ge pair site. From XPS measurement, Ge fraction on Si(100) is almost equal to that on SiO@sub 2@ within 10% error. The relationship among lattice constant, Ge and C fraction is under investigation.

SS+SC-TuP4 Mechanisms of Vapor Phase Growth of Chalcopyrite Semiconductors*, **D.-X. Liao**, A. Rockett,* University of Illinois

Epitaxial growth of the chalcopyrite-structure semiconductor Cu(In,Ga)Se2 alloys on (111)A and B, (110), and (100) GaAs was studied and a growth model is proposed. These semiconductors are prime candidates for high-efficiency thin film solar cells and have potential in thin film transistor applications. Surface morphologies result from a mixture of surface-energy and nucleation and growth dominated phenomena. Surface energy considerations drive all observed surface planes to decompose into close packed facets, some including large numbers of surface steps. Comparison of the bulk structure and morphologies of the different surfaces indicate that nucleation of surface terraces on close-packed Se-terminated planes and their growth dominates the evolution of surface morphologies. Relatively slow nucleation of terraces on metal terminated close packed planes leaves these very smooth relative to the Se-terminated faces. Structural and electronic properties measurements show that point-defect clusters occur in large numbers in this material and can spontaneously organize on specific planes. The creation of these clusters during facet growth is proposed to be responsible for the observed step motion and consequently for the surface morphologies. Results show that epitaxial temperatures vary significantly from ~700 C on the (111)B surface to ~540 C on (110). The epitaxial temperature is proposed to be related to the availability of Se- and metal-terminated surface step edges. The organization of the point defects during growth appears to lead to a physical separation between the defects responsible for p-type doping and the conduction path for holes, permitting a nearly constant 300K hole mobility of 300 cm2/V-sec over a wide range of hole concentrations.

SS+SC-TuP5 Studies on Spray Deposited Lanthanum Selenide Thin Films from Non-aqueous Medium*, **G.D. Bagde**, C.D. Lokhande,* Shivaji University, India

Since the discovery of high temperature semiconductor, great efforts have been made to produce high quality thin films of the materials. The rare earth chalcogenides are of interest for applications such as thermoelectric cooler, photoelectric cells, solar cells, cold cathode emitting devices, far infrared window materials etc. The rare earth selenide have shown semiconducting properties used for high temperature device formation. Spray pyrolysis is simple and inexpensive technique for large area deposition of thin films. Spray pyrolysis technique is employed to prepare La@sub 2@Se@sub 3@ thin films from non-aquous (methanol) medium. The preparative parameters are optimized to get good quality films. The optimized pyrolysis temperature is 200@super o@C. The La2Se3 film show polycrystalline cubic structure with dominant plane (310). The calculated average grain size is about 40 nm. Scanning Electron Microscopic studies revels that La@sub 2@Se@sub 3@ films have porous fibrous network structure and presence of irregular shaped particles. From the analysis of the optical absorption data a direct allowed transition at 2.45 eV has been observed. The room temperature electrical resistivity is of the order of 10@super 4@-10@super 5@ @ohm@-cm. The films are found to be p-type semiconductor by themoemf measurement study.

SS+SC-TuP6 Studies on Deposition of Indium Sulphide Thin Films by Silar Method*, **H.M. Pathan**, S.D. Sartale, G.D. Bagde, C.D. Lokhande,* Shivaji University, India

Indium Sulphide is a promising material used as a buffer layer in Cu(InGa)Se@sub 2@ based solar cells and mini models. Successive ionic layer adsorption and reaction (SILAR) is a modified version of chemical bath deposition (CBD) method for thin film deposition. In CBD, when solutions are mixed together, the precipitation on the substrate and in the solution takes place. This results into wasteful and unavoidable formation of bulk precipitation in the solution since the reaction is not controllable. To overcome this difficulty, CBD is modified as SILAR in which substrate is immersed into separately placed cationic and anionic precursors and rinsing before every immersion with ion exchanged water to avoid homogeneous precipitation in the solution. In the present investigation, nanocrystalline semiconducting indium sulphide thin films were deposited onto glass substrates using SILAR method. For the deposition of indium sulphide thin films, preparative conditions such as concentration and pH of precursor solution and adsorption, reaction and rinsing time duration were optimized at room temperature (27 @super o@C). These deposited films were characterized for their structural, optical and electrical properties. The films are found to be nanocrystalline. The films have 2.7 eV direct optical band gap with n-type electrical conductivity.

SS+SC-TuP7 The Effects of the Microstructure Factor in Chemical Texturization of Crystalline Si Solar Cells*, **F. Krok**,* Jagiellonian University, Poland*; Z. Swiatek, E. Beltowska-Lehman,* Polish Academy of Science*; M. Szymonski,* Jagiellonian University, Poland

The texturization of the silicon solar cell front surface improves the cell efficiency due to its antireflection properties and light trapping effect. The chemical texturization of single grains in well-defined multi-crystalline Si wafers was performed in a standard alkaline (anisotropic etching) as well as in acid (isotropic etching) solutions. The microstructure of textured wafers was investigated using SEM, TEM, and NC-AFM methods. The crystallographic orientation of each grain was determined by means of electron back scattered diffraction (EBSD) technique. It comprises the analysis of detected Kikuchi patterns, observed in the SEM. The texturization in alkaline etching solutions causes development of steps between particular grains because of different etching rate in different crystal plane orientation in the wafers. In these cases, although the grains were textured, the grain boundaries became developed and steps were observed. Depending on the grain initial crystallographic orientation (hkl) and the individual disorientation, different final morphologies have been observed. Based on the NC-AFM measurements, the nanostructural nature of the texturized surface was evident for some grain orientations. Moreover, these nanocrystals (ca. 20 nm) have a well-defined preferred crystallographic orientation. The texturized surface with good homogeneity of particular grain orientations of m-c Si has been achieved. The final morphology of the texturized m-cSi surface strongly depends on the process parameters as well as on the polar and azimuthal disorientation of the grain.

SS+SC-TuP8 Polycrystalline Si Thin Film Growth on Glass using Magnetron Sputtering*, M.J. Jung*, *Y.M. Jung, J.U. Kim, J.G. Han,* Sungkyunkwan University, Korea

Polycrystalline Si thin film is widely applied materials for thin film transistor of Flat Panel Display (FPD), and photovoltaic applications because of its high mobility, electrical conductivity, and high-energy conversion efficiency compared to a-Si.@footnote 1@ Over the past few years, there have been a variety of techniques on thin film growth of poly-Si. Among theses techniques, Solid Phase Crystallization (SPC) and Excimer Laser Annealing (ELA) have been the most frequently used methods. The SPC method has too high crystallization temperature (650°C) for glass substrate. On the other hand, ELA method is suitable for low temperature on the glass substrate, however, there are still problems such as non-uniformity of grain growth on the large area glass substrate as well as expensive processing cost.@footnote 2@ Recently, Metal-Induced Crystallization (MIC) of amorphous silicon has been studied for poly-Si thin films on low temperature glass@footnote 3@. We have deposited crystalline poly-Si thin films on soda-lime glass and SiO@sub2@ glass substrate as deposited by PVD at low substrate temperature using high power magnetron sputtering method. The electron mobility of the poly-Si grown on soda-lime glass and SiO@sub2@ glass at substrate temperature of 115° show 138 @cm square per Volt dot second@ and 191@cm square per Volt dot second@. Therefore, to investigate the relationships between surface and film microstructure as well as the nucleation, growth mechanism and its electrical properties of poly-Si thin film, we have studied the variation of plasma state for nucleation and growth mechanism by Langmuir probe and Optical Emission Spectroscopy (OES). The epitaxial orientation, microstructual characteristics and surface properties of the films were analyzed by TEM, XRD, and AFM. For the electrical characterization of these films, its properties were obtained from the Hall effect measurement by the Van der Pauw measurement.

SS+SC-TuP9 Arsenic Incorporation into Indium Phosphide (001) Surfaces during Metalorganic Vapor-Phase Epitaxy*, R.F. Hicks,* ***D.C. Law****, C.H. Li, S.B. Visbeck, Y. Sun,* University of California, Los Angeles

The quality of heterointerfaces is of great importance for high performance optoelectronic devices. In this work, we report on a detailed study of the effect of arsenic exposure to indium phosphide (001) during metalorganic vapor-phase epitaxy (MOVPE). Indium phosphide surfaces were exposed to several Torr of tertiarybutylarsine (TBAs) at temperatures ranging from 200 to 600°C. Scanning tunneling micrographs reveal that arsenic exposure below 400°C yields atomically smooth surfaces with ordered reconstructions. These surfaces consist of either a single monolayer of As and P with a (2x1) structure, or half a monolayer of As incorporated into a (2x4) structure. Conversely, at temperatures above 450°C, three-dimensional islands are formed during TBAs exposure. The arsenic coverage in these structures exceeds several monolayers, indicating diffusion into the bulk. The implications of these results for the fabrication of III- V heterojunction devices will be discussed at the meeting.

SS+SC-TuP10 Synthesis of Sb2Se3 Nanorods under Mild Hydrothermal Conditions*, J. Wang,* ***Z. Deng****, Y. Li,* Tsinghua University, P.R. China

A hydrothermal reduction route was employed for the synthesis of Sb2Se3 semiconductor nanorods. The reaction temperature for the formation of Sb2Se3 nanorods was found to be above 130Â°C, otherwise some impurities, such as Sb2O3 and unreacted Se, would exist in the final products. In addition, the role of hydrazine, which serves as both the reducing agent and the coordinator, was also found to be crucial for the formation of the rod-like products. The resulted products were characterized by XRD, TEM, XPS, UV-vis adsorption spectroscopy and Raman spectroscopy. @FootnoteText@ Email: ydli@@tsinghua.edu.cn Tel.: +86-10-62772350 Fax: +86-10-62788765 .

Surface Science
Room 134/135 - Session SS1-TuP
Semiconductor Surfaces Poster Session

SS1-TuP3 Reduction of Oxidation Rate during the Initial Stages of the Oxidation of Heavily Phosphorus Doped Silicon in Dry Oxygen*, Y. Kamiura*,** *K. Hasegawa, Y. Mizokawa,* Osaka Prefecture University, Japan*; K. Kawamoto,* Denso Co. Ltd., Japan

The oxidation of heavily phosphorus doped Si(100) and polycrystalline Si in RT to 800°C range in dry oxygen was studied by Auger electron spectroscopy(AES). The oxidation rate of the phosphorus doped Si(100) was larger than the P-doped poly-Si for each O@sub 2@ exposure at RT. Phosphorus segregation didn't take place in RT oxidation of the P-doped Si(100). The Dioxide formation gradually occurred from ca. 500L in thermal oxidation at 650°C in the P-doped Si(100). The reduction of oxidation was found above 5x10@super 5@L. At the same time, the amount of the phosphorus piled-up at Si/SiO@sub 2@ interface slightly degreased. The accurate AES measurements of 97 to 137eV range showed that phosphorus slightly oxidized in the initial stage of the oxidation of P-doped Si for each O@sub 2@ exposure and the phosphorus peak in P@sub 2@O@sub 5@ was clearly found at ca. 110eV above 10@super 3@L. It seemed that the modification of this substance fairly desorbed in UHV and the residual partially held into the Si/SiO@sub 2@ interface at this temperature. Therefore the oxidation of silicon didn't proceed until about ca. 1x10@super 6@L. On the other hand, the suppression of oxidation of silicon wasn't caused for P-doped poly-Si, the amount of SiO@sub 2@ strongly increased above 5x10@super 5@L. The thermal oxidation behavior at 800 °C was quite different from low temperature results. Oxygen uptake on the silicon surfaces didn't almost take place below 10@super 3@L for both samples because the volatile SiO molecules were formed and the silicon surfaces were etched away by oxygen atoms. Dioxide formations rapidly took place above 10@super 4@L, and then a large amount of phosphorus piled up at the interfaces due to the formation of SiO@sub 2@. The P@sub 2@O@sub 5@ was formed through low O@sub 2@ exposures even at this temperature for both samples.

SS1-TuP5 The Investigation of the Semiconductors Surfaces by Method of the Low Energy Ion Scattering*, U. Kutliev*,** *B. Kalandarov,* Urgench State University, Uzbekistan

In the present work the scattering processes of 5 keV Ne @super +@ ions on the GaP(100) surface under grazing ion bombardment have been investigated by computer simulation in the binary collision approximation. The particle interaction were described by the universal BZL-potential. Elastic and inelastic energy losses of scattered ions were summed along their trajectories. Trajectories of incident ions experienced correlated sliding scattering on discrete atomic chains, in semichannels and channels in the , <-100> directions were traced in several nearest to surface atomic layers. The monoatomic steps of the different length, one atomic layer high on the surface were simulated. Energy, angular and spatial distributions of Ne @super +@ ions scattered from stepped GaP(100) surface at different crystal directions were calculated. The computer simulation allowed an investigation of the effect of the atomic steps on the real single crystal surface upon the trajectory features and capture in subsurface channeling and dechallening of the ions being scattered on the surface. It has been shown that the presence of atomic steps on the surface lead to increase of the capture probability of channeling ions in the layers under the steps and to increase of probability of their dechanneling. Character of ions movement under the step (their range, energy losses and dechanneling) is determined both the grazing angle and capture angle under the step.

SS1-TuP6 Femtosecond Time-Resolved Photoemission Study of Two-Dimensional Layered Semiconductor MoS@sub 2@ Surface*, A. Tanaka*,** Tohoku University, Japan and University of Rochester, JAPAN*; N.J. Watkins, Y. Gao,* University of Rochester

A femtosecond time-resolved two-photon photoemission study of 2H-MoS@sub 2@ surface has been carried out in order to investigate in detail the relaxation dynamics of hot electrons in the two-dimensional layered semiconductor. Among the lamellar transition metal dichalcogenides, MoS@sub 2@ is a semiconductor with an indirect gap of about 1.2 eV. The observed two-photon photoemission spectrum with a photon energy of 3.3 eV exhibits a single feature in the intermediate state energy between 2.1 and 3.3 eV above the valence-band maximum (i.e., between 0.9 and 2.1 eV above the conduction-band minimum). From the detailed time-resolved two-photon photoemission measurements as a function of electron excitation energy, it is found that the inverse relaxation lifetime of hot electrons depends linearly on the excess energy above the conduction-band minimum. This result is in strong contrast to the results based on the Fermi liquid theory, which takes into account the electron-electron scattering as the dominant relaxation process and gives the quadratic energy dependent lifetime in the both three- and two-dimensional electron systems within logarithmic corrections. From these results, we discuss the relaxation process of hot electrons in the two-dimensional layered semiconductor.

Surface Science
Room 134/135 - Session SS2-TuP
Semiconductor Reactions Poster Session

SS2-TuP1 XPS Investigation of Trimethylsilane Dosed Ge (100) Surfaces*, P.W. Wang,* The University of Texas at El Paso*; Y. Qi,* University of Massachusetts*; J.H. Craig,* Bradley University

Trimethylsilane (TMSi) was dosed onto a sputter cleaned Ge (100) surface at 145 + 5 oC and X-ray photonelectron spectroscopy (XPS) was used to study the cumulative effect of dosage, electron irradiation, temperature, and X-ray photon irradiation. The core level C 1s, Si 2p and Ge 3d photoelectrons were monitored. Arguments based on electronegativities of C, Si, and Ge and bond strengths of C-C, C-Si and C-Ge are invoked to interpret the interaction of TMSi with the Ge (100) surface under various external conditions. It is demonstrated that TMSi dissociatively chemisorbs initially at low coverage, but physisorbs molecularly at high coverage. Both electron irradiation and thermal effects cause the breaking of C-C or C-H bonds. New bonds of C-Ge are formed as a consequence. X-ray photon induced secondary electrons and local heating result in the dissociation of the adsorbed C-H or Si-H species which causes the initial concentration increase of Ge-C bonds. This study clearly shows the different pathways to form new species on the Ge (100) surfaces under various external conditions.

SS2-TuP3 Generation of Type-C Defects on Si(100) by Bimolecular Adsorption of Water: A FT-IR, STM, AES and QMS Study*, M. Nishizawa,* *T. Yasuda, S. Yamasaki,* Joint Research Center for Atom Technology (JRCAT), Japan*; K. Miki,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; M. Shinohara, N. Kamakura, Y. Kimura, M. Niwano,* Tohoku University, Japan

STM studies on various processes on Si(100)-(2x1) are often interfered with a high density of surface defects. Among three types of defects reported on this surface,@footnote 1@ the structure of the so-called type-C defect has been under debate. We show that the C-defects are generated by adsorption of water from the UHV environment. This conclusion is based on our systematic investigations using FT-IR, STM, AES, and QMS. Our STM experiments have reproduced the commonly observed phenomenon that the C-defect density increases with time even when the vacuum is as good as 10@super -11@ Torr. The surface with many C-defects shows a small but detectable O@sub KLL@ signal in AES. A possible source of O is the residual H@sub 2@O, CO, and/or CO@sub 2@ in UHV. To identify the source of surface O, we examined the correlation between the generation rate of the C-defects and the partial pressures for these gases. We have found that H@sub 2@O, which adsorbs at a sticking probability near unity, is the only candidate that can account for the defect generation rate. Dissociative adsorption of residual H@sub 2@O has been indeed detected by our IR measurements in which Si-H and O-H stretching modes are observed. The Si-H band has two components indicating that there are two kinds of Si-H bonds of different configurations. In addition, kinetic analyses of the Si-H evolution have revealed that the adsorption takes place via highly mobile precursor states. These observations suggest that C-defects are generated by bimolecular adsorption of H@sub 2@O, which readily explains the STM observation that the C-defects occupy two dimers. The detailed structure of the C-defect will be discussed at the presentation. This study, partly supported by NEDO, was performed at JRCAT under the joint research agreement between AIST and ATP. @FootnoteText@ @footnote 1@ Hamers et al., J. Vac. Sci. Technol. A 7 (1989) 2854.

SS2-TuP5 Investigation of Surface Intermediates in Thermal Decomposition of Diethylmethylsilane on Si(111) using Low Energy Cs Ion Scattering and Thermal Desorption Spectroscopy*, H.-G. Chi,* *Y. Kim, J.-H. Boo, S.K. Kim, S.-B. Lee,* Sungkyunkwan University, Korea*; H.T. Kwak,* Kook Min University, Korea

The intermediate species produced in the decomposition of diethylmethylsilane on Si(111) were investigated in the range of 110 1200 K by using Cs@super +@ reactive ion scattering (RIS), low energy secondary ion mass spectrometry (SIMS) and thermal desorption spectroscopy. We will show that RIS gives more reliable evidence than SIMS for identification of surface species of this system. The results of low energy Cs@super +@ ion scattering indicate that molecular diethylmethylsilane and various alkylsilyl species such as (C@sub 2@H@sub 5@)@sub 2@Si, C@sub 2@H@sub 5@SiCH@sub 3@, C@sub 2@H@sub 5@Si, and CH@sub 4@Si as well as hydrocarbon species such as C@sub 2@H@sub 4@ and C@sub 2@H@sub 5@ exist on surface between 110-150 K. Above 300 K, all the alkylsilyl species are converted to CH@sub 4@Si, which decomposes completely to form SiC above 900 K. We will propose a possible mechanism for the SiC formation from the results of low energy ion scattering and thermal desorption spectroscopy.

SS2-TuP6 Interface Reaction of Cesium Layers Deposited on a H-terminated CVD Diamond*, S. Yoshida,* *T. Inaba, T. Urano, S. Hongo,* Kobe University, Japan

CVD diamond is potential for negative electron affinity (NEA)materials. Therefore, H-terminated and alkali adsorbed diamond surfaces have been studied intensively. It has been known that getting clean diamond surface is difficult. Because Ar ion sputtering and electron irradiation may result in amorphization of the diamond structure and heating the amorphous layer results in the formation of graphitic clusters. Cyclic adsorption and desorption of hydrogen also degrades the surface. Like this, the diamond surface is complicated and has inherent instability compared with Si surface. Therefore it is neccessary to reveal interface reaction to produce stable NEA devices. In this study hot-filament CVD diamond was used. All experiments were carried out in a UHV chamber equipped with thermal desorption spectroscopy, metastable deexcitaion spectroscopy, ultra violet photoelectron spectroscopy and Auger electron spectroscopy (AES). Cesium was deposited using SAES gettters Cs dispenser at 150 K. Atomic hydrogen produced by hot filament was used to terminate the diamond surface. It was found that 1)Multilayer(island) Cs is formed on Ar ion sputtered surface, 2)Multilayer(island) Cs desorption peak is not observed on a H-terminated surface, 3)Clear H@sub2@ desorption peak attributed to Cs-H bond foirmation (which is seen for Cs/H-terminated Si(100) sample) is not observed for Cs/H-terminated CVD diamond, 4)As raising the sample(Cs/H-terminated CVD diamond) temperature from 150 K to 470 K, AES peak of Cs decreases and that of C increases, though no Cs and H@sub2@ desorption peak are observed during heating. These experiments may suggest the formation of Cs-C-H mixture at low temperatures.

Surface Science
Room 134/135 - Session SS3-TuP
Adsorption/Desorption Poster Session

SS3-TuP3 The Evolution of Surface Topography of Alkali Halides Crystals During Ion Stimulated Desorption*, F. Krok, J.J. Kolodziej, B. Such, P. Czuba, P. Piatkowski,* ***M. Szymonski,*** Jagiellonian University, Poland

Ion-stimulated-desorption (ISD) of alkali halide (RbI, KBr) surfaces under 5 keV He+ bombardment is investigated in UHV by means of non-contact Atomic Force Microscopy (nc-AFM) and Quadrupole Mass Spectroscopy (QMS). Irradiated surface topography and corresponding desorption fluxes are studied. Although, for the energy range of He+ ions used in the present work, desorption of alkali halides occurs predominantly via electronic processes, there are significant differences between ISD and the electron stimulated desorption (ESD). Recently, present authors@footnote 1,2@ have demonstrated that ESD of alkali halides proceeds in a layer-by-layer mode and oscillating desorption fluxes are observed. These ESD oscillations have been explained to be due to creation of Frenkel pairs in the bulk, their diffusion, and their recombination with surface modulated accordingly to changing surface topography. For ISD studied in the present work AFM images show that the surface erosion does not follow the layer-by-layer scheme and no oscillation in desorption fluxes are found. We propose that these (not anticipated) differences between electron- and ion- stimulated desorption are caused by ballistic processes at the surface. While most of the primary ion beam energy is deposit deep in the bulk leading to production of Frenkel pairs some projectiles colliding violently with top-layer ions may introduce additional nucleation centers for vacancies on surface. Moreover the shallow collision cascades, which extend to the top crystal layers are likely to induce mobility in alkali halide top crystal layer. These ballistic processes interfere with electronic processes and destroy the layer-by-layer desorption scheme. @FootnoteText@@footnote 1@B.

Such, J. Kolodziej, P. Czuba, P. Piatkowski, P. Struski, F. Krok and M. Szymonski, Phys. Rev. Lett., 85 (2000) 2621. @footnote 2@R. Bennewitz, S. Schar, V. Barwich, O. Pfeiffer, E. Meyer, F. Krok, B. Such, J. Kolodziej, M. Szymonski, Surf. Sci. Lett., 474 (2001) L197.

**SS3-TuP4 Nano-scale Modification of Ionic Surfaces by ESD*, B. Such,* *J.J. Kolodziej, P. Czuba, P. Piatkowski, P. Struski, F. Krok, M. Szymonski,* Jagiellonian University, Poland

Surface modification of alkali halide crystals by electron beam was investigated with the use of dynamic force microscope (DFM). It was found that randomly spread rectangular pits of monolayer depth, in the topmost layer of the crystals, were formed during irradiation. Growth and coalescence of the pits led to almost layer-by-layer desorption mode. Average size and density of the pits could be changed by varying parameters of an electron beam and surface temperature leading to controlled nano-modification of the surface. Moreover, by comparison of DFM and mass spectroscopy data we were able to establish that the surface stepdensity, changing in time, controlled the desorption process. The new model of electron-stimulated desorption (ESD) of alkali halides was proposed to explain observed behavior, based on the idea of existence of two kinds of F-centers in the crystal: ground state (immobile) and excited (mobile) ones.

**SS3-TuP5 The Simultaneous Observation of Adsorption Isobars of Xe/Ag(111) and Xe/Ag(100)*, A. Tosaka,* *T. Mitake, T. Hirayama, I. Arakawa,* Gakushuin University, Japan

The growth and the structure of a Xe film physisorbed on the surface of a silver single crystal, Ag(111) or Ag(100), have been investigated by means of an ellipsometry and an eXtremely-low-current LEED (XLEED). We obtained adsorption isobars of Xe/Ag(111) and Xe/Ag(100) simultaneously: one was observed by the ellipsometry and the other by the spot intensity measurement of XLEED in the temperature range between 60K and 90K and the equilibrium Xe pressure range between 5X10@super -6@Pa and 2X10@super -4@Pa. The first layer condensation of Xe/Ag(111) occurs at the temperature 0.3±0.1 K higher than that observed for Xe/Ag(100), while the second layer condensation occurs at the same temperature within the experimental accuracy . On the assumption (1) that this temperature difference is mainly caused by the difference of the induced dipole moment between the Xe atom on Ag(111) and that on Ag(100) and (2) that the system follows the two dimensional van der Waals equation, we calculated the difference of the induced dipole moment μ to reproduce the experimentally determined temperature difference. The result shows that μ on Ag(100) is 5% larger than that on Ag(111). @FootnoteText@ *T. Hirayama Present Address: Department of Physics, Rikkyo University, Toshima, 171-8501 JAPAN.

**SS3-TuP6 Measurement and Quantitative Analysis of Photon or Electron Stimulated Desorption Yields of Solid Argon and Krypton*, T. Adachi,* *T. Hirayama,* Gakushuin University, Japan*; M. Sakurai,* Kobe University, Japan*; I. Arakawa,* Gakushuin University, Japan

Electron or photon irradiation of the surface of rare gas solids produces the electronic excitations which can be followed by the desorption of various kinds of particles. Investigation of the desorption characteristics such as desorption yields, kinetic energy distributions and angular distributions, will reveal the dynamics of the electronic excitations and relaxations in rare gas solids. We have reported the absolute photo-desorption yields of solid neon at the excitonic excitation energy range and shown that the yields were quantitatively explained by an internal sputtering mechanism.@footnote 1@ Here, we present the absolute desorption yields of the solid argon and krypton for the both case of photon impact and low energy electron impact. At the films thicker than 400 atomic layers, the absolute photo-desorption yields were about 1.5, 0.07, and 0.03 atoms/photon for neon, argon, and krypton, respectively, at the excitation energy of first order bulk exciton. In the case of 220 eV electron impact, the desorption yields were about 1 and 0.1 atoms/electron for argon and krypton, respectively. We will present the quantitative evaluation of the absolute desorption yields and these thickness dependencies for argon and krypton using the the classical molecular dynamics calculation results.@footnote 2,3@ @FootnoteText@ *T. Hirayama Present address: Department of Physics, Rikkyo University, Toshima, Tokyo 171-8501 JAPAN. @footnote 1@ Arakawa, I., et al. Surf. Sci. 451, 136 (2000). @footnote 2@ Cui, S., et al. Surf. Sci. 207, 186 (1988). @footnote 3@ Dutkiewicz, L., et al. Nucl. Instr. Meth. B 101, 188 (1995).

**SS3-TuP7 The Adsorption and Thermal Decomposition of Trimethylamine on Si(100)*, L.H. Zhang,* *A.J. Carman, J. Liswood, S.M. Casey,* University of Nevada, Reno

Trimethylamine (TMA) adsorption on Si(100)-(2x1) has been investigated using low-energy electron diffraction, Auger electron spectroscopy (AES), and thermal desorption spectroscopy (TDS). TMA appears to undergo molecular adsorption on this surface at room temperature. By comparison to the AES results from the adsorption of methyl iodide on Si(100), it was concluded that the initial surface saturation coverage of TMA on Si(100) is 0.5 monolayers. TDS reveals a parent TMA desorption channel, as well as competing surface decomposition channels. In order to gain further physical insight into the available reaction pathways for this molecule on this surface, we have used density functional theory (DFT) to study the adsorption of TMA on simplified silicon clusters. By experimental and theoretical studies of the adsorption of TMA and its subsequent surface pyrolysis, we try to understand the bonding characteristics and possible deposition reaction pathways for TMA and similar amines on the surfaces of semiconductor wafers.

SS3-TuP8 Resonances in Electron-Stimulated Desorption of Europium Atoms from Oxidized Tungsten: Effects of Temperature*, V.N. Ageev,* Academy of Sciences of Russia, Russia*; Yu.A. Kuznetsov, N.D. Potekhina,* Academy of Sciences of Russia*; T.E. Madey,* Rutgers, The State University of New Jersey

The electron-stimulated desorption (ESD) yield for neutral europium (Eu) atoms from Eu layers adsorbed on oxidized tungsten surfaces has been measured as a function of electron energy, europium coverage and degree of oxidation of tungsten, with an emphasis on effects of substrate temperature. The measurements have been carried out using a time-of-flight method and surface ionization detector. We expand on an earlier report, and compare ESD of multivalent Eu with ESD of monovalent alkali atoms, studied previously. The Eu atom ESD is a complicated function of Eu coverage, electron energy and substrate temperature. In the coverage range 0.05 to 0.35 monolayer (ML), overlapping resonant-like Eu atom yield peaks are observed at electron energies of 36 and 41 eV that might be associated with Eu 5p and 5s level excitations. Additional resonant - like peaks are seen at electron energies of 54 and 84 eV that are associated with W 5p and 5s level excitations. The Eu atom yield peaks at 36 and 41 eV are seen only in the temperature range 220 to 300 K at an europium coverage of 0.07 ML, and the temperature range becomes narrower with increasing europium coverage. In contrast, the peaks at 54 and 84 eV persist above 500 K. The surface ionization current calculations show that the yield associated with the tungsten core level excitations may arise from the ESD of EuO molecules rather than Eu atoms. This is the only reported system for which the electron energy dependence of neutral ESD yield has a resonant character, in the absence of a non-resonant background.

**SS3-TuP9 Cs Adsorbed Structure and Change of Magnetism in fcc Co Thin Films Grown on Cu(001) Surfaces*, F. Komori,* *M. Xu, T. Iimori, K. Lee, M. Yamada, K. Nakatsuji,* ISSP, University of Tokyo, Japan

Magnetic properties of ferromagnetic thin films are often largely modified by adding foreign atoms on the surface. Some of the adsorbed non magnetic atoms or molecules make the magnetization small and change the magnetic anisotropy. To study the effect of Cs adsorption on magnetism as a simple metal, we have deposited Cs on a fcc Co(001) thin film grown on a clean Cu(001) surface, and measured correlation between the ordered structure of Cs adsorbed surface and the ferromagnetic hysteresis loops of the thin film. A fcc Co thin film (about 5 mono-atomic layers thick) was prepared on a clean Cu(001) surface in an ultra-high vacuum, and the surface structure was monitored by LEED with increasing the amount of adsorbed Cs both at 300 K and at 100 K. In both cases, a ring pattern appeared at the first stage of the deposition, and then quasihexagonal LEED spots with two domains were observed. These features are similar to the Cs adsorption on a clean Cu(001) surface, and the distance between the adjacent Cs atoms on the Co surface is the same as that on the clean Cu surface. The relation between the ferromagnetic hysteresis loops and the amount of the adsorbed Cs was in situ studied using magneto-optical Kerr effect. Cs adsorption does not change the magnitude of the magnetization. This is quite in contrast with hydrogen adsorption on the same surface. With increasing the amount of Cs on the surface, the coercive force once decreases and then increases at 100 K while it is almost constant after the initial decrease at 300 K. These are interpreted the increase of the uni-axis magnetic anisotropy due to the steps on the surface at 100 K..

SS3-TuP10 Real-Time Monitoring of Desorption and Restoration on Cl/Si(111) Surface with Second Harmonic Generation*, **K. Shudo**, T. Sasaki, M. Tanaka,* Yokohama National University, Japan

Surface etching with halogen is most elementary process in semiconductor fabrication. To elucidate thermal process on Cl-covered Si(111)-1x1 surface, second harmonic (SH) generation was measured in real time with 1.17 eV photons from a pulsed laser (8 nsec). From isothermal change in the SH signal, energetics on related reactions can be discussed. On clean Si(111)-7x7 dimer-adatom-stackingfault (DAS) surfaces, SH intensity was calibrated in Cl-adsorption compared with temperature programmed desorption. The weakened SH signal by disappearing dangling bonds was interpreted as chlorine coverage on the surface. Initial sticking probability of Cl on the surface was determined to be 0.58, that is actually the same as obtained with SDR.@footnote 1@ Under the isothermal treatment of the Cl/Si(111)-1x1 surface from 843 to 963 K, time-evolution of SH recovery showed that fast and slow steps are involved in the process. The fast one turned out to be of a first order process. Temperature dependence of the rate in the fast component indicates a barrier of 2.1 eV. It corresponds to an energy against emerging of dangling bonds at desorption of silicon chlorides. The following slow component has 2.4 eV of barrier, being activation energy to reform the surface into 7x7 DAS structure. To reduce the dangling bond, 5x5 or 9x9 structures are known to appear temporarily before 7x7 DAS appears. The barrier is considered as the energy required for the slow structural restoration to form and/or move stacking faults. @FootnoteText@ @footnote 1@ Desorption from Cl/Si(111) is also discussed with surface differential reflectance (SDR) spectroscopy, presented elsewhere of SS17 in the conference.

SS3-TuP11 Adsorption and Decomposition of Dimethylisopropylsilane on Si(111) Surface*, **T.S. Yang**, S.J. Cho, J.-H. Boo, J.-W. Lee, S.-B. Lee,* Sungkyunkwan University, Korea*; Y. Kim,* Korea Research Institute of Chemical Technology, South Korea

The adsorption and decomposition of dimethylisopropylsilane,(CH@sub 3@)@sub 2@CHSiH(CH@sub 3@)@sub 2@ on Si(111) surface have been studied in the temperature range of 100 - 1200 K in ultrahigh vacuum by X-ray photoelectron spectroscopy, thermal desorption spectroscopy, and low-energy Cs ion reactive scattering. Dimethylisopropylsilane adsorbs molecularly on the surface at 115 K and its thermal desorption spectrum shows a board peak centered at about 250 K. Even at this low temperature, the results of the low-energy Cs ion reactive scattering indicate that the adsorbed dimethylisopropylsilane was found to partially decompose to adsorb as the Si(CH@sub 3@)@sub 2@ and (CH@sub 3@)@sub 2@CHSiH species. The former decomposes to form CH@sub 4@Si and C@sub 2@SiH@sub x@ species with increasing temperature up to about 600 K and the latter may be converted C@sub 3@H@sub y@ on the surface. Above 900 K the intermediate species completely decomposes to form SiC. The possible decomposition mechanism of dimethylisopropylsilane will be proposed.

SS3-TuP12 Negative Ion Formation in Electron-Stimulated Desorption of CF@sub2@Cl@sub2@ Co-adsorbed with Polar and Non-polar Gases on Ru(0001)*, **S.M Solovev**,* A. F. Ioffe Physico-Technical Inst., Russia*; D. Kusmierek, T.E. Madey,* Rutgers University

Photon-induced dissociation of CF@sub2@Cl@sub2@ (freon-12) in the stratosphere contributes substantially to atmospheric ozone depletion. We report recent results on dissociation and negative ion formation in electron-stimulated desorption of CF@sub2@Cl@sub2@ on Ru(0001), when CF@sub2@Cl@sub2@ is coadsorbed with a polar gas (NH@sub3@) and non polar Xe, for electron energies from 50 eV to 300 eV. Two different time-of-flight methods were used in this investigation : (a) an ESD ion angular distribution (ESDIAD) detector with wide collection angle, and (b) a quadrupole mass spectrometer with narrow collection angle and high mass resolution. Many negative ESD fragments are seen (F@super-@, Cl@super-@, FCl@super-@, CF@super-@, F@sub2@@super-@, Cl@sub2@@super-@, CFCl@sub2@@super-@, whose intensities depend on the surface preparation. Using both detectors we observe a giant enhancement of Cl@super-@ and F@super-@ yields for ESD of CF@sub2@Cl@sub2@ coadsorbed with ~1ML of NH@sub3@; this enhancement (> 10@super3@ for Cl@super-@) is specific to certain ions, and is attributed to an increased probability of dissociative electron attachment due to "trapped" low-energy secondary electrons.@footnote 1@ The magnitude of Cl@super-@ yield enhancement as a function of electron energy scales with the secondary electron yield, demonstrating the role of low-energy secondaries. In further studies, the influence of polar NH@sub3@ and non-polar Xe space layers (1-10 ML) on ESD of top-layer CF@sub2@Cl@sub2@ is determined, and compared with thick films of condensed CF@sub2@Cl@sub2@. The magnitudes and energy-dependences of the Cl@super-@ yields are different in these cases, due to several contributing factors. @FootnoteText@ @footnote 1@ Q. - B. Lu and T. E. Madey, Surf. Sci. 451(2000) 238.

SS3-TuP13 Collision Induced Process of Adsorbates on Ni(100)*, T. Takaoka, M. Inamura, S. Yanagimachi, **I. Kusunoki**,* IMRAM, Tohoku University, Japan

Surface reactions are usually described as reactions between adsorbates on surfaces. However, effect of collision of molecules in gas phase to surfaces is drawing attention at present. In this work, the collision effect on a N@sub 2@ monolayer, a benzene multilayer, and CO and H coadsorbates on Ni(100) surfaces were investigated. The experiment was carried out in the homemade molecular beam apparatus, which was equipped with a FTIR spectrometer. A supersonic molecular beam technique was used for the control of translational energy of Xe atoms. (1) N@sub 2@ on the Ni(100) surface In FTIR spectra of a Ni(100) c(2x2)-N2 surface, a peak was observed at 2205 cm@super -1@. From the analysis of FTIR spectra recorded after the surface began to be irradiated with Xe beam, it was found that the desorption of N2 molecules is induced by collision with the Xe atoms. The desorption is induced when Xe energy is above threshold energy of 0.8 eV. The threshold energy can be explained with a classical collisional model. (2) benzene multulayer on the Ni(100) surface The effect of the collision onto a multilayer of molecules has been studied. No desorption was observed when a benzene multilayer on the Ni(100) surface was irradiated with Xe atoms with energy of 1.2 eV. The energy transferred from the Xe atom was probably dissipated in condensed molecules and no desorption was observed. (3) CO and H coadsorbates on the Ni(100) surface After the Ni(100) surface was pre-exposed to H@sub 2@ and subsequently exposed to CO, a peak at 2100 cm@super -1@ was observed. In FTIR spectra recorded after the surface began to be irradiated with the Xe beam, decrease of the intensity of the 2100 cm@super -1@ peak and increase of the intensity of a 1950 cm@super -1@ peak with increasing Xe irradiation were observed. It was found that the adsorption site of CO is changed owing to the collision of Xe atoms and a cross section for the change is dependent on the Xe energy.

SS3-TuP14 Desorption of Silicon Chloride and Formation of Dimer-Adatom-Stacking Fault Structure on Si(111) Studied by Surface Differential Reflectivity Spectroscopy*, **M. Tanaka**, S. Minami, K. Shudo,* Yokohama National University, Japan

The processes of isothermal desorption of silicon chloride from the chlorine-saturated Si(111)1x1 surface has been investigated by means of in-situ real-time surface differential reflectivity (SDR) spectroscopy. Temperature range was 873-933K. SDR spectra at each temperature were obtained by the normalization with the reflectance spectrum of the clean surface having 7x7 dimer-adatom-stacking fault (DAS) structure. The spectral features observed at 1.8 and 2.5eV come from missing of adatom dangling bonds and adatom back bonds of DAS structure, respectively. The feature at 1.8eV is found to be removed faster than that at 2.5eV due to the desorption of silicon chloride, which means that the feature at 1.8eV originates from not only adatom dangling bonds but also dangling bonds on the 1x1 surface. The restoration of the dangling bonds therefore represents the development of the desorption. The desorption process is found to follow first order kinetics, suggesting the mechanism that SiCl supplied from clusters and/or steps on the chlorine-saturated Si(111)1x1 surface recombines with Cl on the surface and SiCl@sub 2@ species is desorbed. The activation energy of this process is obtained as 2.2eV from the temperature dependence of the rate constant. On the other hand, the restoration of the back bonds represents the formation of DAS structure after the desorption. The restoration process is found to follow also first order kinetics, and the activation energy is obtained as 2.8eV. The mechanism of the desorption of silicon chloride and the formation of DAS structure is discussed from these activation energies in terms of potential barriers.

SS3-TuP15 Spatially Resolved Thermodynamic and Kinetics of Adsorption on BaTiO@sub 3@ Surface by Variable Temperature Scanning Probe Microscopy*, S.V. Kalinin, D.A. Bonnell, **S. Gupta**,* University of Pennsylvania

Variable temperature scanning surface potential microscopy is used to determine thermodynamic and kinetic parameters associated with polarization and charge dynamics on BaTiO@sub 3@ (100) surface. Potential retention above the ferroelectric phase transition, observation of domain wall motion, and local piezoresponse indicate that the temperature dependence of surface potential results from the interplay between the fast dynamics of atomic polarization and slower dynamics of screening charge. At room temperature surface potential has the sign of the screening charges and is reverse to that expected from polarization orientation. Increasing the temperature results in a decrease of polarization charge leaving the screening charges uncompensated, thus increasing the effective surface potential. On decreasing the temperature spontaneous polarization increases and for a short period of time sign of domain potential is determined by the polarization charge. This phenomenon is referred to as temperature induced potential inversion (TIPI). Under isothermal conditions, polarization and screening charges equilibrate and the potential returns to an equilibrium value. The relaxation kinetics are found to be weakly dependent on temperature with activation energy E@sub a@ ~ 4 kJ/mole. The equilibrium domain potential difference was found to be linearly dependent on temperature. A thermodynamic description of ferroelectric screening based on the Ginzburg-Devonshire theory was developed and enthalpy and entropy were obtained as @Delta@H@sub ads@ = 164.6 kJ/mole, @Delta@S@sub ads@ = -126.6 J/mole K for BaTiO@sub 3@ (100) surface in air. These values are within the range expected for adsorption from the gas phase. Thus, in the case where the charge compensation mechanism is surface adsorption, scanning probe microscopy allows kinetics and thermodynamics of adsorption to be studied with the advantage of spatial localization over techniques such as temperature programmed desorbtion.

SS3-TuP16 COsmic COcktails: CO-ice Chemistry under Interstellar Conditions*, **H.J. Fraser**, W.A. Schutte, E.F. van Dishoeck,* Leiden University, Netherlands

Ices are observed throughout the universe: on planetary bodies, comets, in the Interstellar Medium and in protoplanetary disks. In the laboratory it is possible to study the chemistry and physics of molecular ices under pseudo interstellar conditions. Our experiment combines UHV surface science techniques with an atomic beam to study chemical reactions occurring on interstellar ice grain mimics. The experiment is aimed at identifying the key barrierless reactions and desorption pathways on ices of H@sub 2@O and CO that generate simple molecular species in the gas phase. In this poster we will present results illustrating the desorption rate of CO ice when H@sub 2@ is formed from H recombination reactions on the ice surface, and identify the reaction products formed during thermal warm-up, e.g. HCO, CO@sub 2@, H@sub 2@O, HCOOH. We will also present results on the reaction between CO and O, before, during and after ice processing by UV irradiation. The chemical and astronomical implications of these results will be discussed.

SS3-TuP17 Phosphorus Behaviors upon the Annealing of the Heavily Phosphorus Doped Silicon with Thin Native Oxide Film Evaluated by XPS and AFM*, **Y. Mizokawa**, W.B. Ying, H. Iguchi, Y. Kamiura,* Osaka Prefecture University, Japan*; K. Kawamoto,* Denso Co. Ltd., Japan

Phosphorus redistribution and its chemical structure of the heavily phosphorus doped Si(100) upon the annealing were investigated using x-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM). The samples were prepared by predeposition of POCl@sub 3@, and annealing was performed on the HF-treated samples with about 2nm-thick native oxide film in nitrogen atmosphere at 450°C, 660°C and 750°C for 1 hour. The depth profiling was carried out by the chemical etching using 0.1-1% HF solutions. The true in-depth profiles of P obtained after correcting the mean free path effect showed that the segregated-P was piled up at the interface, and its concentration decayed exponentially toward both directions of oxide film and substrate. Although the dominant chemical structure of P was unoxidized states throughout the oxide/Si, the peak position of the P2p photoelectron shifted toward higher binding energy side with approaching the interface. The results suggest that upon annealing a part of the segregated P atoms located in the top surface region of silicon lattice protrude into the oxide film as a form of P-cluster with P-P bonding. The amount of protruded-P in the oxide film increased with annealing temperature, where the activation energy was about 1 eV. The amount was estimated to be about 1x10@super 15@ P-atoms/cm@super 2@ after 750°C annealing. The AFM image showed an unique pattern of various-sized plateaus of about 2nm height, and after 750°C annealing, some of the plateaus grew in height keeping their lateral shape. The total increments were in rough accord with the estimated volume of protruded-P in the oxide film.

SS3-TuP18 Vibrational Excitation of Methane Physisorbed on Ag(111) using HREELS*, **M. Sakurai**, S. Nishida,* Kobe University, Japan

We measured the incident energy dependence of the relative cross section of both elastic scattering and vibrational excitation of methane molecule physisorbed on the surface of Ag(111) using high-resolution electron energy loss spectroscopy (HREELS). The substrate was mounted on a closed-cycle refrigerator attached on a manipulator for XYZ translation and rotation, and is cooled down to 15K. It has been measured that the elastic cross section shows double dips suggesting the existence of surface resonance.@footnote 1@ At the present experiment with improved resolution, the variation of resonance structure was measured depending on the ambient pressure of CH@sub 4@, which possibly corresponds to the variety of the structure of adsorbed CH@sub 4@ . In addition, the shape of the loss peaks in EEL spectra has a tail which might indicate the rotation of CH@sub 4@ molecule on the surface. @FootnoteText@ @footnote 1@ M. Sakurai, T. Okano and Y. Tuzi, Vacuum 41, 234 (1990).

SS3-TuP19 Adsorbate Induced Electronic Relaxation at Transition Metal > Surfaces*, **G. Fahsold**, A. Priebe, M. Sinther, A. Pucci,* Universität Heidelberg, Germany

We investigate the relaxation of electrons at transition metal surfaces by means of IR-spectroscopy. The adsorbate induced relaxation of electrons is responsible for the DC-resistivity of metal thin films, it is connected to the damping of adsorbate motion, and it contributes to enhancement effects observed in adsorbate vibrational spectroscopy. We measured the contribution of adsorbates (CO, O) to the relaxation of electrons at iron and copper surfaces by observing adsorbate induced broadband changes, firstly, in the IR-reflectivity from thick (opague) epitaxial films and, secondly, in the IR-transmission through ultrathin (< 5 nm) smooth epitaxial films. The higher (compared to IRAS measurements) sensitivity for adsorbate resistivity in IR-transmission is well demonstrated by our experimental results. We understand our results on the basis of a proper description of the optical properties of bulk metals and metal thin films. The talk will focus on the importance of the inclusion of non free-electron-like properties for calculating both the magnitude, the sign, and the spectral shape of adsorbate induced broadband effects.

SS3-TuP20 Electron-hole Pair Generation in Adsorption of Gas-phase H(D) Atom on Pt(111) and Cu(111)*, **J.H. Kim**, S.J. Lee, J.S. Choi, J. Lee,* Seoul National University, Korea

Adsorption of gas species at solid surface proceeds via trapping of incident atom(or molecule) in the surface potential well, which requires an energy transfer to the surface. It is generally believed that multi-phonon creation is the dominant mechanism for the energy transfer. However, for the gas-phase H(D) atom, the lightest of all, phonon creation is expected to be negligible because of an extremely poor mass matching, and therefore other loss mechanism such as electron-hole pair creation may be the dominant mechanism.@footnote 1@. We have investigated adsorption on Pt(111) and Cu(111) surfaces at 100K of the gas-phase H(D) atom generated in a hot tungsten capillary tube at 1900K. The hot electrons and holes generated upon adsorption of H(D) atom were detected as an external short-circuit current using metal/n(p)-type Si(100) Schottky diodes. We will compare the results for the two surfaces and interpret in terms of the different electron density of states near the Fermi level. Based on these results, we will also discuss about the widely different sticking probability, saturation coverage, and abstraction reaction probability of H(D) atom on the two surfaces. @FootnoteText@@footnote 1@Nienhaus et al., Phys. Rev. Lett. 82 (1999) 446.

SS3-TuP21 Thermal Accommodation Coefficients Measurement of Inert Gas on Surface of Stainless Steel Sphere*, **B.S. Jun**, T.K Ghosh, R.V. Tompson, S.K Loyalka,* University of Missouri-Columbia

Heat transfer in the fuel-clad gap in a nuclear reactor impacts the overall temperature distribution, stored energy and the mechanical properties of a nuclear fuel rod. Therefore, an accurate estimation of the gap conductance between the UO2 fuel and the clad is critically important for reactor design and operations. To obtain the requisite accuracy in the gap conductance estimation, it is necessary to take into account the thermal accommodation coefficients of the various gases that are involved. This paper summarizes some recent efforts to obtain stainless steel accommodation coefficients experimentally. To get these values, a high-vacuum system was constructed incorporated in tandem a mechanical vacuum pump and a turbo molecular pump. Thermal accommodation coefficients for helium on stainless steel have been obtained by measuring the cooling rates of a stainless steel sphere suspended in the vacuum chamber. The cooling rate in vacuum is measured and subtracted from the cooling rate in helium at various pressures to yield the approximate net cooling rate of the sphere due to molecular impacts. Knowing the heat capacity of the sphere, its net cooling rate, the temperature difference between the sphere and the ambient gas far from the sphere, the pressure, and the rate of impingement of the gas molecules on the surface of the sphere, one can calculate the efficiency of the energy transfer to the impinging molecules. These measurements have been made on so-called engineering surfaces where no special attempt other than standard baking under high vacuum to remove volatile surface contaminants was used to clean the surfaces. It has been found for helium and argon gas that the thermal accommodation coefficient values with stainless steel are quite constant over the range of pressures studied.

SS3-TuP22 Hyperthermal Product Velocity Detected as a Signature of Electron Harpooning in Gas-Surface Reactions, ***G.C. Poon**, J.-C. Gumy, K.A. Pettus, A.C. Kummel,* University of California, San Diego

Multiphoton Ionization (MPI) and Time-of-Flight Mass Spectroscopy (TOF-MS) have been used to demonstrate that the reaction of ICl on the low work function Al(111) surface proceeds by a nonadiabatic electron harpooning process. In the nonadiabatic model of this reaction, as ICl approaches the Al(111) surface, an electron harpoons from the surface, suddenly converting ICl to ICl@super -@. This places the molecule high on the repulsive portion of the ICl@super -@ potential curve leading to rapid dissociation of ICl@super -@ into I@super -@ and Cl fragments. Following this remote dissociation of ICl above the surface, I@super -@ proceeds towards the surface and sticks while Cl is ejected into the gas phase. This is referred to as chemically selective abstraction and is consistent with the observed excess iodine on the surface by Auger Electron Spectroscopy and the detection of ejected Cl atoms. The experimentally observed signature of this harpooning process is the hyperthermal translational energy of the ejected fragment. A harpoon process should give fast Cl whose energy is determined by the vertical transition between ICl and ICl@super -@ and be independent of incident translational energy. Conversely, a conventional adiabatic abstraction reaction should provide only a small translational energy for the ejected Cl and should increase with increased incident translational energy. Hyperthermal Cl (0.36 eV ± 0.14 eV) ejected from the surface has been observed using MPI/TOF-MS, which is evidence for the aforementioned nonadiabatic process. Furthermore, DFT calculations of the vertical transition energy from ICl to ICl@super -@ are in good agreement with experiment. Comparison of the translational energy of ejected Cl from the abstractive chemisorption of Cl@sub 2@ and ICl will also be presented. Cl@sub 2@ should lead to even faster Cl ejected from the surface than for ICl, since Cl@sub 2@@super -@ is formed even higher on the repulsive portion of the potential curve.

SS3-TuP23 Growth Process of Self-organized Ge Quantum Dots on Si(111)-(7x7) Surface Studied by STM, *Y. Zhang, L. Yan, S. Xie, **S. Pang**, H. Gao,* Chinese Academy of Sciences, P.R. China, China

The influence of substrate temperature on the nucleation and self-organized growth of submonolayer Ge on Si(111)-(7x7) surfaces grown by solid phase epitaxy (SPE) has been studied using scanning tunneling microscopy (STM). Ordered Ge quantum dots on the surface are formed through controlling the annealing temperature after submonolayer Ge deposition at room temperature. The formation of ordered Ge quantum dots is due to the preferential adsorption sites of Ge on Si(111)-(7x7). The formed ordered nanostructures may have a potential in the application of nanodevices.

SS3-TuP24 Halogen Adsorption on Pt(110): A Coverage-dependent Charge Density Wave Transition, ***K. Swamy**, C. Deisl, R. Beer, A. Menzel, E. Bertel,* University of Innsbruck, Austria

STM and LEED results of halogen (Cl, Br) adsorption on Pt(110) show a sharp, coverage-dependent phase transition into a charge density wave ground state for a coverage of @THETA@ = 0.5 ML. At this coverage Br orders in a c(2x2) and Cl in a (2x1) structure. The (1x2) missing-row reconstruction of clean Pt(110) is lifted. Contrary to our previously published mode,@footnote 1@ LEED-IV data and ab-initio calculations reveal that the halogens are not substitutionally adsorbed, but in every second short-bridge site.@footnote 2@ Both, the Br-c(2x2) and the Cl-(2x1) phase can be transformed into a (3x1) phase by minute amounts of excess halogens (@THETA@ = (0.5 + @delta@) ML), but also of molecular species (CO and NO). The Br-c(2x2) derived (3x1) phase is stable up to T > 500 K, while the Cl-(2x1) derived (3x1) phase is long-ranged ordered only at T < 200 K. Low-temperature ARUPS spectra prove that the Br-(3x1) and the Cl-(3x1) phases have an almost identical electronic structure. We interpret the (3x1) structure as a charge density wave. This is compatible with the ARUPS data, i. e. we find a corresponding nesting vector and a Peierls gap. @FootnoteText@ @footnote 1@ K. Swamy, A. Menzel, R. Beer, and E. Bertel, Phys. Rev. Lett. 86, (2001) 1299. @footnote 2@ K. Swamy, C. Deisl, E. Bertel, V. Blum, L. Hammer, K. Heinz, C. Franchini, and J. Redinger, in prepration.

SS3-TuP25 A LEED Investigation of Xe Adsorbed on Pd(111), ***J. Zhu**, H. Ellmer, H. Malissa, D. Semrad, P. Zeppenfeld,* Johannes Kepler Universität Linz, Austria

Xe adsorption on the Pd(111) surface was investigated by means of low energy electron diffraction (LEED) in a UHV chamber with 1.2x10@super -11@ mbar base pressure. Depending on the Xe coverage and substrate temperature, a large number of different phases were identified, including a 2D gas phase and a 2D liquid phase, a commensurate (@sr@3x@sr@3)R30° solid phase (C), a compressed striped incommensurate phase (SI), ordered multilayer structures, and a clear Xe(111) crystal with sharp spots rotated 30° with respect to the substrate. In addition, a hexagonal incommensurate solid phase (HI) and a hexagonal incommensurate rotated phase (HIR) were observed as well as a C -> SI -> HI -> HIR phase transition. The (@sr@7x@sr@7)R19.2° and (@sr@19x@sr@19)R23.5° commensurate phases reported by Hilgers et al.@footnote 1@ were not obtained after Xe adsorption on the clean surface in the entire temperature and coverage range. However, small amounts of contaminants (CO and/or H@sub 2@) on the Pd(111) surface have a striking influence on the Xe post-adsorption. With ~0.1 L of CO pre-adsorbed at 55 K, a clear (@sr@7x@sr@7)R19.2° commensurate phase is obtained. After pre-adsorption of ~0.1 L of H@sub 2@ at 55 K, a commensurate phase (@sr@19x@sr@19)R23.5° appears in the high Xe coverage region. A combination of 0.1 L H@sub 2@ and 0.1 L CO pre-adsorbed at 55 K leads to a phase transition sequence from (@sr@3x@sr@3)R30° -> (@sr@19x@sr@19)R23.5° -> (@sr@7x@sr@7)R19.2° similar to the one reported for Xe on Pd(111) in Ref. 1. From these observations, therefore, we conclude that the high-order commensurate (@sr@7x@sr@7)R19.2° and (@sr@19x@sr@19)R23.5° phases of Xe are related to CO and H@sub 2@ impurities, respectively. @FootnoteText@ @footnote 1@ G. Hilgers, M. Potthoff, N. Müller and U. Heizmann, Surf. Sci. 322 (1995) 207.

SS3-TuP26 Adsorption and Absorption of Hydrogen by Ti(0001): A Study Combining Surface Characterization and Non-destructive H-Depth Profiling, ***M. Wilde**, M. Matsumoto, K. Fukutani, T. Okano,* University of Tokyo, Japan*; Y. Mizuno, T. Homma,* Chiba Institute of Technology, Japan

In the present work the interaction of the Ti(0001) single crystal surface with molecular H@sub 2@ and atomic H is studied at temperatures of 100-300 K. We combine standard UHV techniques of clean surface preparation and characterization with hydrogen depth-profiling by nuclear reaction analysis (NRA, via the @sup 1@H(@sup 15@N,@alpha@@gamma@)@sup 12@C reaction), which allows straightforward assigning of the features in H@sub 2@ thermal desorption spectra (TDS). Molecular H@sub 2@ admitted at T650 K is unaffected. The outgassing rate is characterized by an activation energy in excellent agreement with the heat of H solution in @alpha@-Ti of 21.6 kcal/mole.

Applied Surface Analysis
Room 134 - Session AS-WeM

Biomaterials and Polymers

Moderators: D.H. Fairbrother, Johns Hopkins University, S.L. McArthur, University of Washington

8:20am **AS-WeM1 Surface Characterization of Biomaterials for Medical Applications***, **H.J. Mathieu,*** Swiss Federal Institute of Technology Lausanne (EPFL), Switzerland **INVITED**

Biomaterials are non viable materials used as medical devices interacting with biological systems and are increasingly being applied as substitutes and/or sensors in human hosts. This paper describes the specific surface functionalization and characterization of biomaterials for Medical Applications by use of methods such as x-ray photoelectron spectroscopy (XPS) and imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) as well as contact angle measurements and scanning force microscopies (SFM). Bio-molecules (peptides, polysaccharides, proteins, etc) are grafted to various types of materials ranging from metals, semiconductors to polymers. It is the bulk composition which determines the physical, mechanical and rheological properties, whereas surface chemistry and topography influence the response to a foreign implant. The control of chemistry, forces and topography of surfaces and thin films with femtomol sensitivity, nanometer in-depth information and submicron lateral resolution will be highlighted. Practical applications cover photo-grafting of hydrocarbons for the development of bio-sensors - glycoengineering -, plasma modification of polymers to reduce bacterial adhesion on endotracheal devices and cell adhesion on metallic surfaces. References: 1. D. Leonard and H.J. Mathieu, Fresenius' Journal Analytical Chemistry 365 (1999) 3-11 2. H. J. Mathieu, Surface and Interface Analysis 32 (2001) in print.

9:00am **AS-WeM3 Micromechanical Properties of 'Smart' Gels: A Study of PNIPAAm by Scanning Force and Scanning Electron Microscopy***, **T.R. Matzelle,*** Universite Libre de Bruxelles, Belgium*; R. Reichelt,* University of Muenster, Germany*; N. Kruse,* Universite Libre de Bruxelles, Belgium

PNIPAAm [poly-(N-isopropylacrylamide)] is one of the most interesting and promising 'smart' gels. It undergoes a reversible phase transition in response to external temperature changes. The PNIPAAm matrix, swollen in aqueous solution, collapses as the temperature is increased above the lower critical solution temperature (LCST), which is about 33°C. Due to this thermoresponsive ability, these gels are promising candidates for thermal switches, micro/nanoactuators or controlled-release systems. In order to provide information on the local structural and mechanical properties of PNIPAAm we employed scanning force microscopy (SFM) in air or in water at various temperatures below and above the LTSC. SFM images of the gel surface were compared with those obtained in dry, swollen, and collapsed states using field emission scanning electron microscopy (FESEM). Images of SFM and FESEM of the dry hydrogel surface revealed similar structural features. The surface is rather smooth except for small spherically shaped protrusions with a diameter and a height ranging from 10 to 50 nm and from 5 to 15 nm, respectively. FESEM of a cryogenically dried PNIPAAm sample swollen in water at 20°C revealed a coral-like structure with cavities of @tdA@40 nm. Force vs. cantilever displacement curves were measured with both, spherical (µmm-sized) and commercial probes. Indentation of the hydrogel surface as a function of the probe load was evaluated using the Hertz model to determine the local elastic moduli at different temperatures. For the swollen state at 10°C Young's modulus was found to be 1.11 kPa, which is more than 100 times lower than for the collapsed state at 35°C. More generally, this modulus is significantly lower than the moduli measured for biological cells.

9:40am **AS-WeM5 Tailored Polymer Surfaces Controlled by XPS***, **J.-J. Pireaux,*** Facultés Universitaires Notre-Dame de la Paix, Belgium **INVITED**

If polymer materials are now so widely used that it is hard to imagine life without them - billions of kilograms of plastics are sold every year-, a significant set of applications rests on polymers in juxtaposition with another material, as in composites or (multi)layered structures. All properties of these ensembles depend on successful and controlled adhesion, a very complex technology indeed that encompasses various physico-chemical interactions between two surfaces. This presentation will review the different methods used in the laboratory, or at the production plant, to modify, if possible in a very controlled way, a polymer surface. To remove superficial contamination, to modify surface morphology, to tune hydrophobicity, to functionalize a polymer surface ... can be achieved by various chemical or physical methods. Surface treatment is particularly versatile when using a plasma discharge, a vacuum technique, while X-Ray Photoelectron Spectroscopy (XPS) appears a method of choice to control the tailored polymer surface. Potentials of the cold (reactive) plasma treatment will be shown; advantages and problems of the XPS characterization method will be pointed out; complementary information gained by FT-infrared and contact angle measurements will be illustrated. Two sample cases will be commented on: (1) plasma treatment of polyester, in various reactive gases that shows ageing (surface oxidized species slowly disappear with time), while an optimum amount of functionalization allows better adhesion of an evaporated aluminium layer (mechanical adhesion test); (2) some parameters governing the physico-chemical interactions at the SiO@sub x@ -functionalized polypropylene interface will be explained with the help of the acid-base concept.

10:20am **AS-WeM7 Synthesis and Characterization of Poly(imidesiloxane) Copolymers Containing Two Siloxane Segment Lengths: Surface Composition and Its Role in Adhesion***, **C.M. Mahoney,*** State University of New York at Buffalo*; J.C. Rosenfeld,* Occidental Chemical Corporation*; J.A. Gardella, Jr.,* State University of New York at Buffalo

Polyimidesiloxane (SIM) copolymers are extremely important materials for microelectronic applications due to their excellent adhesive properties, low dielectric constants and good overall thermal and mechanical properties. Hence it is of importance to study the surface and interfacial properties of this polymer system. A series of poly(imidesiloxane) (SIM) copolymers have been synthesized, where the total composition of PDMS was maintained at 10% (by weight) with two different PDMS segment lengths of different relative composition. (e.g. 5% PDMS containing 1 repeat unit, designated G-1 and 5% PDMS containing 9 repeat units, designated G-9 incorporated into the same polymer vs. 1% G-1 and 9% G-9 in the same polymer). Two main polymer series were synthesized, one containing G-1 and G-9 in varying ratios, and the other containing G-5 and G-9. Both of these series have been analyzed using angle dependent X-Ray Photoelectron Spectroscopy (XPS). The results suggest that there is preferential segregation of longer siloxane segment lengths to the surface. The angle dependent data was then used to obtain an in-depth profile by using a deconvolution process. From the profiles, it was determined that the thickness of the surface PDMS layer of all polymers containing both G-9 and G-1 were the same for all compositions studied, while that of the pure 10% G-1 was much less. The adhesion strengths of these polymers were measured using peel strength tests and the adhesion values were correlated to the XPS results. It was found that the adhesion of the pure 10% G-1 was much higher than that of any other polymer in the series. The remainder of the polymers in the series all had similar adhesion values. These results are consistent with a model of the surface, which has longer segment lengths preferentially segregating and dominating the adhesive properties.

10:40am **AS-WeM8 Phase Contrast AFM Analysis of Polymers: Use of Correlative Classification Methods for Phase Identification***, **J. Farrar**[1], K. Artyushkova, J.E. Fulghum,* Kent State University

Phase contrast AFM is increasingly utilized in the analysis of polymers and polymer blends. The phase contrast images potentially contain chemical information, although image interpretation can be challenging. In this study we evaluate methods for the correlation of XPS and AFM data, in order to facilitate chemical interpretation of phase contrast AFM images. Polymer grids are used to evaluate the image pre-processing required before the application of classification methods. Processing for image correlation includes resizing, image alignment and resolution matching. Considerations specific to each technique will also be discussed. Following the image processing, classification methods are used to correlate components present in the XPS and AFM images. After validating the approach on test samples, heterogeneous polymer blends are analyzed using image classification methods. This work has been partially supported by NSF ALCOM (DMR89-20147).

11:00am **AS-WeM9 A Surface Chemistry Study of Laser Ablated Polymers Used for Microfluidic Devices***, **D.L. Pugmire**, E.A. Waddell, C.J. Taylor, L.E. Locascio, M.J. Tarlov,* National Institute of Standards and Technology

Polymer substrates are being investigated for use in microfluidic devices because of their low cost, ease of fabrication, and wide range of materials properties. It is well established that the surface chemistry of a plastic substrate greatly influences the electroosmotic flow (EOF) behavior of microfluidic channels made from that material. Typical channel imprinting techniques do not offer direct control of surface chemistry. Laser ablation

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[1] **ASSD Student Poster Competition Participant**

shows promise as a versatile method for directly forming a variety of microchannel geometries in plastics. In addition, we have demonstrated that surface chemistry, and, therefore, EOF behavior can be controlled by changing the atmosphere under which laser ablation of the plastic is performed. The surfaces of several plastics ablated in a variety of environments were studied with x-ray photoelectron spectroscopy (XPS), attenuated total reflection infrared spectroscopy (ATR-IR), and scanning electron microscopy (SEM). XPS results indicate that laser ablation generally resulted in an increase in the oxygen content of the polymers studied, regardless of ablation atmosphere. However, this oxygen uptake was often more pronounced when ablation was performed under O@sub 2@ as opposed to N@sub 2@ or Ar. Ablation of commercially obtained PVC, with an organotin stabilizer, resulted in concentration of tin species at the ablated surface. These results will be discussed and compared to EOF rates of ablated microchannels.

11:20am **AS-WeM10 RBS-based Characterization of Hyper-Thin Silicon Compound Deposits on Polymers***, **G. Dennler**,* Ecole Polytechnique de Montreal, Canada*; A. Houdayer,* University of Montreal, Canada*; Y. Ségui,* Université Paul Sabatier, France*; M.R. Wertheimer,* Ecole Polytechnique of Montreal, Canada

Rutherford Backscattering Spectroscopy (RBS) with 1 and 1.5 MeV alpha particles has been used to investigate the growth of SiO@sub 2@ and Si@sub 3@N@sub 4@ films deposited by Plasma-Enhanced Chemical Vapor Deposition (PECVD) on three different polymers, namely polyimide, polyethyleneterephthalate and polycarbonate. The thicknesses of the various films considered in this work vary from 0.1 to 50 nm. In the case of Kapton PI, using the IBM geometry at 150°, we verified that the ratio of Silicon to Carbon does not change during irradiation; this signifies that the specimen does not suffer a significant amount of damage. Thus, using this RBS geometry, we were able to follow the surface density of Si atoms versus time of deposition, t, that is, to measure film thickness, d, down to 1 Å. The calibration of d was accomplished using thicker samples, characterized by Variable Angle Spectroscopic Ellipsometry (VASE) and X-Ray Fluorescence (XRF); a perfectly linear relationship between d and t was observed over the entire range, for both coating types on PI. RBS was also used at near-grazing angle (95°) to investigate the interphase between SiO@sub 2@ and polymeric substrates. RUMP simulations predicted a precision of about 5 nm under these conditions. Thus, we investigated a 50 nm SiO@sub 2@ film on Kapton PI and found that the interphase thickness does not exceed 7 nm. The same methods, applied to deposits on the other two polymers, were unsuccessful because of serious modifications of the polymeric substrate, induced by the incident ion beam, even under conditions of very low beam current (1nA) : Scanning Electron Microscopy (SEM) allowed us to observe the damage caused at the surface by the volatile molecular fragments created in the irradiated bulk of the polymer during their escape through the coated sample surface. This work shows clearly that an interphase of the order of 5 nm can be observed in certain cases, but that this IBA technique is not generally applicable for all polymers, because of radiation damage.

Biomaterials
Room 102 - Session BI+SS-WeM
Biological Interface & Surface Science

Moderator: C. Wöll, Ruhr-University Bochum, Germany

8:20am **BI+SS-WeM1 Hybridization Reactions between Surface Attached Oligonucleotides and Complements from Solution***, **W. Knoll**, D. Kambhampati, T. Neumann, M. Chen,* Max-Planck-Institut für Polymerforschung, Germany **INVITED**

The quantitative evaluation of hybridization reactions between surface-attached 15mer oligonucleotides and their complements from solution will be described. Reaction kinetics, as well as equilibrium binding studies are conducted in order to reveal the association/dissociation mechanism. Different strategies to prepare the interfacial probe layers are tested and compared to each other: These are 1) direct coupling of the catcher oligonucleotides to a gold substrate by thiol groups, 2) a streptavidin monolayer-based coupling scheme via biotinylated probe oligos, 3) a similar approach but based on a commercial dextran-streptavidin structure, 4) 15mers attached to polymer brushes grown by a "grafting-from" approach, and finally 5) a layer prepared by electropolymerization of hydroxyphenol-derivatized oligonucleotides. In cases where surface plasmon spectroscopy was not sensitive enough for label-free detection of the hybridization we employed our recently developed surface-plasmon field-enhanced fluorescence spectroscopy. Different versions based on having either the catcher strand labeled, or the target, or both (e.g., for energy transfer studies) will be discussed. Parameters that are studied include the effect of temperature, ionic strength, mismatch (number of bases, position) length of complement, charge density (DNA versus PNA) etc.

9:00am **BI+SS-WeM3 Functionalization of Metal-Oxide-Based Biomaterials and Biosensor Surfaces by Molecular Self-Asssembly Processes***, **M. Textor**, S. Tosatti, M. Zwahlen, S. Finken, J.A Hubbell, G. Haehner,* Swiss Federal Institute of Technology (ETH), Switzerland

Modifications of metal oxide surfaces based on spontaneous adsorption of alkane phosphates and polycationic copolymers and subsequent film formation are shown to be potentially very useful for designing the chemical and biochemical properties of metallic implants and optical biosensors. Alkane phosphates were found to self-assemble on a number of transition metal surfaces such as titanium oxide, tantalum oxide and niobium oxide through direct coordination of the phosphate head group to high-valency metal cations. The chemical and structural properties of the adlayers were investigated using XPS, ToF-SIMS and NEXAFS. Introducing terminal functionalities other than methyl, e.g. hydroxy, amine or oligo(ethylene oxide) groups, allows one to tailor physico-chemical properties such as wettability, surface charge or the strength of protein-surface interactions. A second class of molecular assembly systems, PEG-grafted polycationic copolymers, spontaneously form monomolecular adlayers on negatively charged metal oxide surfaces, imposing high resistance towards biomolecule adsorption. Through further functionalization of the PEG-chains with biotin or peptide moieties, specific interactions of the treated oxide surface with streptavidin or with cell receptors can be induced while preserving the low degree of non-specific events. w-functionalized alkane phosphate SAMs, as well as peptide-modified PEG-grafted copolymers have been applied to both smooth and rough titanium surfaces to produce model surfaces for the study of fibroblast and osteoblast cell-surface interactions, with independent control of surface topography and chemistry. Furthermore, the two novel molecular assembly systems are shown to have a substantial potential for the reproducible and cost-effective modification of chips in optical-waveguide-based bioaffinity sensing of proteins and of DNA/RNA, including their application to microarray-type sensor surfaces.

9:20am **BI+SS-WeM4 Buildup Mechanism for Hyaluronic Acid/polysine Films onto a Solid Interface***, C. Picart, Ph. Lavalle, F.J.G. Cuisinier,* INSERM U424, France*; P. Schaaf,* Institut Charles Sadron (CNRS) Strasbourg, France*;* ***J.C. Voegel***, INSERM U424, France

The formation of a new kind of biocompatible films based on Poly-L-Lysine and Hyaluronic Acid (PLL/HA) by alternate deposition of PLL and HA was investigated. It is shown that the driving force of the buildup process appears, as for "convential" polyelectrolyte multilayer systems, to be the alternate overcompensation of the surface charge after each PLL and HA deposition. The construction of (PLL/HA) films appears to take place over two buildup regimes. The first regime is characterized by the formation of isolated islands dispersed on the surface and which grow both by addition of new polyelectrolytes on their top and by mutual coalescence of the islands. The second regime sets in once a continuous film is formed at the after the 8th bilayer deposition in our working conditions. QCM measurements at different frequencies evidences a viscoelastic behavior of the films which have a shear viscosity of the order of 0.1 Pa.s. During this second regime the mass of the multilayer film increases in an exponential rather than in a linear way. This exponential growth is explained the diffusion of free PLL chains into the interior of the film when it is brought in contact with a PLL solution and by the diffusion out of the film of a fraction of these free chain followed by their interactions with HA chains at the outer limit of the multilayer when the film is further brought in contact with a HA solution. The diffusion of free PLL chains into the film is also found to be accompanied by an expulsion of water out of the film. This new kind of biocompatible film incorporating a natural polymer of the extracellular matrix and a widely used polypeptide makes it a potential candidate for cell-targeted action and for the coating of different types of surfaces, such as implants or capsules, in order to mimic a natural extracellular gel.

9:40am **BI+SS-WeM5 Orientational Effects and Surface Free Energies in the Amino Acids Adsorption Process onto Silicon-based Surfaces***, G.L. Gambino, **C. Satriano**, G. Marletta,* University of Catania, Italy

The present paper deals with the study of the adsorption process of Lysine (Lys) and Cysteine (Cys) from aqueous solutions as a function of the substrate structure and solutions pH. The substrate effect has been studied for three silicon-based substrates, i.e. silicon dioxide, poly(hydroxymethyl)siloxane (PHMS) and oxygen plasma-treated PHMS. The pH role on the adsorption process has been investigated by performing the incubations in the amino acid solutions both at their isoelectric pH and at the physiological pH, i.e. pH = 7.4. The in situ characterization of the substrates-amino acids molecules interaction was performed by means of the Quartz Crystal Microbalance with Dissipation (QCM-D) technique. On the other hand, ex-situ measurements were performed by means of Angular Resolved X-Ray Photoelectron Spectroscopy (ARXPS) and Contact Angle (CA) measurements. In particular, ARXPS, by varying the sampling depth from @tdA@10 nm to @tdA@2 nm, allowed to elaborate a coverage model, while the CA technique, by using three test liquids, allowed to calculate the surface free energies and their relative dispersive and acid-base contributions. QCM-D data shows that Lys and Cys strongly adsorb onto the plasma-treated PHMS while on the untreated PHMS surfaces the adsorption of both amino acids does not occur. ARXPS measurements indicate that the adsorbed molecules exhibit a preferential orientation respect to the plane of the surface, however no uniform coverage is obtained for any kind of substrate. Finally, the CA measurements indicate that the polar component of the surface free energy is directly related to both the amount and the orientation of the adsorbed amino acid molecules.

10:00am **BI+SS-WeM6 Surface-bound Liposomes for Biomedical Applications***, P. Vermette,* CSIRO, Australia*; E. Gagnon,* Universite Laval, Canada*; L. Meagher,* CSIRO, Australia*; D. Dunstan,* Melbourne University, Australia*;* ***H.J. Griesser****,* CSIRO, Australia*; C. Doillon,* Universite Laval, Canada

Injectable liposomes, in particular PEG-coated liposomes, are well known in the pharmaceutical industry for drug delivery. However, much of the drug never reaches the intended target site. We have developed methods for binding liposomes onto surfaces of biomedical devices for controlled local delivery of drugs adjacent to implanted biomedical devices. In this way we aim to reduce drug amounts and wastage, and control the local host response to the implant, a response which with most current biomaterials typically is dominated by fibrous tissue encapsulation. We have produced liposomes with encapsulated drugs and model substances, characterized them in terms of size and release performance, and bound them onto polymeric surfaces. PEGylated phospholipid liposomes were produced by extrusion through polycarbonate membranes of various pore sizes. The diameters of the liposomes were characterized by photon correlation spectroscopy. For binding liposomes, polymer surfaces were coated with streptavidin, which was used for affinity capture of biotinylated PEGylated liposomes. Streptavidin was covalently bound onto polymer surfaces via an amine plasma (glow discharge) polymer interlayer and a layer of polyacrylic acid, onto whose carboxylate groups the streptavidin was attached by carbodiimide chemistry. Detailed surface analyses were used to characterize and verify each step in the fabrication of the liposome coated surfaces. To test the in vivo efficacy of liposome coated biomaterials, an angiogenesis promoting drug was encapsulated and the liposomes attached. Both in vitro and in vivo there occurred markedly enhanced angiogenesis. Another way of using the same concept may be to implant streptavidin coated biomedical implants and then inject drug-loaded liposomes. Experiments are currently underway to investigate whether circulating biotinylated liposomes can thus be enriched at an implant surface by affinity capture with surface-immobilized streptavidin.

10:20am **BI+SS-WeM7 Thiol-Reactive Surfaces for the Specific Immobilization of Biomolecules***,* ***R.L. Cicero****, D. Martin, S. McManus-Munoz, C.E.J. Dentinger, P. Kernen, P. Wagner,* Zyomyx Inc.

We present multi-component self-assembled monolayers on Au(111) surfaces that extend thiol-reactive groups and chemical moieties known to resist non-specific adsorption of proteins. Particular attention will be paid to the structural characterization of these surfaces using X-ray photoelectron spectroscopy, reflection absorption infrared spectroscopy and ellipsometry. We also investigate the effect surface density of thiol-reactive groups presented at the solid-liquid interface has with respect to homogeneity, efficiency and specificity of immobilizing thiol-containing biomolecules to these surfaces. Several methods for detecting and quantifying biomolecule immobilization are used including surface plasmon resonance spectrometry, radiometry and fluorimetry.

10:40am **BI+SS-WeM8 Control and Detection of Surface Immobilized DNA Interactions Using Electrostatically Assisted Surface Plasmon Resonance***,* ***R.J. Heaton****, A.W. Peterson, L.K. Wolf,* Boston University*; R.M. Georgiadis,* Boston University, usa

Using Surface Plasmon Resonance (SPR) spectroscopy, we demonstrate that the formation of an immobilized DNA film on gold can be controlled by non-Faradaic electrostatic charging. Furthermore, electrostatic charging can be used to enhance interactions between the immobilized probe film and target oligonucleotides in solution. By simply adjusting the potential across the surface thiol-modified single stranded oligonucleotide films can be formed with good reproducibility in coverage. The application of an attractive potential can speed up and maximize the hybridization of complementary and mismatched oligonucleotides to the probe film. We demonstrate the efficacy of this technology with application to both single area and array-mode SPR.

11:00am **BI+SS-WeM9 Non-Uniform Mixing in Fluid Surfaces***,* ***J.S. Hovis****, S.G. Boxer,* Stanford University

Cell membranes are two-dimensional heterogeneous fluid surfaces comprised of lipids, proteins, and carbohydrates. Understanding their organization at the molecular level is of critical importance for understanding cellular function. One of the key features, of the cell membrane is it's fluidity, which precludes long range order. However, due to the heterogeneous nature of the system it is possible that non-uniform mixing occurs, resulting in the local enhancement of certain membrane components. We will present results from our studies designed to probe for one type of domain, termed 'lipid rafts', using model membranes. In particular, we use supported lipid bilayers that are partitioned; the partitioning enables us to spatially contain the membrane components. By applying an electric field in the plane of the bilayer we can rearrange the membrane components in the partitioned regions. Sphingolipids and cholesterol, the major components of lipid rafts are electrically neutral and will not reorganize in response to a field; however, GM@sub 1@, a minor component, will as it has a net negative charge. Using epi-fluorescence microscopy we monitored the resultant electric field induced reorganization of the membrane components. Our results indicate that the reorganization of the GM@sub 1@ induces a reorganization of the sphingolipids and cholesterol. However, this reorganization does not appear to be concerted, suggesting that the rafts are not long-lived structures. That is, there is an increased propensity for certain components to be in close proximity to one another, but due to the fluid nature of the lipid bilayer, individual components are not in close proximity for long. This work will hopefully provide additional insight into understanding how non-uniform mixing occurs in these fluid surfaces and what the functional consequences are.

11:20am **BI+SS-WeM10 Vesicle to Supported Bilayer Transformation Kinetics; Influence from Vesicle Size, Temperature and Surface Support***,* ***E. Reimhult****, K. Dimitrievski, V.P. Zhdanov, F. Höök, B. Kasemo,* Chalmers University of Technology, Sweden

Supported phospholipid bilayers (SPB) on solid surfaces are biologically functional components of high current interest, e.g., for biosensors, tissue engineering, and basic science (Sackman, Science 271:43 (1996)). We investigate how the kinetics of vesicle to bilayer transformation on SiO@sub 2@ depend on vesicle size using small Extruded Unilamellar Vesicles (EUV; diameter~30-200 nm) and Small sonicated Unilamellar Vesicles (SUV; diameter~25 nm)) and temperature (T~5 to 30°C).). The experimental results are complemented by computer modeling and MC simulations. Our results reveal weak but significant vesicle size-dependent kinetics. The rate and completeness of the vesicle-to-bilayer transformation is strongly dependent on temperature and the vesicle-to-bilayer formation on SiO@sub 2@ can under certain circumstances be completely inhibited at low temperatures. In addition, the vesicle-surface interaction was investigated for various surfaces, including oxidized Au, Pt and Ti, which all demonstrate adsorption of vesicles in an intact state independent of vesicle size and temperature. The obtained results extend our previous studies at constant vesicle size and temperature (Keller et al, Phys Rev B 61: (3) 2291 (2000)) and constitute a platform that will significantly improve the possibility to control the process on µmm-nm fabricated surfaces, from which more complex functional supported bio-membranes are constructed.

11:40am **BI+SS-WeM11 Functional Tethered Lipid Membranes on Gold***,* ***K. Bender****,* Stanford University

A solid supported, biomimetic lipid bilayer was formed on a gold substrate by adsorbing lipid vesicles on a self-assembled monolayer (SAM) consisting of thiol-lipopeptides mixed with thiol-peptides. The membrane was bound to the surface by the thiol-lipopeptides, the thiol-peptides being used to change the surface concentration of thiol-lipopeptide and hence control membrane fluidity. The lipid bilayer was formed by fusion of L-@alpha@-Phoshatidylcholine (eggPC) liposomes onto the mixed thiol-lipopeptide / thiol-peptide SAM. The free lipids replenish the tethered lipid layer and also form the second layer to complete the bilayer. A functionalized lipid bilayer was formed by incorporating H@super +@-ATP-synthase (extracted and purified from spinach chloroplastes) with the eggPC. This enzyme is a membrane integral protein that can synthesize or hydrolyze adenosine triphosphate (ATP) from or to adenosine diphosphate (ADP) and in doing so pumps H@super +@ through the bilayer. Impedance spectroscopy measurements demonstrated that the enzyme had not lost its biological functionality and was still active. The formation of the lipid bilayer was detected by using surface plasmon resonance spectroscopy (SPS). Finally Annexin V, a pore forming protein, was immobilised on a lipid bilayer by using Ca@super 2+@-ions to bind (by chelation) the negatively charged parts of the protein to the negatively charged lipids (1,2-Dimyristoyl-sn-Glycero-3-Phoshatidylserin) in the bilayer. Annexin V as a non-integral protein and its function as a passive ion transporter through the lipid bilayer was used for comparison of the active ion transporter H@super +@-ATP-synthase. The same techniques as described above were used to observe the formation and activity of this system.

Organic Films and Devices
Room 131 - Session OF+NS+SS+BI-WeM
Self Assembled Monolayers/Ordered Films

Moderator: R. Maboudian, University of California, Berkeley

8:20am **OF+NS+SS+BI-WeM1 Preparation and Characterization of Nano-Scale Mixed Self-Assembled Monolayers***, S. Chen, L. Li, C. Boozer,* ***S. Jiang,*** University of Washington

Fabrication of nano-scale structures by mixed self-assembled monolayers (SAMs) has recently attracted much attention due to its scientific importance and potential applications to chemical and biological sensors, and biocompatible materials. However, it is still difficult to prepare nano-scale mixed SAMs since phase segregation occurs when two components are quite different. Recently, we proposed a new kinetically-trapped method to prepare nano-scale uniform mixed SAMs. In this work, we prepared various mixed SAMs, such as dodecanethiol(C12)/octanethiol(C8), tetradecanethiol (C14)/C8, 11-mercaptoundecanol(C11OH)/C8, and 11-mercaptoundecanoic acid(C10COOH)/C8 at a range of compositions using the kinetically-trapped method. Our results by low-current scanning tunneling microscopy (STM) revealed homogenous mixed SAMs with various terminal groups and a solution composition up to 25% of long chains formed at higher solution temperatures. Possible mechanism for forming uniform mixed SAMs will be discussed.

8:40am **OF+NS+SS+BI-WeM2 The Role of Linker Molecules in the Controlled Adsorption of Polystyrene (PS) Nano Particles***,* ***M. Himmelhaus,*** Universität Heidelberg, Germany*; H. Takei,* Hitachi Central Research Laboratory, Japan

Controlled adsorption of PS nano particles onto specific regions of flat surfaces has found increasing interest as potential applications for surface-adsorbed PS particles, such as fabrication of quantum dots, optical switches, mesoscopic lasers, biosensors, as well as dosing of biomolecules, require an easily applicable adsorption scheme capable of addressing macroscopic areas. Among the various techniques those utilizing linker molecules to promote particle-particle as well as particle-surface interaction have only recently been applied as to date the role of the linker molecules in the various physical and chemical adsorption mechanisms is only poorly understood. We have studied the effect of several water-soluble linker molecules on the adsorption behavior and packing density of surfactant-free polystyrene latex spheres from suspension. By variation of several parameters, such as molarity of the linker molecules, pH of the suspension, as well as choosing differently functionalized PS particles we can distinguish several adsorption mechanisms from each other, reaching from purely physical ones to covalent bonding. This basic study is a first step to the fabrication of 2D crystalline monolayers of macroscopic lateral extension by means of chemically driven self-assembly.

9:00am **OF+NS+SS+BI-WeM3 Characterization of Biphenyl-substituted Alkanethiol Self-assembled Monolayers by High-resolution X-ray Photoelectron Spectroscopy***, K. Heister, H.-T. Rong, M. Buck,* University Heidelberg, Germany*; L.S.O. Johansson,* University Karlstad, Sweden*;* ***M. Zharnikov****, M. Grunze,* University Heidelberg, Germany

Synchrotron-based high resolution X-ray photoelectron spectroscopy was applied to characterize self-assembled monolayers (SAM) of biphenyl-substituted alkanethiols CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH (BPn, n = 1-4) on Au and Ag substrates. Beyond previously identified odd-even changes in the packing density and the tilt angle of the biphenyl moieties, the high resolution spectra reveal a number of additional odd-even effects upon variation of the number of methylene groups in the aliphatic part in the BPn molecule. Their occurrence and mutual correlation suggests that a BPn SAM represents a strongly correlated, highly ordered molecular assembly. In particular, periodical changes of a shake-up feature in the C 1s region are observed, which are related to the differences in the arrangement of the aromatic matrix. The width and binding energy of the S 2p signals also exhibit odd-even changes. The width changes are associated with the occupation of either equivalent or non-equivalent adsorption sites on the polycrystalline (111) Au and Ag substrates. The comparison of the width values with those for conventional alkanethiols implies that the substrate bonding of alkanethiols on gold cannot be described by a single adsorption site. At the same time, the FWHM of the S 2p@sub 3/2,1/2@ peaks in the loosely packed BPn/Au (~0.50 eV) was found to be the smallest one among all thiol-derived SAMs investigated by HRXPS until present. Therefore, this value can be associated with the occupation of equivalent adsorption sites on the Au(111) surface. This work has been supported by the German BMBF (05 SF8VHA 1 and 05 SL8VHA 2), DAAD (313/S-PPP), and DFG (Bu820/11-2).

9:20am **OF+NS+SS+BI-WeM4 Separation via Self-assembly of Enantiomers of Chiral Aromatic Hydrocarbons Adsorbed on Metal Surfaces***,* ***K.-H. Ernst****, Y. Kuster, R. Fasel,* EMPA Duebendorf, Switzerland

We studied the interaction of heptahelicene ([7]H), a helically shaped, polyaromatic phenanthrene derivative, with well-defined single-crystal metal surfaces under ultra high vacuum (UHV) conditions. The molecules, racemate as well as the pure enantiomers, were deposited via molecular beam technique and subsequently characterized with surface sensitive techniques like temperature programmed desorption (TPD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), time-of flight secondary mass spectrometry (ToF-SIMS), X-ray absorption spectroscopy (NEXAFS), and X-ray photoelectron diffraction (XPD). On Ni(111), the [7]H-molecule is adsorbed intactly at room temperature. TPD, however, shows only desorption of molecular [7]H from the multilayers. The first layer undergoes decomposition into carbon and hydrogen at 650 K. From Cu(111), molecular desorption is also observed at low coverages. The closed packed monolayers of [7]H on Ni(111) and Cu(111) show two-dimensional lattice structures. Adsorption of racemic [7]H leads to self-alignment into domaines on the surface, which are mirror images of each other. This is not observed after exposure to pure enantiomers and can be explained with a lateral separation of the enantiomers into homochiral domaines on the surface. For the pure M-enantiomer on the stepped Cu(332) surface, an azimuthal alignment of the molecular spirals is observed. Models for the monolayer structures and the mechanism of the separation will be discussed. Support by the Swiss National Science Foundation (NFP 36) is gratefully acknowledged.

9:40am **OF+NS+SS+BI-WeM5 Mesoscopic Correlation of Supramolecular Chirality in One-Dimensional Hydrogen-Bonded Assemblies***,* ***J.V. Barth,*** Ecole Polytechnique Federale de Lausanne, Switzerland*; J. Weckesser,* Max-Planck-Institut fuer Festkoerperforschung, Germany*; A. De Vita,* Institut Romand de Recherche Numerique en Physique des Materiaux, Switzerland*; C. Cai,* University of Houston*; K. Kern,* Max-Planck-Institut fuer Festkoerperforschung, Germany

We studied enantioselective self-assembly in two dimensions employing the molecule 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid. Scanning tunneling microscopy observations at noble metal surfaces reveal the formation of hydrogen-bonded supramolecular twin chains in two mirror-symmetric species, each containing only molecules of a given chirality. The twin chains are ordered in µmm-gratings, where a mesoscopic correlation of supramolecular chirality over the entire domain size without intimate molecular contact persists. This novel phenomenon reflects mesoscopic chiral segregation due to chiral recognition in the formation of the supramolecular assemblies. Theoretical modelling in conjunction with direct observations indicate that twin chains act as enantioselective templates for transient molecular attachment, which process mediates self-replication of supramolecular chirality and the enantiopure gratings' evolution.

10:00am **OF+NS+SS+BI-WeM6 Controlling Molecular Orientation in Solid Films Via Self-organization in the Liquid-crystalline Phase***, I.K. Iverson, S.-W. Tam-Chang,* ***S.M. Casey,*** University of Nevada, Reno*; B.A. Pindzola,* University of California, Berkeley

We report the control of molecular orientation in solid films through self-organization and induced-orientation processes. We synthesized water-soluble cationic 3,4,9,10-perylene diimide (1) and studied its self-organization in aqueous solution. By UV-vis spectroscopy, H-aggregates of 1 are observed forming in solutions with concentrations as low as 10@super -7@ M. At concentrations above approximately 0.1 M (7% w/w) these solutions are observed with polarized microscopy to form a chromonic N phase (a nematic lyotropic liquid crystalline phase) at room temperature. Upon induced alignment (by shearing) of the chromonic N phase on a glass substrate and removal of solvent, anisotropic solid films of the dichroic dye are produced. These films have dichroic ratio values that routinely exceed 25 and in some cases 30, making them excellent sheet polarizers over the blue and green region. Using a combination of polarized UV-vis and FT-IR spectroscopies, the orientation of the average molecular plane in these films is determined to be perpendicular to both the shearing direction and the substrate plane. X-ray diffraction studies indicate that the molecules in the solid film possess a high degree of order.

10:40am **OF+NS+SS+BI-WeM8 Effect of Lipid Vesicle Fusion on the Ordering and Redox Activity of 11-(ferrocenyl carbonyloxy) Undecanethiols Self-assembled Monolayers***, A.T.A. Jenkins,* University of Bath, U.K., Great Britain*;* ***J.F. Le Meur,*** University of Bath, U.K.

Self-assembled Monolayers (SAMs) of 11-(ferrocenyl carbonyloxy) undecanethiol were made following a procedure given by Chidsey et @footnote 1@ The formation of the 11-(ferrocenyl carbonyloxy) undecanethiol SAM on gold was followed in-situ by Surface Plasmon Resonance (SPR)and showed a film of thickness 13 Å was formed. Impedance measurements indicated a high level of film coverage. Cyclic voltammetry was subsequently used to electrochemically characterise the SAM, and check its stabilty with respect to immersion in electrolyte. Egg-Phosphatidylcholine lipid vesicles were created by extrusion through a 50 nm membrane and were adsorbed on the SAM. SPR was used to follow the lipid adsorption on the SAM. Cyclic voltammetry measurements on the SAM-lipid system showed a large and reproducible increase in the peak anodic and cathodic currents after lipid adsorption, although the total quantity of charge transfered stayed the same. This is likely to be due to an increase in order of the ferrocene units in the SAM, allowing for a faster transfer of electrons on the lipid covered SAM than the SAM alone. The above experiments were repeated with binary mixtures of SAMs containing both 11-(ferrocenyl carbonyloxy) undecanethiol and mercaptoundecanol moities. It was found that the increase in anodic and cathodic current maximums measuresed by cylic voltammetery was disproportionately lower than the single component SAM (relative to the coverage). From this we propose a model for how the SAM structure changes upon lipid adsorption. @FootnoteText@ @footnote 1@ Chidsey, C.E.D.; Bertozzi, C.R.; Putvinski, T.M.; Mujsce, A.M. Journal American Chemical Society, 1990, 112, 4301-4306.

11:00am **OF+NS+SS+BI-WeM9 Temperature-dependent Morphology of Crystalline p-sexiphenyl Thin Films on KCl(001)***,* ***E.J. Kintzel, Jr.,*** Florida State University*; D.-M. Smilgies,* Cornell University*; J.G. Skofronick, S.A. Safron,* Florida State University

Investigations of the morphology of ultrathin films of p-sexiphenyl (p-6P) vapor deposited onto KCl(001) have been carried out using the complementary techniques of X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM). XRD studies have shown that the molecular orientation of the p-6P is dependent on the substrate temperature during deposition. For films prepared at low temperatures, the p-6P molecules take a lying orientation, with the long axis of the molecule aligned parallel to the substrate. As the substrate temperature was increased during deposition, XRD results indicate two coexisting molecular orientations, corresponding to lying and standing p-6P molecules. AFM images provide independent confirming evidence of the influence of substrate temperature on molecular orientation, consistent with the XRD results.

11:40am **OF+NS+SS+BI-WeM11 Characterization of Photoisomerization Reaction of Azobenzene-contanining SAMs: Reaction Kinetics and Thermal Stability***,* ***K. Tamada,*** National Institute of Advanced Industrial Science and Technology (AIST), and Frontier Research System, RIKEN, Japan*; H. Akiyama, T. Wei,* AIST, Japan

We studied the change of photoreactivity of azobenzene disulfide SAMs under thermal stress. Azobenzene-containing unsymmetrical disulfide (C6AzSSC12) SAM was annealed at each temperature (70, 85, 100, 120, 140°C) for 1 hr, then the photoreaction was monitored with surface plasmon resonance spectroscopy (SPR) in hexane. The photoreaction was stable under 100°C when no decomposition of adsorbed molecules was detected, while it was suddenly reduced at over 100°C when the decomposition was taking place. After annealing at 140°C, the reactivity of the unsymmetrical disulfide SAM reached to the level of the corresponding azobenzenethiol SAMs (single component), suggesting the phase segregation of the adsorbed molecules by annealing. We designed new azobenzene thiol/disulfides (C6Az(Me)thiol, C6Az(Me)SSC12) to achieve more thermally stable photoresponse. In these molecules, CH@sub 3@-group is introduced to the azobenzene ring directly to avoid dye aggregation sterically. The C6Az(Me)thiol SAM exhibited much higher photoreactivity than conventional azobenzenethiol, which suggests that dye functions are less aggregated even in the single component SAMs. The C6Az(Me)SSC12 exhibited much higher photoresponse compared with C6AzSSC12 after annealing, since these azo dyes can react even in phase segregated domains. We also discuss photoisomerization reaction kinetics (cis to trans, trans to cis) in correlation with dye alignment.

Surface Science

Room 122 - Session SS+SC-WeM

Adsorption on Semiconductor and Metal Oxide Surfaces

Moderator: R.J. Lad, University of Maine

8:20am **SS+SC-WeM1 Empirical Density Functionals and the Adsorption of Organic Molecules on Si(100)***,* ***M.A. Phillips,*** *N.A. Besley, P.M.W. Gill, P. Moriarty, P.H. Beton,* The University of Nottingham, UK

Density Functional Theory (DFT) has been used in the study of the adsorption of organic molecules such as ethene and ethyne for a number of years. Typically, for semiconductor surfaces, DFT methods are used in conjunction with a cluster model of the substrate.@footnote 1@ However, the computational expense of DFT calculations implies an upper limit on the size of the substrate model, and thus on the size of adsorbate molecule. As such, the study of larger adsorbates requires some reduction in computational expense, often leading to the use of parameterised semi-empirical methods. Unfortunately, such methods do not give good agreement with experiment for many semiconducting elements: another approach is required for these materials. The Empirical Density Functional, EDF1, has been shown to give very good agreement with values of atomisation energy, ionisation potential and proton affinity for the majority of species included in the G2 experimental data set.@footnote 2@ Furthermore, this functional does not require the evaluation of 'exact exchange' contributions, and is therefore significantly less computationally expensive than 'hybrid' functionals. However, the success of EDF1 in the determination of any other physio-chemical properties, in particular adsorption geometry, adsorption energy and vibrational structure, has never been tested. Here, we present the results from a density functional study of the adsorption of organic molecules on the Si(100) surface using EDF1, and discuss their validity through comparison to experimental measurements and results from equivalent calculations using the well known functional, B3LYP. We also compare the computational expense when using EDF1 in these calculations to that when B3LYP is used. @FootnoteText@ @footnote 1@ R. Konecný and D. J. Doren, Surf. Sci. 417 (1998), 169-188. @footnote 2@ R. D. Adamson, P. M. W. Gill and J. A. Pople, Chem. Phys. Lett. 284 (1998), 6-11.

8:40am **SS+SC-WeM2 Scanning Tunneling Microscope Investigation of Adsorption of Titanium Atoms on Si(111)-7x7 Surface***,* ***H.F. Hsu,*** *M.C. Lu,* National Tsing Hua University, Taiwan, R.O.C.*; H.-L. Hsiao,* Tunghai University, Taiwan, R.O.C., Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.

C54-TiSi@sub 2@ has been the primary silicide for contact application in ULSI devices. The initial stages of interfacial reactions of Ti thin films on silicon are of both scientific and the technological interests. The strong reactivity of Ti with Si was manifested by the interatomic mixing at room temperature. The atomic scale studies of initial Ti-Si reactions at very low coverage have been scarce. In particular, it is not clear whether Ti atoms react with the Si substrate from the very beginning of deposition or the formation of a silicide-like compound starts at some critical coverage. In the present study, an atomic-scale characterization of room temperature titanium adsorption on the Si(111)-7x7 surface has been investigated. Preferential adsorption of Ti atoms on the Si center adatom sites at very low coverage was found. At higher coverage, a peculiar contrast feature is observed. The observed feature is attributed to the charge redistribution caused by the adsorption of more than one Ti atoms on this subunit cell. At very low Ti coverage (~0.007 ML), some of the Si adatom sites appear to be brighter in both filled-state and empty-state STM images. The contract behavior is likely to be due to the adsorption of Ti atoms on the Si adatom sites. It was found that Ti atoms adsorb preferentially on top of the Si center adatoms and, to a less extent, on top of the Si corner adatoms. Upon further deposition of Ti, two center adatoms and corresponding corner adatom become darker and the center of these three adatoms become brighter. The observed change in the apparent height is caused by the redistribution of charge near the Si adatom sites. The result indicates that more than one Ti atoms were adsorbed on a triangular subunit cell.

9:00am **SS+SC-WeM3 High-Resolution Core-Level Study of the Initial Stage of Oxygen Adsorption on a Si(111)-(7x7) Surface***, **K. Sakamoto**, H.M. Zhang, R.I.G. Uhrberg,* Linköping University, Sweden

As motivated by the technological importance of thin silicon oxide films in semiconductor devices, the initial stage of oxygen adsorption on silicon surfaces has been a topic of experimental and theoretical investigations. Among the various reports on oxygen adsorption, Si 2p core-level studies have played crucial roles in elucidating the structures of the SiO@sub 2@/Si interfaces. However, very few Si 2p studies are available for the initial stage of oxygen adsorption on a Si(111)-(7x7) surface. In this paper, we present a high-resolution Si 2p core-level photoemission study of submonolayer oxygen adsorption on the (7x7) surface. The photoemission measurements were performed at beamline 311 at the MAX-II synchrotron radiation facility in Lund, Sweden. The clean (7x7) surface was exposed to 0.1-20 L of oxygen at 120 K, which correspond to coverages below 1 ML. Significant intensity of the Si 2p component due to the Si@super 2+@ species is observed already at 0.3 L, and the component due to the Si@super 3+@ species is clearly observed at a dosage higher than 1.0 L. These results indicate that more than two oxygen atoms adsorb to one Si atom even at a very low coverage. After annealing the oxygen adsorbed sample at 600 K, the Si 2p component due to the Si@super 2+@ species shows a shift of 0.4 eV to the higher binding energy side. This result suggests different atomic configurations for the Si@super 2+@ species at 120 K and after annealing the sample at 600 K. We will also present detailed studies of the dosage- and temperature-dependent intensities of the Si 2p components due to the suboxide species.

9:20am **SS+SC-WeM4 First-Principles Theory of Finite-Temperature Adsorbate Ordering in Ba/Si(111)-"3x2"***, **S.C. Erwin**, C.S. Hellberg,* Naval Research Laboratory

Alkali metal adsorbates induce a 3x1 reconstruction of Si(111) widely believed to be a "honeycomb-chain channel" structure. This model is based on a true Si=Si double bond in the surface layer, which at 1/3 ML coverage leads to the elimination of all dangling bonds and thus keeps the fundamental gap free of surface states. Alkaline-earth adsorbates also appear to induce 3x1 (as well as higher-order) reconstructions, yet despite the extra electron the resulting surfaces remain fully gapped---an apparent contradiction to the one-electron band picture. Lee et al. recently suggested that for alkaline-earth adsorbates the coverage is in fact 1/6 ML, and showed that a 3x2 honeycomb-chain channel model is indeed fully gapped.@footnte 1@ We use density-functional methods first to confirm that the model of Lee et al. is indeed energetically preferred at low coverages. Second, we predict that structurally related 5x2 and 2x1 reconstructions will appear---if they are not preempted---at higher coverages. Finally, we propose an explanation for why the 1/6 ML phase appears 3x2 in STM but 3x1 in LEED: namely, that at moderate temperatures the adsorbates will exhibit only short-range order, due the near energetic degeneracy of H3 and T4 adsorption sites. To demonstrate this, we extract from our density-functional calculations the adsorbate-substrate and adsorbate-adsorbate interactions, and based on these carry out classical Monte Carlo simulations to explore the detailed temperature dependence of adsorbate ordering. @FootnoteText@@footnte 1@G. Lee, D. Shin, H. Kim, J. Koo, and S. Hong, Bull. Amer. Phys. Soc. 46 (2001).

10:00am **SS+SC-WeM6 Adsorption Induced Deflection and Frequency Changes in a Silicon Nitride Cantilever due to Ca@super 2+@ Ions***, **S. Cherian**, A. Mehta, T.G. Thundat,* Oak Ridge National Laboratory

Cantilever based micromechanical sensors exploit changes in surface stress due to interactions between the analyte species and cantilever surface. Charged groups on the cantilever surface play a significant role in binding induced deflection of the micro-cantilever. The deflection and frequency response of triangular silicon nitride cantilevers when exposed to calcium chloride solution was investigated in a flow system. The silicon nitride cantilever used was 200µm long and 20µm wide. Calcium chloride solutions of increasing concentrations were injected sequentially into the flow cell and the cantilever response measured. The fundamental resonance frequency of the cantilever shifted to lower values with increasing solution concentrations. The deflections due to interaction with the CaCl@sub 2@ were towards the gold side. The concentration versus deflection curve followed a Langmuir adsorption isotherm. The cantilever response is attributed to chemisorption of calcium ions onto the silicon nitride side. To verify this a calcium binding protein, calmodulin, was used. A cantilever that was exposed to CaCl@sub 2@ solution was subsequently exposed to calmodulin. Calmodulin binding to Ca @super 2+@ ions on the cantilever surface resulted in a deflection. This deflection was significantly different from that observed when calmodulin was exposed onto a fresh cantilever. These observations were further confirmed by fluorescent measurements using a fluorescently tagged calmodulin. These results demonstrate that consideration of ionic interactions of charged species in the medium with cantilever surfaces is critical in interpreting deflection data of cantilever based sensors. This also suggests the importance of passivating one of the surfaces in order to make the deflection of the functionalized cantilever specific to the species of interest.

10:20am **SS+SC-WeM7 Adsorption of NO and NO@sub 2@ on Barium Oxide: Surface Nitrition and Nitration***, P.J. Schmitz, R.J. Baird,* Ford Motor Company*; **M. Miletic**, J.L. Gland,* University of Michigan

Alkaline earth oxides surfaces are known to trap NOx species by chemisorption even under excess oxygen conditions typical of lean burn engines exhaust. These oxides, particularly barium oxide, have been proposed as active components in cyclic automotive NOx abatement strategies because of their ability to store and release NOx under rich/lean exhaust cycling. However, molecular understanding of the adsorption and reactions of NO, and NO2 on alkaline earth oxide surfaces remains incomplete. A series of XPS and temperature programmed studies of NO and NO2 adsorption and reaction on model barium oxide thin films prepared in-situ are reported here. These experiments indicate that charge transfer and reactive chemisorption play an important role even during low temperature adsorption on barium oxide surfaces. Nitrite and nitrate species form preferentially on reactive adsorption sites and can be reactively desorbed in the 400 to 600 K temperature range. The coverage of the precursor molecular species plays an unexpected role both in reactive adsorption and desorption on barium oxide surfaces. These results are discussed in terms of recent DFT calculations which highlight the importance of reactive configurations, charge transfer, and surface oxidation/reduction processes.

10:40am **SS+SC-WeM8 Electronegative Adsorbates on TiO@sub 2@: Reducing Effects of S and Cl***, **E.L.D. Hebenstreit**[1], W. Hebenstreit,* Tulane University*; H. Geisler,* Xavier University of Louisiana*; C.A. Ventrice, Jr.,* University of New Orleans*; D.A. Hite, P.T. Sprunger,* Louisiana State University*; U. Diebold,* Tulane University

TiO@sub 2@(110) is a well-studied model catalyst with an abundance of technical applications. Sulfur and chlorine are common impurities in many catalytic systems which poison catalytic reactions. The adsorption of molecular S and Cl on TiO@sub 2@(110)(1 x 1) has been studied with scanning tunneling microscopy (STM), x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), and low energy electron diffraction (LEED). At room temperature both adsorbates bind dissociatively to 5-fold coordinated Ti atoms and oxygen vacancies. At elevated temperatures (120°C - 440°C), S and Cl replace surface oxygen atoms. S forms different types of superstructures in dependence on coverage and adsorption temperature. No long-range ordering was found in the a dsorbed layer for Cl. Both adsorbates reduce the surface but S leads to a stronger oxygen depletion than Cl. In photoemission experiments, adsorption of either S or Cl at elevated temperatures cause additional emission at the high binding energy side of t he valence band and increases emission from the defect state. Adsorption of S leads to band gap states which fill the band gap

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

completely. Evidence was found that the reduction state of TiO@sub 2@ crystals strongly affects the surface coverage of S and Cl at elevated temperatures. The rate of the site exchange of the adsobates between a weakly bound precursor state on Ti and the replacement of oxygen is kinetically limited by the arrival of diffusing bulk defects at the surface.

11:00am **SS+SC-WeM9 Electronic and Chemical Properties of Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) Surfaces: Photoemission, XANES, Density Functional, and NO@sub 2@ Adsorption Studies***, **G. Liu**, J.A. Rodriguez, J. Hrbek, J. Dvorak,* Brookhaven National Laboratory*; C.H.F. Peden,* Pacific Northwest National Laboratory

Synchrotron-based photoemission,conventional XPS, XANES, and first-principles density functional (DF) calculations were used to study the electronic properties of a Ce@sub 0.8@Zr@sub 0.2@O@sub 2@ mixed-metal oxide. The results of DF calculations show that the band gap in bulk Ce@sub 0.8@Zr@sub 0.2@O@sub 2@ is ~ 0.6 eV smaller than in bulk CeO@sub 2@, with the Zr atoms in the mixed-metal oxide showing smaller positive charges than the cations in ZrO@sub 2@ or CeO@sub 2@. When present in a lattice of CeO@sub 2@, the Zr atoms are forced to adopt larger metal-O distances than in ZrO@sub 2@, leading to a reduction in the oxidation state of this element. Due to non-equivalent Zr-O distances, at least three different types of oxygen atoms are found in the Ce@sub 0.8@Zr@sub 0.2@O@sub 2@ system. O K-edge XANES spectra for a series of Ce@sub 1-x@Zr@sub x@O@sub 2@ (x=0, 0.1, 0.2, 0.3, 1) compounds show a distinctive line shape for the mixed-metal oxides that can not be attributed to a sum of CeO@sub 2@ and ZrO@sub 2@ features, supporting the idea that the O atoms in Ce@sub 1-x@Zr@sub x@O@sub 2@ are in a special chemical environment. XPS Ce 3d spectra show the presence of Ce@super 3+@ cations which may be related to the relative stability of oxygen vacancy defects upon incorporation of zirconia into ceria. The interaction of NO@sub 2@ gas with Ce@sub 0.8@Zr@sub 0.2@O@sub 2-x@(111), CeO@sub 2-x@(111), and Zr(Y)O@sub 2-x@(111) reduced surfaces was examined. Ne@super +@ ion sputtering was used to generate substantial concentrations of Ce@super 3+@, Zr@super 2+@ and Zr0 centers on the oxide surfaces. On CeO@sub 2-x@(111), NO@sub 3@, NO@sub 2@ and N were seen upon adsorption of NO@sub 2@. In contrast, only NO@sub 2@ and N were detected after adsorption of NO@sub 2@ on Ce@sub 0.8@Zr@sub 0.2@O@sub 2-x@(111) and Zr(Y)O@sub 2-x@(111). Adsorption of NO@sub 2@ induced an increase in the oxidation state of the metal cations (Ce@super 3+@ to Ce@super 4+@; Zr0 to Zr@super 2+@).

11:20am **SS+SC-WeM10 Probing Chemical and Topological Heterogeneity of Carbonaceous Surfaces via Temperature Programmed Desorption of Simple Molecules from Model Carbonaceous Surfaces***, **J. Kwon**, R. Vidic, E. Borguet,* University of Pittsburgh

Carbonaceous surfaces find applications in fields ranging from tribology to environmental remediation to catalysis. These surfaces are generally characterized by varying extent of chemical and topological heterogeneity that affects key elementary processe s such as adsorption and desorption. Temperature programmed desorption of model adsorbents (propane and acetone), representative of polar and non-polar organic compounds, was used to investigate the role of surface chemical and topological heterogeneity on the physical and chemical properties of model carbonaceous surfaces (air cleaved and plasma oxidized highly oriented pyrolytic graphite - HOPG). We observed that hydrogen and oxygen containing functional groups, which tend to block available adsorption sites, exist on air cleaved and plasma oxidized HOPG. Thermal treatment leads to removal of these groups and to over an order of magnitude increase in adsorption capacity. Thermal treatment (> 900 oC) of carbonaceous surfaces appears essential for maximum accessibility to adsorption sites. The surface defects induced by plasma oxidation yield greater surface area available for adsorption and higher energy sites. This novel approach promises a better understanding of chemically and topologically heterogeneous nanoporous carbons used in practical applications.

Surface Science
Room 120 - Session SS1-WeM
Surface Diffusion

Moderator: G.L. Kellogg, Sandia National Laboratories

8:20am **SS1-WeM1 Diffusion on and in Surfaces: The Atomic Slide Puzzle***, **J.W.M. Frenken**, R. Van Gastel, E. Somfai, S.B. Van Albada, W. Van Saarloos,* Leiden University, The Netherlands **INVITED**

Usually, surface mobility is thought to be restricted completely to the steps and kinks on crystal surfaces. These sites form the natural locations for atoms to come and go. Atoms in the close-packed terraces are often considered to be completely static, since they are tightly packed by their neighbors. In this talk, measurements will be shown that have been obtained with the scanning tunneling microscope, that show that a close-packed terrace of a metal surface can be far from static, even at temperatures as low as room temperature! We make the motion visible of the atoms in a Cu(001) terrace, by embedding a low density of In atoms in the first Cu layer. The peculiar characteristics of the motion of the In show that the diffusion of surface vacancies is responsible for a continual reshuffling of all the (In and Cu) atoms in the first layer.@footnote 1@,@footnote 2@ @FootnoteText@ @footnote 1@ R. van Gastel, E. Somfai, W. van Saarloos and J.W.M. Frenken, Nature 408 (2001) 665. @footnote 2@ R. van Gastel, E. Somfai, S.B. van Albada, W. van Saarloos and J.W.M. Frenken, Phys.Rev.Lett. 86 (2001) 1562.

9:00am **SS1-WeM3 Nothing Moves a Surface: Probing Surface Vacancy Dynamics with a Surface Alloy***, **R. Van Gastel**, E. Somfai, S.B. Van Albada, W. Van Saarloos, J.W.M. Frenken,* Universiteit Leiden, The Netherlands

Indium atoms that are deposited on the Cu(001) surface at room temperature rapidly diffuse to steps where they are incorporated into the first layer of the crystal surface. We use the In/Cu(001) surface alloy to probe the dynamics of surface vacancies. The motion of embedded indium atoms enables us to use these atoms as `tracer' particles for the direct visualization of vacancy mediated diffusion of surface atoms.@footnote 1@ Steps on the surface act as sources and sinks for surface vacancies. This crucial role of steps is exposed as the mobility of embedded indium atoms is spatially mapped out. The temperature dependence of the diffusion of embedded indium atoms is investigated through high speed STM movies. The temperature dependence provides us with a direct measurement of the surface vacancy mobility, and yields the sum of the vacancy formation and migration energies. In addition to this, we present first results from experiments, in which monatomic surface vacancies are artificially created. From these the vacancy migration energy can be obtained so that we can experimentally separate out the formation and migration energies. @FootnoteText@ @footnote 1@R. van Gastel et al., Phys. Rev. Lett. 86 (2001), 1562.

9:20am **SS1-WeM4 Surface-diffusion Mechanism vs. Electric Field: Pt/Pt(001)****, **P.J. Feibelman***, Sandia National Laboratories

Identifying macroscopic variables that affect the rates and mechanisms by which surface atoms move should enhance our ability to control surface morphology. The search for new "knobs to turn" is at the root of the decade-long effort to modify thin-film growth by depositing appropriately chosen "surfactant" species. It also motivates the work reported here, in which ab-initio total energy calculations are used to understand how an externally imposed electric field should affect the mechanism and rate of adatom self-diffusion on Pt(001), a surface for which Field Ion Microscopy experiments@footnote 1@ suggest that the low energy process, concerted substitution, is supplanted by hopping when the external field is high enough. The result is that theory agrees with FIM that the barrier to concerted substitutional diffusion of a Pt atom on Pt(001) varies linearly with external electric field (slope ~0.1eÅ), increasing for fields oriented to push electrons into the surface. But, with a computed hopping barrier remaining >0.5 eV higher than that for substitution, the calculations contradict the idea that a change in FIM site visitation at fields of 1.5-2 V/Å and temperatures ~265-284K can be attributed to the onset of hopping. @FootnoteText@ @footnote *@Work supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. Department of Energy. @footnote 1@G. L. Kellogg, Phys. Rev. Lett. 70, 1631(1993).

9:40am **SS1-WeM5 Temperature-Dependent Surface Diffusion Parameters on Amorphous Materials***, **E.G. Seebauer**, D. Llera-Hurlburt, A. Dalton,* University of Illinois, Urbana

Diffusion on amorphous surfaces represents a little-studied physical phenomenon that controls several important kinds of material processing. To elucidate some general features of this phenomenon, we have determined Arrhenius parameters for the surface self-diffusion of amorphous silicon (a-Si) by measuring the formation kinetics of hemispherical grained silicon. The results exhibit significant temperature dependence in the activation energy for total mass transport. We develop a physical model and associated mathematical formalism to show that this behavior should characterize diffusion on amorphous surfaces in general. Adatom formation on amorphous surface can arise from a near-continuum of structures and energy states. The formation energy for mobile atoms is therefore described by a continuous distribution function f(E). The breadth of f(E) on a-Si and related surfaces contrasts sharply with the sum of delta functions corresponding to kinks, steps and terraces on crystalline surfaces. Thus as T increases on amorphous surfaces, the average formation energy for mobile adatoms increases continuously, and the Arrhenius plot for total mass transport bends upward. The sharpness of the curvature depends upon the breadth of f(E); a broader distribution yields more gentle curvature.

10:00am **SS1-WeM6 Hopping Induced by the Vibrational Excitation of Adsorbed Molecule through Inelastically Tunneled Electrons***, **M. Kawai**, T. Komeda, Y. Kim,* RIKEN, Japan

There is a rising interest for the phenomena caused by inelastic tunneling in the experiments using scanning tunneling microscope (STM).@footnote 1@ In this report, we show surface-diffusion of adsorbate is induced by inelastic tunneling of electron for the molecules of CO and ethylene on Pd(110) at 4.8K. When a certain amount of tunneling electron is dosed on a single adsorbate, the change of their bonding site along [1 0] direction is observed. We study this phenomenon systematically and found that the diffusion probability shows a very sharp increase at the bias voltage of 250 mV, which corresponds to the excitation of CO stretch vibrational mode. In similar manner, ethylene molecule adsorbed on the same surface is also enhanced to hop to the neighboring sites by irradiating electrons that correspond to the excitation of the internal stretching modes. These clearly demonstrate that the vibrational mode excited by inelastically tunneled electrons opens a route to induce hopping of the adsorbed molecules on surfaces. In the case of CO on Pd(110), thermal diffusion of CO was previously studied. At 100 K, one-dimensional CO arrays are formed and attaching and detaching of CO molecules are observed. The motion is restricted on [1 0] direction. The estimated diffusion barrier for a CO molecule in an array is ~180 meV, but the value for an isolated molecule should be much smaller in energy. Here we propose a model that the diffusion of CO is induced by an excitation of high lying vibrational mode (C-O stretch mode) which is further coupled with T-mode and R-mode through anharmonic coupling to induce surface diffusion . @FootnoteText@ @footnote 1@J.R. Hahn, H.J. Lee, and W. Ho, Phys. Rev. Lett. 85 1914 (2000) and references there in.

10:20am **SS1-WeM7 Determination of Atomic Potential Energy for Pd Adatom Diffusion Across the W (111) Islands and Surfaces***, **T.-Y. Fu**,* National Taiwan Normal University, R.O.C., R. O. C.*; L.-C. Cheng,* National Taiwan Normal University, R.O.C.*; T.T. Tsong,* Academia Sinica, Taiwan, R.O.C.

Using field ion microscopy (FIM), we have probed the diffusion behavior of Pd adatoms on W (111) surfaces and in the vicinity of surface steps. From the behavior of an adatom approaching the step from the upper terrace, we find the step to be reflective to Pd adatoms. The extra reflective barrier is determined to be 0.64±0.03 eV. The behavior of adatoms approaching the step from the lower terraces has also been studied. The activation energy for the step-up motion of Pd atoms of W (111) steps is 1.84 eV. The potential energy difference toward and away from the W (111) pole exhibits a free energy anisotropy of 0.013 eV. These experimental results of atomic processes are related to the phenomenon of impurity induced pyramidal facet formation.

11:00am **SS1-WeM9 Surface Dynamics During Etching of GaAs(001)***, **S.W. Robey**,* National Institute of Standards and Technology

We present results from an experimental investigation of the surface dynamics controlling morphology during CH@sub 4@/H@sub 2@ plasma and wet etching of GaAs (001) surfaces. In the case of plasma etching, height-difference correlation functions (extracted from AFM data) indicate that morphology development is dominated by diffusion below ~ 100 nm, while desorption/etching effects dominate on larger length scales. The crossover between these two regimes is temperature dependent. Below 600 K, oscillatory structure in the height correlation function, associated with a "rippled" surface morphology, arises due to an instability in the etching dynamics. We attribute this instability to Ehrlich- Schwoebel step-edge barriers. The behavior of the height-difference correlation function and the time-dependent roughening is found to be in good agreement with studies of continuum models based on the Kuramoto-Sivashinsky (KS) equation. However, the Laplacian term in the KS equation has components arising from both the ES barrier and etching/desorption effects so that the effect of the ES barrier in producing the instability is weakened, compared to thin film growth examples. Using theoretical expressions for the kinetic coefficients in the KS equation, we find that the Ehrlich-Schwoebel barrier is ~ 0.05 eV in this system. We will also present initial results studying "facetting" during wet etching of GaAs (001). The initial formation of anisotropic "hillock" structures develops in time to form a hill-and-valley structure along the (110) direction, with faces close to [111]. The length scale coarsens in time and is dependent on the etchant composition. Comparisons with theoretical studies of kinetically controlled crystal growth and etching will be discussed.

11:20am **SS1-WeM10 Step Motion on the Cu(100)-(@sr@2x2@sr@2)R45°-O Surface***, C.L.H. Devlin,* Air Force Research Lab, U.S.*; J.P. Landry,* University of California, Davis*; N.C. Bartelt,* Sandia National Laboratories*; **S. Chiang**,* University of California, Davis

Low energy electron microscopy (LEEM) was used to study the motion of single-atom-high steps on a Cu(100) surface covered with the (@sr@2x2@sr@2)R45°-O structure. Curved steps exhibited capillary wave motion, which was analyzed using Langevin Dynamics.@footnote 1@ From this analysis, the dominant mode of adatom diffusion (i.e., along steps or over terraces) was deduced. Parameters such as the step stiffness and kink activation energy were also discovered. @FootnoteText@ @footnote 1@ N.C. Bartelt and R.M. Tromp, Phys Rev B 54 (1996) 11731.

Surface Science
Room 121 - Session SS2-WeM

Surface Reactions on Metals

Moderator: D.R. Mullins, Oak Ridge National Laboratory

8:20am **SS2-WeM1 CO Oxidation on Au Crystals: Studies on the Nanoscale***, T. Bär, T. Visart de Bocarmé,* Free University of Brussels, Belgium*; B.E. Nieuwenhuys,* Leiden University, The Netherlands*; **N. Kruse**,* Free University of Brussels, Belgium

Until recently gold was regarded as a metal of little interest for applications in heterogeneous catalysis. The discovery that supported gold catalysts are among the most active ones in CO oxidation has completely changed this picture. The mechanism of the reaction is, however, still under debate. In particular, the question for the role of the support material and for possible impurity effects must be asked. With this background we have studied oxygen activation and reaction with CO on pure Au single crystal specimens, in the absence of any oxidic support material, using Field Ion Microscopy (FIM) and atom-probe techniques. FIM-images (using H@sub 2@ and Ne as imaging gas at 55 K and at field strengths of up to 35 V/nm) indicated clean, nearly hemispherically shaped Au crystals of (111) orientation. Exposure of such a specimen to O@sub 2@ gas at 100 mbar and temperatures between 300 and 450 K, in the absence of an electric field, led to oxygen chemisorption and formation of a "surface oxide". In particular, layer edges of (111) and (100) planes were decorated by oxygen atoms. In situ studies of surface oxide formation performed in an O@sub 2@ gas atmosphere of 1,0*10@super -4@ mbar showed that the presence of an electric field of 12-15 V/nm significantly enhances oxygen adsorption. Exposure to CO gas at 300 K led to the removal of the surface oxide, i.e. CO@sub 2@ formation. This was associated with the occurrence of a reaction front which started in the apex centre, i.e. the (111) pole, and extended in nearly concentric circles to the outskirts of the Au specimen. Using video-FIM several cycles of oxide build-up and titration with carbon monoxide were performed to demonstrate the reversibility of the surface processes. Using atom-probe techniques during the ongoing reaction AuO and AuCO ionic species could be observed in variable amounts. We conclude that pure gold crystals are active catalysts for the CO oxidation at 300 K.

8:40am **SS2-WeM2 Surface Phase Transitions of Pt(110) Studied by Desorption Dynamics of Product CO@sub 2@ in Steady-state CO Oxidation***, **I. Rzeznicka**, M.G. Moula, T. Matsushima,* Hokkaido University, Japan

This paper reports the first confirmation of the transition from (1x2) to (1x1) through angular distribution analysis of desorbing product CO@sub 2@. Clear distribution changes were observed in the inhibited region where CO retards its oxidation. The surface phase transition of Pt(110)from (1x1)to(1x2) yields differently-oriented adsorption sites of oxygen. The CO oxidation on these sites induces differently-collimated CO@sub 2@ desorption, since this desorption mostly collimates along the local normal of the site. Both the angular and velocity distributions of desorbing CO@sub 2@ will switch sharply around the transition condition. This phenomenon was examined in steady-state CO oxidation on Pt(110) in a wide range of surface temperature and reactant pressures by means of cross-correlation time-of-flight techniques. In the active region where the surface is covered by O(a), desorbing CO@sub 2@ mostly collimated in a two-directional way along +25° or -25° off the surface normal in the (001) plane. This indicates CO@sub 2@ formation on the declining (111) terraces of the (1x2) form. On the other hand, in the inhibited region where the surface is mostly covered by CO(a), the normally directed desorption was sharply enhanced at a critical CO pressure where the two-directional components were suppressed. Below 3x10@super -4@ Torr of fixed O@sub 2@, this critical pressure shifted from the kinetic transition pressure (where the inhibition by CO starts) to higher values with increasing surface temperature. This critical point was confirmed to indicate the completion of the phase transition from LEED and CO adsorption measurements.

9:00am **SS2-WeM3 Dynamic Spatial Patterns in a Surface Reaction - The Microscopic and Mesoscopic Scales***, **J. Wintterlin**, C. Sachs, M. Hildebrand, S. Voelkening, G. Ertl,* Fritz-Haber-Institut, Germany **INVITED**

One of the most spectacular observations in surface catalytic reactions is the formation of dynamic spatial patterns that are connected with non-linear terms in the reaction kinetics. We have investigated such phenomena, both on the atomic and the mesoscopic scales, for the catalytic water formation from adsorbed oxygen and hydrogen on a Pt(111) surface. By means of scanning tunneling microscopy (STM) propagating reaction fronts were observed on a 10 to 1000 nm scale. Simulations were performed with a reaction diffusion model that contains an autocatalytic reaction sequence. The model predicts reaction fronts, formed by travelling interfaces between adsorbed oxygen and water. The fronts contain the reaction intermediate OH, in full qualitative agreement with the experiment. However, quantitative simulations reveal deviations from the experiment, demonstrating the limitations of this description. The atomic scale processes in the fronts, which were resolved by STM, indicate that the reasons for these deviations lie in the simplifications of standard reaction-diffusion models, namely the assumptions of a random occupation of adsorption sites and of spatially independent kinetic constants.

9:40am **SS2-WeM5 Hydrogenation of Oxygen on Pd(111)***, **T. Mitsui**,* Lawrence Berkeley National Laboratory*; M.K. Rose, E. Fomine,* University of California, Berkeley*; F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The reaction of hydrogen with (2x2) oxygen islands on Pd(111) has been studied with scanning tunneling microscopy under UHV conditions. Hydrogenation of oxygen, to form OH, was observed at 25 K. The reaction destabilizes the (2x2) ordering of oxygen and results in the formation of new (@sr@3x@sr@3) islands above 120 K. The OH islands remain stable up to 210 K even after the H@sub 2@ gas phase has been removed. Above this temperature, however the OH species decompose back to oxygen which reorganizes into (2x2) structures. The (@sr@3x@sr@3) OH islands can be formed again by additional hydrogen. If H@sub 2@ gas phase (10@super -8@ torr) is maintained during heating at 220 K, the (2x2) oxygen islands disappear completely from the surface by forming of H@sub 2@O that desorbs. Based on these results, the mechanisms of the formation of H@sub 2@O on Pd(111) from oxygen and hydrogen will be discussed.

10:00am **SS2-WeM6 Abstraction of Si and SiH@sub x@ (x=1,2,3) Adsorbed on Cu(100) Surfaces with Gaseous D towards Silane***, **D. Kolovos-Vellianitis**,* EPIII, University of Bayreuth, Germany*; Th. Kammler,* Focus GmbH, Germany*; Th. Zecho, J. Kueppers,* University of Bayreuth, Germany

The study of metal-silicide interfaces is of significant imterest because of their important technological applications. In particular, a better understanding of the formation of silicon structures on metal surfaces using chemical vapor deposition (CVD) of silane and disilane can provide valuable information about the elementary processes of adsorption, dissociation and reaction with other gaseous atoms. The interaction of silane and disilane with Cu(100) surfaces was studied in the temperature range 77 K to 650 K with thermal desorption and Auger electron spectroscopies. Silane admission to Cu(100) at low temperatures initially leads to a complete decomposition of the silanes into adsorbed Si and H. Close to saturation of the surface with H, SiH@sub x@ species remain intact on the surface. They were identified as SiH@sub 3@ and to a smaller extent SiH@sub 2@ by monitoring the silane abstraction products and their kinetics during admitting gaseous D to the surface between 77 K and 200 K. Silane desorption through recombination of SiH@sub 3@ and SiH@sub 2@ with adsorbed H occurs around 157 K and 224 K, respectively. After hydrogen desorption around 300 K a Si covered surface remains, which can be converted to a clean Cu(100) surface by activating Si bulk diffusion around 700 K. Adsorbed Si is abstracted from the surface below 200 K by gaseous H via formation of silane through a sequence of 4 hydrogenation steps. The first hydrogenation reaction is rate determining and is significantly accelerated by increasing the temperature between 77 K and 200 K. Above 200 K a thermally unstable SiH@sub x@ species blocks the abstraction reaction. The reaction kinetics phenomenology is in accordance with an Eley-Rideal scenario.

10:20am **SS2-WeM7 Catalytic Reactions on Alkali-modified Vicinal Cu(100) Surfaces***, **J Onsgaard**,* Aalborg University, Denmark*; J.P. Godowski,* University of Wroclaw, Poland*; S.V. Hoffmann,* Aarhus University, Denmark*; L. Bech,* Odense University, Denmark

Coadsorption of atoms and molecules with alkali-metal(AM) atoms on single crystal metal surfaces is of importance in heterogenous catalysis. The roles of AM (K or Cs) coverage and steps on vicinal Cu(100) surfaces - Cu(115) and Cu(117) - have been studied with respect to reactivity with low-molecular gases. It is demonstrated that the presence of steps and AM in the submonolayer coverage regime enhances the reactive properties of these surfaces. The Cu(115) surface, particularly, but also the Cu(117) surface modified with AM exhibit a high surface reactivity. The processes studied include dissociation of CO and synthesis of formate from coadsorption of H and CO@sub 2@. The C and O 1s core level shifts and the changes in the intensities of the satellite peaks are discussed in terms of the CO-substrate and/or the interatomic C-O interactions. A series of techniques, including photoelectron spectroscopy based on synchrotron radiation, thermally programmed desorption, work function measurements and LEED has been used.

11:00am **SS2-WeM9 Formation of Methylaminomethylidyne(>CNH(CH@sub 3@)) by Hydrogenation of Methyl Isocyanide and by Dehydrogenation of Dimethylamine on Pt(111)***, **D.H. Kang**, M.W, Trenary,* University of Illinois at Chicago

Fourier transform-reflection absorption infrared spectroscopy(FT-RAIRS) and temperature programmed desorption (TPD) have been used to study the adsorption and the surface reaction of methyl isocyanide (CNCH@sub3@) and dimethylamine ((CH@sub3@)@sub2@NH)) on the Pt(111)surface. Our previous studies have shown that the CN containing molecules, like azomethane (CH@sub3@N=NCH@sub3@), methylamine (CH@sub3@NH@sub2@) and hydrogen cyanide (HCN), have a common highly stable intermediate, aminomethylidyne (>CNH@sub2@), which is an aminocarbyne (>CNR@aa R@) species. An aminocarbyne species is a likely surface intermediate that could be formed by hydrogenation of the isocyanides and by dehydrogenation of amines.It is, therefore, of great interest to understand the adsorption and surface reaction of isocyanides and amines on metal surfaces. At low coverage and 85 K, methyl isocyanide adsorbs at on-top sites with an upright structure and then adsorbs on bridge sites at higher coverage. The RAIR spectra show new peaks by exposing hydrogen to the sample at or above 200 K, indicating a new surface species formed by hydrogenation. This species is identified as methylaminomethylidyne (MAM),(>CNH(CH@sub3@)),and exists as a stable species up to 350 K. Dimethylamine (DMA) adsorbs molecularly at 85K and the RAIR spectra show the same characteristic peaks as the hydrogenation of methyl isocyanide after annealing the sample to 350 K. This MAM species could be formed by the dehydrogenation of DMA as shown by TPD. At 400 K, the MAM species changes to a (>CNCH@sub3@) species, by dehydrogenation of the N-H bond and part of the (>CNCH@sub3@) species rearranges to the on-top site methyl isocyanide. When coadsorbing hydrogen at 300 K following annealing the sample to 400 K, part of the (>CNCH@sub3@) species changes to MAM by hydrogenation. The RAIR spectra also show peaks corresponding to aminomethylidyne (>CNH@sub2@), suggesting the existence of CN on the surface at 400 K.

11:20am **SS2-WeM10 Experimental and Theoretical Imaging of the Decomposition of Furan on Pd(111)***, **A. Loui,*** University of California, Davis*; D.N. Futaba,* Hokkaido University, Japan*; S. Chiang,* University of California, Davis

Experimental and theoretical studies have been performed on the decomposition of furan, C@sub4@H@sub4@O, adsorbed on Pd(111). The reaction of furan on this substrate has been previously studied using LITD/FTMS.@footnote 1@ In that study, furan was observed to decompose to H, CO, and C@sub3@H@sub3@ in the temperature range of 280-320 K; the latter species can then dimerize to form benzene above 350 K. Using scanning tunneling microscopy, our observations of the pre-reaction surface at 126 K show features adsorbed along the upper step edges, which match theoretical images of furan@footnote 2@ (generated using Extended Hückel Theory) in overall shape, size and internal structure. Comparison of the calculated and experimental furan features show that these molecules seem to preferentially orient with the oxygen atom facing away from or towards the step edge. Data obtained in the temperature range of 280-320 K show evidence of decomposition, which is consistent with the previous desorption studies. We have observed two distinct types of features that are discernible based on size, location and internal detail. The larger features populate the upper step edge region and are consistent with the data obtained at 126 K for unreacted furan. The smaller features appear to be clumped along the lower step edges. Based on the size and the known reaction products, we attribute these features to C@sub3@H@sub3@. In some reaction data, this species is resolved as an oblong feature with a bisecting node, agreeing well with the calculated images for flat-lying C@sub3@H@sub3@ molecules in shape, size and internal structure. These experiments indicate that there is a fundamental difference in the properties of the upper step edge versus the terrace with respect to this decomposition reaction. @FootnoteText@ @footnote 1@ Caldwell, T. E. and Land, D. P., Polyhedron, 16(18), 3197 (1997). @footnote 2@ Futaba, D. N. and Chiang, S., J. Vac. Sci. Technol. A, 15(3), 1295 (1997).

Tribology
Room 132 - Session TR+SS-WeM
Fundamentals of Tribology & Adhesion

Moderator: S.M. Aouadi, University of Nebraska - Lincoln

8:20am **TR+SS-WeM1 Bonding and Debonding in Nanometer-Scale Viscoelastic Contacts***, **M. Giri,** D.B. Bousfield, W.N. Unertl,* University of Maine

Contact to viscoelastic materials, unlike elastic or elastomeric materials, are poorly understood, primarily because of the hysteretic effects caused by the time dependent mechanical properties. We present a quantitative analysis of contacts to viscoelastic materials, specifically crosslinked styrene-butadiene and uncrosslinked styrene-acrylate copolymers. Contacts were made with ultra-low load indentation using diamond probes of various axisymmetric shapes. Both creep and loading-unloading (bonding-debonding) measurements were made for penetration depths ranging from a few nanometers up to a few micrometers. This data was analyzed using the cohesive zone model recently developed by Hui and coworkers.@footnote 1@ This model demonstrates that the most information that can be extracted from a contact experiment is the Mode I Stress Intensity Functional K@sub I@. We show that no knowledge of the interfacial bonding mechanism is required to determine K@sub I@ from the displacement versus load data. In effect, K@sub I@ is analogous to the rate constant of a chemical reaction. Its measurement does not require knowledge of the bonding mechanism, but once measured, it can be used to test models of the mechanism. We illustrate this by testing the widely used bonding-debonding theory of Schapery@footnote 2@ for propagation of cracks at viscoelastic interfaces. We show that this model is inadequate to explain our results and attribute this failure to the assumption of a rate-independent interaction potential. @FootnoteText@ @footnote 1@Y.Y. Lin, C.K. Hui, J.M. Baney, J. Phys. D: Appl. Phys. 32 (1999) 2250. @footnote 2@R.A. Schapery, Intl. J. Fracture 39 (1989) 163.

8:40am **TR+SS-WeM2 A Multi-Scale Elasto-hydrodynamic Contact Model of Chemical Mechanical Planarization***, **A. Kim,** J. Tichy, T.S. Cale,* Rensselaer Polytechnic Institute

We present a physically based multi-scale finite element model to help better understand the CMP process. We extend a model that is presented in Ref. 1. This extended "soft" elasto-hydrodynamic contact model captures the fundamental mechanical and tribological aspects of the CMP process and requires few ad hoc assumptions or adjustable parameters. Recent experimental results show that fluid suction pressures exist,@footnote 2@ and the friction coefficient decreases as the Hersey number (i.e., viscosity*velocity/ pressure) increases.@footnote 3@ These results indicate that there exist mixed direct solid-solid contact and partial fluid lubrication, i.e., elasto-hydrodynmic lubrication. The theoretical results presented in this work support elasto-hydrodynamic contact (abrasion) at the pad-wafer interface. The constitutive equation for the soft polymer pad material must be some form of large strain nonlinear elasticity such as hyperelasticity as the strains of a well-deformed asperity are of order one. A physically based asperity-scale hyperelastic model, which includes a frictional effect, is presented to calculate local stresses at asperity tips. These local stresses are directly related to widely accepted material removal models. In most CMP tools, the external downward force is applied to the wafer-carrier head through a ball joint, which in principle cannot transmit a moment. In order to obtain closure of the analysis, the mean depth into the pad and tilt angle of the wafer are determined by the normal global force applied and momentum balances using the Levenberg-Marquardt method. Finally, we summarize our approach to linking the asperity scale contact analysis to the wafer scale model through a statistical method. @FootnoteText@@footnote 1@J. A. Tichy, J. Levert, L. Shan and S. Danyluk, J. Electrochem. Soc. 146(4), 1523 (1999). @footnote 2@L. Shan, Ph.D. Thesis, Georgia Institute of Technology, 2000. @footnote 3@Y. Moon, Ph. D. Thesis, University of California, Berkeley, CA, 1999.

9:00am **TR+SS-WeM3 Comparative Energy Dissipation in Nanoscale Shear and Tensile Interactions***, **G. Haugstad,*** University of Minnesota

A case study of ultrathin polyvinyl alcohol films is presented, comparing energy dissipation in three modes of scanning force microscopy: friction force, pulsed force mode and "tapping mode". Relative energy dissipation is measured on three distinct film components: a continuous first layer (~1 nm thick) strongly adsorbed to mica; a thicker, discontinuous overlayer, autophobically dewetted from the first layer; ordered overlayer islands (1 nm thick) located within the breaks of component #3. These films are chemically homogeneous but structurally heterogeneous. The components differ in amorphous content (free volume) and confinement, giving rise to differences in energy dissipation. Energy dissipation during sliding is quantified as friction force multiplied by a sliding distance of one contact diameter. Dissipation per cycle during vertical cantilever oscillation is quantified from the cantilever phase lag and the ratio of reduced to free resonance amplitude, via the method proposed by Cleveland et al.@footnote 1@ Dissipation during pull-off in pulsed force mode is quantified with a newly proposed method: by measuring the cantilever deflection with high time resolution (5 MHz) and comparing the (slowly damped) free oscillation amplitude (squared) immediately following pull-off to the quasistatic deflection (squared) immediately prior to pull-off. Corrections arise from (a) the relationship between linear deflection and (measured) angular tilt near the end of the cantilever;@footnote 2@ (b) the excitation of higher cantilever eigenmodes@footnote 2@ upon pull-off. Our results demonstrate that energy dissipation contrast in pulsed force and "tapping" modes is very similar, though the time scales of interaction are very different, whereas contrast in sliding friction is markedly different from either. @FootnoteText@ @footnote 1@J. P. Cleveland, B. Anczykowski, A. E. Schmid and V. B. Elings, Appl. Phys. Lett. 72, 2613-2615 (1998). @footnote 2@H. J. Butt and M. Jaschke, Nanotechnology 6, 1 (1995).

9:20am **TR+SS-WeM4 A Nanoscale JKR Test for Adhesive Contacts to Polymers***, S.A.S. Asif,* Geo-Centers*; **K.J. Wahl,*** Naval Research Laboratory

Contact mechanics measurements at the nanoscale are important for understanding the behavior of ultrathin films developed for adhesives, electronics packaging, microelectromechanical devices, colloidal particles, and lubrication. Determining surface mechanical properties of small devices, thin films or small volumes may be impossible by traditional methods, which lack either high spatial resolution or surface sensitivity. In this paper, we present a dynamic nanoscale Johnson-Kendall-Roberts (JKR) test to examine adhesive contacts to polymers and thin films. The nanoscale JKR test, based on a depth-sensing nanoindenter with AC force modulation capabilities,@footnote 1@ combines measurements of load and contact or interaction stiffness as a function of tip-surface separation and indenter penetration depth. With this method, and appropriate contact mechanics, it is possible to make localized mechanical property measurements (e.g. loss and storage moduli, adhesion energy, cohesive stress, and strain energy release rate) for contacts with diameters smaller than the optical limit. We present results of studies using probes with tip radii between 1 and 10 microns against polydimethyl siloxane surfaces with varying cross-link densities. Smaller probe diameters and increased cross-link density shifted the measured response away from a pure JKR model into the Maugis-Dugdale transition regime. The storage modulus and surface energy measured from nanoscale JKR results are compared to both calculated values and those measured with conventional nanoindentation. @FootnoteText@ @footnote 1@ S.A. Syed Asif, K.J. Wahl, and R.J. Colton, Rev. Sci. Instrum. 70 2408-2413 (1999).

9:40am **TR+SS-WeM5 Combined Nanoindenter and Quartz Crystal Microbalance Studies of Realistic Tribological Contact***, **B. Borovsky**, J. Krim,* North Carolina State University*; S.A.S. Asif, K.J. Wahl,* Naval Research Laboratory

There has recently been increased interest in studying friction at nanometer and micron length scales at much higher speeds than are obtainable with instruments such as atomic force microscope and surface forces apparatus. Sliding contacts in computer hard drives, micromachines, and many macroscopic applications move at speeds on the order of 1 m/s. This speed regime is routinely accessed by the vibrating surface of a quartz crystal microbalance (QCM). We have therefore constructed a device capable of studying both high-speed sliding friction and contact mechanics by combining a nanoindenting probe and QCM. By measuring normal load, contact stiffness, and QCM response simultaneously, this combination is well-suited to developing the theoretical understanding of probe-QCM systems. In order to establish the relationship between the QCM response and the properties of the interface, we have carried out detailed studies of glass-metal and metal-metal contacts in air. The interfaces are characterized by a contact area (derived from the square of the contact stiffness) proportional to the normal load, consistent with multi-asperity contact and elastoplastic deformation.@footnote 1@ We observe that the frequency shift of the QCM is proportional to the true area of contact as inferred from the contact stiffness. Following an earlier suggestion, we model the interaction in the near-field acoustic regime.@footnote 2@ We find that our results are explained by accounting for the roughness of the opposing surfaces. The magnitude of QCM frequency shift is found to reflect the elasticity of the interface, the number and size of contact regions, and the degree of slippage. Research supported by NSF, AFOSR, and ONR. @FootnoteText@ @footnote 1@ J.A. Greenwood, in Fundamentals of Friction: Macroscopic and Microscopic Processes, NATO ASI Series, I.L. Singer and H.M. Pollock, eds., (Kluwer, Boston, 1992) p. 37. @footnote 2@ A. Laschitsch and D. Johannsmann, J. Appl. Phys. 85, 3759 (1999).

10:00am **TR+SS-WeM6 Molecular Layer Effects on Friction Between Single Crystalline Metal Surfaces***, **A.J. Gellman**,* Carnegie Mellon University*; J.S. Ko,* Merck & Co.

The combined use of an ultrahigh vacuum tribometer and a variety of surface science techniques has enabled us to explore the tribological properties of interfaces between Ni(100) surfaces and to observe phenomena attributable to molecular layering. Friction measurements have been made between a pair of clean Ni(100) surfaces, modified by the presence of adsorbed atomic sulfur with and without adsorbed ethanol. Friction measurements made with ethanol coverages ranging from 0 â€“ 10 monolayers on each Ni(100) surface reveal that the friction coefficient is discontinuous in coverage and can be correlated to the coverage dependence of the ethanol desorption energy. During shearing sliding never commences between clean Ni(100) surfaces or sulfided Ni(100) surfaces without adsorbed ethanol. In the submonolayer coverage regime of either atomic sulfur or adsorbed ethanol the behavior is characterized by a high friction coefficient (µ@sub s@ > 5.5) accompanied by high adhesive forces (µ@sub ad@ = 1.5 Â± 0.7). An abrupt decrease in both the friction coefficient and adhesion coefficient occurs at a coverage of one monolayer of ethanol on each surface. The friction coefficient drops to (µ@sub s@ = 3.1 Â± 1. while the adhesion coefficient is lowered to µ@sub ad@ ~ 0.25. At coverages between 1.0 and 2.5 monolayers of ethanol on each Ni(100) surface the static friction coefficient decreases in a step-wise manner that is correlated with discontinuities in the ethanol desorption energy. This step-wise decrease in both the friction coefficient and the desorption energy may be due to molecular layering of the ethanol.

10:20am **TR+SS-WeM7 The Effect of Packing Density on the Friction of Alkane Monolayers***, **J.A. Harrison**, P.T. Mikulski,* United States Naval Academy **INVITED**

Hydrocarbon materials have traditionally been used to prevent the friction and wear of mechanical components in sliding contact. One important example of this is the use of oil in conventional combustion engines. The advent of chemical vapor deposition technology has piqued interest in the use of solid hydrocarbons as lubricants in systems such as microelectromechanical devices. A detailed knowledge of the molecular-scale mechanisms responsible for lubrication would be invaluable in the design of novel solid lubricants. We are using molecular dynamics to examine the atomic-scale phenomena governing the tribology of hydrocarbon-containing systems. Because liquid hydrocarbons and boundary layer lubricants, such as self-assembled monolayers, are to be studied, the potential energy function must include intermolecular interactions. The new adaptive intermolecular reactive empirical bond-order potential (AIREBO)@footnote 1@ can simulate reactive and non-reactive processes in a wide range of environments, including graphite, liquid hydrocarbons, and self-assembled monolayers. We have conducted extensive simulations that have examined the friction of alkane monolayers attached to diamond surfaces or model self-assembled monolayer systems. We have examined friction as a function of packing density, chain length,@footnote 2@ and sliding direction. Recent AFM results of Perry and coworkers@footnote 3@ unambiguously demonstrate that decreasing the packing density, or the disorder of the film, increases the friction. Simulations reproduce this trend and provide an atomic-scale explanation for this observation. *Supported by ONR and AFOSR. . @FootnoteText@ @footnote 1@ S. J. Stuart, A. B. Tutein, and J. A. Harrison, J. Chem. Phys. 112, 6472-6486 (2000). @footnote 2@ A. B. Tutein, S. J. Stuart, and J. A. Harrison, Langmuir 16, 291-296 (2000); Ibid. , J. Phys. Chem. B 103, 11357-11365 (1999). @footnote 3@ Lee et al., Langmuir 16 2220 (2000).

11:20am **TR+SS-WeM10 A Study of Triboelectricity on Dielectric Surfaces by Measuring Electric-discharge Luminescence during Friction***, **T. Miura**, I. Arakawa,* Gakushuin University, Japan

Triboluminescence during friction between a spherical surface and a flat surface of dielectrics, i.e., a typical pin-on-disk technique, was observed by a spectrometer and an optical microscopy. Spectrum measurement of the luminescence in ambient air made it clear that electric discharge occurs around a contact point. To investigate a relation between the electric discharge and triboelectricity the luminescent intensity distribution along the sliding direction was measured using the microscope with only UV-translucent filter. In short, the breakdown characteristics depending on the gap distance was aimed. When it is assumed that the UV distribution indicates electric discharge currents at each gap distance, the distribution is accounted for a well-known equation of semi-empirical discharge-current. As a result, voltage between the both sides was evaluated. Then the surface charge density at immediately after the friction in several ms was shown. We believe this is innovative technique to evaluate electric potential difference of triboelectricity between dielectric surfaces. In this conference we will present our experimental results, methods, analysis, and discussions in detail.

Surface Science
Room 120 - Session SS1-WeA

New Opportunities in Surface Microscopy

Moderator: C.S. Fadley, Lawrence Berkeley National Laboratory

2:00pm **SS1-WeA1 Imaging with Helium Atoms: Developments in Scanning Atom Microscopy**, ***D.A. MacLaren***, *W. Allison,* University of Cambridge, U.K.

We report on the preparation and production of ultra-smooth helium atom mirrors and on recent advances in the development of a Scanning Atom Microscope (SAM). A bent Si(111)-(1x1)H crystal is an ideal mirror for helium atoms and can be used as the focusing element of a SAM. @footnote 1@ Based upon a focused microprobe of thermal helium atoms, a SAM provides the opportunity for sub-micron, non-destructive and surface-sensitive imaging and could have a profound impact on surface science, particularly in studies of delicate organic systems. A low aberration, high intensity atom mirror requires control over both the macroscopic and microscopic surface properties. Our approach is to bend an ultrasmooth single crystal into the optimum macroscopic profile by application of precise electrostatic fields; we have demonstrated that aberration-free focusing is possible using this method.@footnote 2@ The atom mirror must also have a high helium reflectivity, which requires careful manipulation of the surface microstructure. Here, we discuss refinements to the ex-situ preparation of Si(111)-(1x1)H. Atomic Force Microscopy is used to study the kinetics of the etching mechanism used to produce the mirror surface. We show that small changes in miscut angle can alter the kinetic steady state to promote the formation of deep etch pits and stable self-aligned 'etch hillocks' on the micron scale. Our study has led to the production of surfaces that are homogeneous over tens of microns and which have substantially improved atom reflectivity. The results are a significant improvement in silicon preparation and are a crucial step in the development of a scanning atom microscope. @FootnoteText@ @footnote 1@ B. Holst and W. Allison, Nature (London) 286, (1997), 244. @footnote 2@ D.A. MacLaren, W. Allison and B. Holst, Rev. Sci. Instrum. 71, (2000), 2625.

2:20pm **SS1-WeA2 Scanning Near-Field Infrared Microscopy**, ***E.S. Gillman,*** Jefferson Lab

Nanoscale chemical identification of objects below the diffraction limit is possible using a scanned probe technique, the Scanning Near-Field Infrared Microscope (SNFIM). In most cases vibrational spectroscopy in the infrared region is restricted due to the limitations of beam focusing to samples of macroscopic dimensions, on the order of one to several microns. The scale of the measured area is completely determined by the diffraction limit of the incident radiation. With a scanned probe technique resolution of chemical features on the order of @lambda@/20 or ~100 nm can be achieved. An overview of previous experimental results using a free electron laser (FEL)@footnote 1@@super,@@footnote 2@, and more conventional infrared sources@footnote 3@@super,@@footnote 4@, will be discussed. A description of the experiment and recent results from the SNFIM at the Jefferson Lab Free Electron Laser facility will be presented. This work was supported by U.S. DOE Contract No. DE-AC05-84-ER40150, ONR Contract No. N00014-99-1-09B, the Commonwealth of Virginia and the Laser Processing Consortium. @FootnoteText@ @footnote 1@ A. Piednoir, C. Licope, and F. Creuzet, Opt. Commun. 129, 414 (1996). @footnote 2@ M. K. Hong, A. G. Jeung, N. V. Dokholyan, T. I. Smith, H. A. Schwettman, P. Huie and S. Erramilli, Nucl. Instrum. Methods Phys. Res. B 144, 246 (1998). @footnote 3@ B. Knoll and F. Keilmann, Nature 399, 134 (1999). @footnote 4@ C. A. Michaels, S. J. Stranick, L. J. Richter, and R. R. Cavanaugh, J. Appl. Phys. 88, 4832 (2000).

2:40pm **SS1-WeA3 Spectroscopy, Microscopy, and Chemistry at the Spatial Limit**, *W. Ho,* University of California, Irvine*;* ***M. Persson,*** Chalmers University, Sweden **INVITED**

The combination of vibrational spectroscopy and microscopy with the imaging, manipulation, and chemical modification capabilities of the scanning tunneling microscope (STM) has made it possible to probe surface chemistry with sub-Angstrom resolution. Direct visualization of the nature of the chemical bonds and their transformations at the single molecule level not only provides convincing evidences but also fundamental understandings of chemical processes. The STM junction is effectively a nanoreator in which the metallic tip and substrate work together to induce chemical transformations of individual molecules adsorbed either on the substrate or the tip. Many aspects of chemistry can be probed by the STM, including the rotational, vibrational, and translational motions, the conformational changes, the energy transfer, the electrical conductivity, the coupling of electrons to the nuclear motions, and the bond breaking and formation of individual molecules.

3:40pm **SS1-WeA6 Focused Inelasticity in Scanning Tunneling Spectroscopy**, ***J.W. Gadzuk,*** National Institute of Standards and Technology*; M. Plihal,* KLA-Tencor

Scanning tunneling microscopy/spectroscopy of magnetic atoms adsorbed upon non-magnetic metal surfaces (possibly Kondo systems) has provided intriguing visual images and spectroscopic signatures in the form of Fano lineshapes in which the asymmetry depends in a diagnostically-useful way on tip location with respect to the adsorbate. Additional STM studies have demonstrated the ability of suitable two-dimensional nanostructures (such as "quantum corrals") to influence the surface electron transport that is part of the total elastic STM process. In a well known paradigm, an elliptical arrangement of Co atoms on Cu(111) gives rise to an apparent enhanced electronic communication between points on the surface which are near the two elliptical foci, showing some behavior consistent with classical ray tracing. The spectroscopic signature of a Kondo atom adsorbed at one focus shows an identical signature (though diminished in intensity) when the STM tip is placed over the vacant focus, suggestive of a mirage or "phantom atom". We report here on similar remote sensing for STM procedures involving inelastic tunneling in which adsorbate-surface or intra-molecular vibrational excitation occurs. We have extended our nonequilibrium theory of scanning tunneling spectroscopy@footnote1@ to include the additional processes, inelastic adsorbate vibrational excitation and elastic surface nanostructure scattering/focusing and the general theory has been applied to an elliptic corral realization. The characteristics of such "focused inelasticity" will be presented within the context of both Kondo systems such as Co/Cu(111) and also simple molecular systems. @FootnoteText@ @footnote 1@ M. Plihal and J. W. Gadzuk, Phys.Rev.B63(2001)085404.

4:00pm **SS1-WeA7 Calculations of Elastic and Vibrational Inelastic Electron Tunneling Images**, ***M. Persson***, *F. Olsson,* Chalmers University, Sweden*; N. Lorente,* IRSAMC, Univ. P. Sabatier Touluose, France

The inelastic electron tunneling spectroscopy (IETS) in the STM is capable of mapping the vibrational excitation of single molecules in real space with sub-Å spatial resolution and meV spectral resolution.@footnote 1@ Despite the obvious promise of a spectroscopy with these unique capabilities, STM-IETS raises several issues that we need to address by theory to fully exploit this spectroscopy. These issues include; (1) why are so few modes detected; (2) what can be learnt from IET images; (3) what is the nature of the coupling between the tunneling electron and the vibration; (4) what determines the vibrational lineshape ? To this end we have studied the excitation mechanism in STM-IETS using a generalization of Tersoff-Hamann theory to IET combined with density functional calculations.@footnote 2,3@ We have shown that this many-electron theory give quantitative agreement with experiments and have identified several general effects: (1) elastic and inelastic contributions to the IET tend to cancel; (2) a symmetry selection rule connecting the symmetries of the IET images, adsorbate-induced states at the Fermi level and the vibrational mode; (3) a Fano-like lineshape for the second derative of the tunneling current with bias. These effects will be illustrated from a comparison of results of calculated vibrational inelastic images from several systems with experiments, in particular, oxygen adsorbed on silver surface, which provides a typical example of inelastic coupling through a single resonance level.@footnote 4@ We will also illustrate the applicability of the Tersoff-Hamann approximation for the calculations of elastic STM images. @FootnoteText@ @footnote 1@ B.C. Stipe, M.A. Rezaei and W. Ho, Science 208, 1732 (1998); Phys. Rev. Lett. 82, 1724 (1999). @footnote 2@ N. Lorente and M. Persson, Phys. Rev. Lett. 85, 2997 (2000). @footnote 3@ N. Lorente, M. Persson, L. Lauhon, and W. Ho, Phys. Rev. Lett. 86, 2593 (2001). @footnote 4@ J.R. Hahn and W. Ho, Phys. Rev. Lett. 85, 1914 (2000).

4:40pm **SS1-WeA9 Progress in Dynamic Force Microscopy: From High-Resolution Imaging of Insulators to the Measurement of Dissipative Interaction Forces**, ***U.D. Schwarz***, *H. Hölscher, W. Allers, S. Langkat,* University of Hamburg, Germany*; B. Gotsmann, H. Fuchs,* University of Münster, Germany*; R. Wiesendanger,* University of Hamburg, Germany

Recent progress in dynamic force microscopy (DFM) operated in ultrahigh vacuum, often also called non-contact atomic force microscopy (NC-AFM), enabled the imaging of the atomic structure of surfaces including the observation of point defects independent from the sample's conductivity. However, only few results on insulators have been published so far, possibly due to difficulties in preparing suitable sample surfaces for NC-AFM, e.g., electrostatic charging of the surfaces in vacuum. In order to illustrate the high-resolution capabilities of DFM on insulators, we present the first part of our talk results obtained on NiO(001) at low temperatures. Transition metal oxides are a class of magnetic insulators, which have been of great interest for several decades due to their electronic and magnetic properties. On this material, monatomic defects and atomic resolution across step edges could be observed, achieving a vertical resolution of 1.5 pm. In a second part, the spectroscopic potential of DFM based on a self-driven oscillator set-up is analysed. Introducing a very general tip-sample force law, we show that one of the two quantities measured, the frequency shift, is determined by the mean tip-sample force, while the other quantity, the gain factor (or excitation amplitude), is directly related to dissipative processes like hysteresis or viscous damping. This insight into the measurement principle can be used to examine the contrast mechanism in more detail. The application to non-reactive surfaces like graphite(0001) and xenon(111) allows us to simulate complete DFM images. A comparison between experiment and simulation shows that on xenon, atoms are imaged as maxima, whereas on graphite, the atomic positions of carbon atoms appear as minima and the hollow sites as maxima, in contrast to a simple interpretation of the experimental images.

5:00pm **SS1-WeA10 Characterization of Structure Transition in Ion-Implanted Amorphous Silicon***, **J.-Y. Cheng,*** University of Illinois at Urbana-Champaign*; J.M. Gibson, P.M. Baldo,* Argonne National Laboratory

We use fluctuation electron microscopy to characterize disordered structures in silicon. In fluctuation electron microscopy, variance of dark-field image intensity contains the information of high-order atomic correlations, primarily in medium-range order length scale (1-3nm). In this study, amorphous silicon is produced by self-ion implantation of silicon at liquid nitrogen temprature, followed by annealing processes. As-implanted and annealed structures have been identified as paracrystalline structures and a continuous random network. However, the connection of structure transition to free energy release has not yet been fully understood. We will present new results from materials prepared by post-anneal He irradiation and post-He-bombardment annealing, and discuss effects of He implantation as the system evolves in consecutive treatments.

Surface Science
Room 121 - Session SS2-WeA
Adsorption on Metal Surfaces

Moderator: M.W, Trenary, University of Illinois, Chicago

2:00pm **SS2-WeA1 Chemical Bonding of Alkanes on Metal Surfaces: Adsorption of n-octane on Cu(110)***, **L. Triguero**, K. Weiss, H. Öström, D. Nordlund, H. Ogasawara,* Uppsala University, Sweden*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Uppsala University; Sweden and Stanford University, Sweden

Using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy and X-ray emission spectroscopy (XES), we have investigated the electronic structure and chemical bonding of n-octane adsorbed on Cu(110). The high degree of NEXAFS dichroism reveals that the molecule is well oriented on the surface. The NEXAFS spectra also reveal large changes in the unoccupied electronic structure of the adsorbed octane relative to the free molecule. XES, which shows the occupied density of states, reveals new states showing up near the Fermi level. In order to understand these changes in the electronic structure, we have performed cluster model calculations in the framework of Density Functional Theory. The calculations indicate significant charge transfer and formation of a chemical bond between the molecule and the substrate. Our study also gives new experimental evidence of chemical interaction and insights into the bonding mechanism of saturated hydrocarbons adsorbed on metal surfaces, which is of importance for the understanding of the C-H bond activation mechanism.

2:20pm **SS2-WeA2 Two Dimensional Crystallisation of Nucleic Acid Bases on Cu{110}***, **N.V. Richardson**, D.J. Frankel, Q. Chen,* University of St Andrews, UK

There is considerable interest in the characterisation and control of biomaterial surfaces. An important step towards this goal is a better, molecular level understanding of model systems based on two dimensional arrays of biorelevant molecules. In this presentation, the adsorption of the nucleic acid bases, uracil (U), thymine (T), cytosine (C), guanine (G) and adenine (A), on Cu{110} has been studied in depth by scanning tunneling microscopy, electron energy loss spectroscopy and low energy electron diffraction. In general, all the molecules form well-ordered 2D structures when vacuum deposited on a room temperature Cu{110} crystal, or at least after moderate annealing. A variety of ordered structures are found for each molecule dependent on coverage and temperature. The pyrimidine bases U, C and T form related structures involving upright molecules and, following loss of hydrogen, adsorbed species in well ordered structures are stable to over 700K. Further heating, results in major re-faceting of the uppermost (ca. ten) layers of the copper substrate giving rise to major new one or two dimensional features. In contrast the purine bases, A and G, form large, two dimensionally ordered domains based on flat-lying molecules without faceting. Hydrogen bonding is a key feature of all the networks. Models of the surface structures will be presented. We also note that although these planar molecules are optically inactive, the single mirror plane is destroyed by adsorption and the resulting surface species is then chiral. This is important in the 2D crystal structures and can result in chiral domains on the surface. .

2:40pm **SS2-WeA3 Electronic State of DNA Molecules on Surface: Cytosine on Cu(110)***, **M. Furukawa,*** Osaka University, Japan*; T. Komeda, M. Kawai,* RIKEN, Japan*; T. Kawai,* Osaka University, Japan*; H. Ogasawara,* RIKEN, Japan*; A. Nilsson,* Uppsala University, Sweden

Electric property of DNA strands and/or molecules being attractive as they are considered to be a candidate for a piece of molecular system in nano-scale technology. The purpose of the present study is to experimentally define the local electronic state of the molecule of the molecular systems by use of x-ray spectroscopies. Here, X-ray photo-electron spectroscopy (XPS) gives the energy level of core sates against the Fermi level, X-ray absorption spectroscopy (XAS) gives the atom specific energy difference between the core state and the state above the Fermi level. Combining all the information then the atom specific view of the energy levels across the Fermi level be understood. Here we give an example for Cytosine adsorbed on Cu(110) surface, where we have observed the core level for C1s, O1s and N1s and XAS from these core levels to the unoccupied states. As for the orientation of the molecule, electric field direction dependence in the XAS experiment for all C, O and N K edge exhibited that the molecular plane of cytosine sits perpendicular to the surface and also parallel to the [1-10] row of the surface. On of the most interesting feature of the electronic states is the fact that the LUMO state of the molecule is found to sit very close to the Fermi level, indicating that the system has a natural tendency to be electron doped conductor is the level is connected in space.

3:00pm **SS2-WeA4 Understanding the Pressure and Structure Gaps in Catalysis: Role of Steps and Terraces in the O@sub 2@ and C@sub 2@H@sub 4@ Interaction with Ag(410)***, L. Savio, L. Vattuone, **M. Rocca,*** Universita' di Genova, Italy

The effort to unravel the dynamics of real catalysts by ultra high vacuum investigations of gas-surface interaction suffers of two major limitations, known as pressure gap (10 order of magnitudes difference) and structure gap (the surface of a real catalyst has a high density of steps and defects in contrast to the almost perfect low Miller index surface of a single crystal). A large effort was devoted to bridge the pressure gap; in order to face the structure gap, attention was focused on defected surfaces, obtained either by ion bombardment or by cutting a single crystal along vicinal planes. We report on a combined supersonic molecular beam and High Resolution Electron Energy Loss Spectroscopy investigation of the angle and energy dependence of the sticking probability, S, of O2 and C2H4 on Ag(410), a vicinal surface with (100) teraces and (110) step edges. In agreement with our previous results for the ion bombarded Ag(100) surface, we find for O2 adsorption that dissociation and molecular chemisorption coexist already at temperatures at which only molecular adsorption is stable on flat Ag(100). The angular dependence of S shows that when the molecules impinge against the step edges the activation barrier for molecular adsorption is strongly reduced or even eliminated. The reactivity of Ag atoms at terrace sites is, on the contrary, reduced with respect to the flat surface. Dissociation takes place preferentially at the upper side of the steps as proven by the temperature and angular dependence of S. For C2H4 we observe nearly unitary sticking probability at the step edge and stable adsorption in the pi-bonded state. S scales approximatively with total energy, but it is slightly larger for molecules impinging grazing on the step edges and decreases when the step edges are in shadow. The interaction is mediated by an extrinsic precursor.

3:20pm **SS2-WeA5 Chemical Bonding in Structurally Complex Chemisorption Systems*, D.A. King,*** University of Cambridge, UK, U.K. **INVITED**

The combination of (i) quantitative LEED, infrared and STM structural analyses of complex adsorbate structures with (ii) SCAC (single crystal adsorption calorimetry) measurements of energetics, on the one hand, and state-of-the-art first principles DFT slab calculations of these systems on the other has provided a unique experimentally benchmarked approach to chemical bonding in structurally complex chemisorption systems.@footnote 1@ Of particular importance to reactivity in molecular systems at surfaces, this has given rise to the new concept of surface and promoter-induced molecular polarisation, and its relationship to stereo-electronically driven chemical reactivity in catalysis.@footnote 2@ The presentation will draw particularly on our recent results for CO + K coadsorption on Co{1010},@footnote 2-4@ C@sub 6@H@sub 6@ adsorption on Ni{111}@footnote 5@ and on Ir{100}@footnote 6@ and coadsorption with O, CO and NO on Ni{111}@footnote 7@ and anisole adsorption on Pt{110}.@footnote 8@ @FootnoteText@ @footnote 1@"Adsorption Energetics and Bonding from Femtomole Calorimetry and from First Principles Theory", Advances in Catalysis, 43 (2000) 207-259. @footnote 2@Q. Ge, R. Kose and D. A. King. "A Role for Induced Molecular Polarisation in Catalytic Promotion: CO Coadsorbed with K on Co{1010}", J. Am. Chem. Soc., 122 (2000) 10610-10614. @footnote 3@S. J. Jenkins and D. A. King. "Full Structure Determination of an Alkali Metal/CO Co-Adsorption Phase, for Co{1010} (2x2)-(K + CO)", Phys. Rev. B, 51 (1995) 17063-17067. @footnote 4@P. Kaukasoina, M. Lindroos, P. Hu, D. A. King and C. J. Barnes. "The Coadsorption of CO and K on Co{1010}", Surf. Sci., 349 (1996) 19-42. @footnote 5@R. L. Toomes and D. A. King "Realistic Molecular Distortions and Strong Substrate Buckling Induced by the Chemisorption of Benzene on Ni{111}", J. Chem. Phys, 105 (1996) 11305-11312. @footnote 6@G. Held, M. P. Bessent, S. Titmuss and D. A. King. "Benzene Adsorption on Ir{100} Studied by LEED I-V Analysis: Evidence for Formation of Tilted Benzyne", J. Chem. Phys., in press. @footnote 7@K. Johnson, B. Sauerhammer, S. Titmuss and D. A. King. S. Titmuss, D. A. King, to be published. @footnote 8@Y. P. Tan, S. Khatua, S. Jenkins and D. A. King, to be published.

4:00pm **SS2-WeA7 The Dynamics of CO and H co-adsorption on Ru(0001)***, B. Riedmüller,* FOM Institute for Atomic and Molecular Physics, The Netherlands*; I.M. Ciobica, R.A. van Santen,* Eindhoven University of Technology, The Netherlands*; **A.W. Kleyn,*** Leiden University, The Netherlands

Chemical reactions at surfaces form an exciting example of co-adsorbate systems on surfaces. The dynamics of such systems is still poorly understood. In this paper we will consider the dynamics of CO and H co-adsorption on Ru(0001). In earlier experiments we have demonstrated that H-adsorption turns the Ru surface in an almost perfect inert mirror for CO molecules. However, the sticking probability does not go to zero. There are adsorbing spots on the mirror. We carried out DFT calculations that demonstrate the nature of the activated adsorption of CO on H-Ru(0001). There is one specific site (atop) exclusively binding CO. In contrast, at the clean surface the entire unit cell strongly binds CO, and the molecule will reside at the most strongly bound site. This means that the reactivity of the H-covered surface strongly varies over distances of much less than an Angstrom. The nature of the bonding will be elucidated. Although we have computed a stable CO-H-Ru(0001) configuration this does not mean that this is the most stable. In fact the system shows phase separation. We studied its formation by Thermal Energy Atom Scattering. We find that on adsorption of CO on a H-Ru(0001) surface the CO nucleates in islands. The island size depends on the CO flux. In contrast to what has been seen for epitaxy of metals on metals at low CO flux small 'magic' CO-7 clusters are formed, at high flux large islands nucleate.

4:20pm **SS2-WeA8 Ordered Structures of CO on Pd(111) Studied by STM*, M.K. Rose,*** Lawrence Berkeley National Laboratory and University of California at Berkeley*; J.C. Dunphy, T. Mitsui,* Lawrence Berkeley National Laboratory*; A. Borg,* Norwegian University of Science and Technology, Norway*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The @sr@3x@sr@3-R30°, c(4x2), and (2x2)-3CO structures of CO on Pd(111) have been studied by STM. Shifts of the CO binding site with increasing coverage are observed. At coverages of 1/3 ML and below, CO occupies three-fold hollow sites. Near 1/2 ML, regions of c(4x2) CO with both FCC and HCP three-fold hollow site occupation coexist with bridge bonded c(4x2) CO. At high coverage, a partially disordered phase with no top site occupation directly precedes formation of the 2x2 structure. With additional adsorption of CO, bright maxima appear with 2x2 periodicity. The maxima at the edge of 2x2 domains exhibit a quasi-continuous range of corrugation, implying a gradual shift of CO to top sites. The high corrugation of top site CO obscures the other two CO molecules per unit cell, resulting in a symmetric 2x2 periodicity. In addition to this symmetric 2x2 structure, previously unreported domains of lower symmetry 2x2 are observed.

4:40pm **SS2-WeA9 Bridging the Pressure Gap at the Atomic Level*, P. Thostrup,*** *L Österlund, I. Stensgaard, E. Laegsgaard, F. Besenbacher,* University of Aarhus, Denmark

Surface science studies conducted under ultrahigh vacuum (UHV) conditions have contributed immensely to our current knowledge about catalytic processes. A fundamental question is however still, whether UHV data are in general applicable at technologically relevant pressures magnitudes higher than those obtainable in UHV studies. We have developed a novel high-pressure scanning tunneling microscope (HP-STM)@footnote 1@ in order to compare eg. the UHV and HP response of the H/Cu(110) and CO/Pt(110) systems. The H/Cu(110) system is a classic model system for activated dissociation. We find that hydrogen reconstructs the surface both at UHV and high pressures. Through a detailed comparison we even find quantitative agreement between HP and UHV data,@footnote 2@ thus providing support for the surface science approach to heterogeneous catalysis. The CO/Pt(110) system has attracted widespread attention since CO displays an unusually strong dependence upon the coordination number of the Pt atom to which it binds. This property makes the open Pt(110) surface ideal for HP experiments since high pressures of CO are expected to induce massive roughening of the surface. Notwithstanding, already in UHV this interesting property reveals itself:@footnote 3@ We find the equilibrium structure at intermediate coverages to be extremely rough to an extent where almost all top-layer Pt atoms are at steps. Interestingly, we have been able to reproduce this behavior quantitatively in Monte Carlo simulations where all energies involved are taken from ab initio density functional calculations. Preliminary experiments indicate that the roughening behavior described above is also present at high pressures, but in this case to an even more extensive degree. @FootnoteText@ @footnote 1@ E. Laegsgaard, P. Thostup et al., submitted to Rev. Sci. Instr. @footnote 2@ L. Österlund, P. Thostrup et al., Phys. Rev. Lett. 86, 460 (2001). @footnote 3@ P. Thostrup et al., submitted to Phys. Rev. Lett.

5:00pm **SS2-WeA10 A Single-crystal Adsorption Calorimeter for Low Vapor Pressure Molecules*, H. Ihm,*** *H.M. Ajo, C.T. Campbell,* University of Washington

We report a new microcalorimeter for measuring heats of adsorption of low vapor pressure molecules on clean single crystals. While temperature programmed desorption (TPD) and isosteric measurements can provide information on heats of adsorption, they are limited to reversible adsorption-desorption processes. In many catalytically interesting cases, adsorbates undergo irreversible chemical changes upon adsorption or heating. Our microcalorimeter enables direct measurement of these adsorption energies. The principle is similar to that pioneered by King's group:@footnote 1@ a pulse of gas from a molecular beam impinges on a 1 µm-thick single crystal surface. The incident molecules adsorb either physically or chemically, causing a transient temperature rise. This heat input is detected by a 9 µm thick pyroelectric polymer ribbon, which is mechanically driven to make gentle contact with the back of the single crystal sample during a calorimetry measurement.@footnote 2@ This process allows the determination of heats of adsorption as a function of coverage with femtomole resolution. While King's group has performed beautiful adsorption calorimetry, their measurements have been limited to high vapor pressure gases. We have added a specially designed molecular beam source for low vapor pressure molecules, thus significantly extending the capabilities of this technique. Sticking probabilities and absolute coverages are measured by quadrupole mass spectrometry (QMS), low energy ion scattering (LEIS), x-ray photoelectron spectroscopy (XPS), and TPD. As a first experiment, we present a microcalorimetric measurement of benzene adsorption on Pt(111). @FootnoteText@ @footnote 1@ W.A. Brown, R. Kose, and D.A. King, Chem. Rev. 98, 797 (1998). @footnote 2@ J.T. Stuckless, N.A. Frei, and C.T. Campbell, Rev. Sci. Instruments, 69, 2427 (1998).

Surface Science
Room 122 - Session SS3-WeA

Electronic Structure I

Moderator: S.D. Kevan, University of Oregon

2:00pm **SS3-WeA1 Medard W. Welch Award Lecture: Intertwined Charge Density Wave and Defect-Ordering Phase Transitions in a 2-D System@footnote 1@**, ***E.W. Plummer,*** The University of Tennessee and Oak Ridge National Laboratory, US*; A.V. Melechko,* The University of Tennessee and Oak Ridge National Laboratory **INVITED**

The study of macroscopic properties of phase transitions in low-dimensional systems provides an understanding of the fundamental aspects of systems of interacting particles. Phase transitions are strongly affected by defects, especially in systems with lower dimensionality. In quasi-1D or -2D systems that exhibit a CDW transition, a small proportion of microscopic disorder can control the global properties because of the collective nature of the phenomena. It has been speculated that the interaction of mobile defects with CDW leads to alignment of defects with the CDW, or the formation of Defect Density Waves.@footnote 2@ In this dynamic picture, the distribution of defects is neither random nor static, instead defects align their positions to optimize the energy of the pinned CDW. Here, we will discuss a complex symmetry lowering (Ã3xÃ3) to (3x3) phase transition in Sn/Ge(111) and similar systems that can be decomposed into two intertwined phase transitions: a second order CDW transition and a first order disorder-order transition in the defect distribution. We present two phenomenological models that describe these transitions and their interrelation.@footnote 3@ These models allow us to understand the formation of the domains and domain walls seen in STM at low temperatures, defect-induced waves above the CDW transition temperature, and ordering of the defects caused by the CDW-mediated defect-defect interactions.@footnote 4@ The models predict a shift in the CDW transition temperature with impurity density and a dependence of the (3x3) lattice structure on the specific defect alignment. @FootnoteText@ @footnote 1@ Supported by NSF DMR 980130. ORNL is supported by the U.S. DOE through contract DE-AC)5-))OR22725 with UT-Battelle, LLCC.@footnote 2@ H. Mutka, in Advances in the crystallographic and microstructural analysis of charge density wave modulated crystals, edited by F. W. Boswell and J. C. Bennet, Kluwer Academic Publishers, Dordrecht, 1999.@footnote 3@ A. V. Melechko, M. Simkin, N. F. Samatova, J. Braun, and E. W. Plummer, submitted for publication.@footnote 4@ A. V. Melechko, J. Braun, H. H. Weitering, and E. W. Plummer, Phys. Rev. Letters, 83, 999 (1999). H. H. Weitering, A. Melesko, J. M. Carpinelli, and E. W. Plummer, Science, 285, 2107-2110 (1999).

2:40pm **SS3-WeA3 Lifetimes of Surface States at Si(001) Surfaces*, M. Weinelt*,** *M. Kutschera, C. Kentsch, Ch. Orth, Th. Fauster,* Universität Erlangen-Nürnberg, Germany

With ultrafast two-photon photoemission spectroscopy the temporal evolution of an excited electronic system can be studied on the femtosecond time scale. A pump pulse excites electrons to distinct intermediate states while a second time-delayed pulse probes the evolving population dynamics. This allows to determine lifetimes of conduction bands and unoccupied dangling-bond states on semiconductor surfaces directly in the time domain. Using time-resolved two-photon photoemission we have studied the c(4 x 2) and (2 x 1) reconstructions of the Si(100) surface. Several bulk and surface transitions involving unoccupied intermediate states below the vacuum energy are identified. In particular, the surface band gap at the center of the surface Brillouin zone, i.e., the gap between occupied and unoccupied dangling-bond states is determined to 0.96 ± 0.05 eV. The unoccupied dangling-bond state shows a rich dynamic ranging from fs to more than 100 ps. Population and decay are dominated by electron-phonon scattering which couples bulk and surface states. The decay rate is strongly influenced by surface defects in the band gap.

3:20pm **SS3-WeA5 Electronic Structure of Complex Manganite Spinels Studied by XPS, XANES, EXAFS and Nanoprobe EELS*, D.A. KuKuruznyak,*** *B.W. Reed, J.G. Moyer, M.C. Gregg, S.-W. Han, E.A. Stern, M. Sarikaya, F.S. Ohuchi,* University of Washington

Ni-Co-Cu-Mn-O spinels, owing to their strong temperature influence on resistivity, are technologically important oxide materials for thermistor applications, among which Ni@sub 0.48@Co@sub 0.24@Cu@sub x@Mn@sub 2.28-x@O@sub 4@ (x = 0.6, and 1.2) are the compositions of specific industrial interests. In this study, we synthesized nanocrystalline thin films and powders using low temperature metallorganic decomposition technique, rather than conventional solid state sintering. The materials were subsequently annealed at temperatures between 500 and 800°C, and it was found that annealing temperature was a decisive factor in controlling transport properties. Electronic structure of the bulk and surface was investigated by combinations of XPS, XANES, and nanoprobe EELS. The analysis revealed that the annealing caused change of the oxidation state from Cu@super 1+@ to Cu@super 2+@, which was accompanied by reduction of manganese cations from Mn@super 4+@ to Mn@super 3+@. EXAFS analysis showed that both the Cu@super 1+@ and Cu@super 2+@ ions occupied the tetrahedral lattice sites, whereas both the Mn@super 4+@ and Mn@super 3+@ were in the octahedral sites in the spinel structure. During the course of annealing, an unusually large negative binding energy shift in both Cu 2p and Cu 3d levels for the Cu@super 1+@ state was observed. This negative shift appears to be unique to this system, and was attributed to the change in the Fermi surface topology due to strong 3d-4p hybridization which occurs in the in the tetrahedral coordination because of the completely filled 3d@super 10@ orbital of Cu@super 1+@ ion.

3:40pm **SS3-WeA6 Quantum Well Behavior without Confining Barrier Observed via the Dynamically Screened Photon Field***, S.R. Barman,* Inter-University Consortium for DAE Facilities*; **P. Haberle,*** Universidad Tecnica Federico Santa Maria*; K. Horn,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; J. Maytorena,* Universidad Nacional Autonoma de Mexico*; A. Liebsch,* Forschungszentrum Julich, Germany

Quantum well states are a striking manifestation of elementary quantum mechanics. An electron confined in a one-dimensional potential well, formed by the vacuum on one side and a band gap in the substrate on the other, may occupy discrete energy levels whose quantum number specifies the number of half-wavelengths spanning the well. Angle resolved photoemission spectra from Na adlayers on Al(111) reveal features which behave as quantum well resonances, even though the substrate does not provide a barrier for electron confinement. These features are observed in a narrow photon energy range where overlayer collective excitations cause resonant enhancement of the photoemission intensity. The quantum well behavior is shown to be due to surface resonances of the Na/Al system. These are observable since the screened photon field is dynamically enhanced and spatially confined to the overlayer. The special role of the photon field distinguishes the present system from ordinary quantum wells. The quantum well-like spectral features are associated with virtual states induced by the large negative potential step between overlayer and substrate. To observe these resonances it is crucial to suppress emission from substrate bands in the same energy region. This is achieved by tuning the photon energy to the collective modes of the overlayer. The local electric field is then enhanced and confined to the overlayer so that the Na resonances can be observed in a wide range of coverages. Thus, while in usual quantum well systems the photon field plays no special role, here it serves as a novel mechanism ensuring the confinement of the excitation region.

4:00pm **SS3-WeA7 Molecular Resonant Quantum Wells at Organic-Metal Interfaces*, G. Dutton*,** *X.-Y. Zhu,* University of Minnesota

Quantum-well like molecular resonances have been observed in electron transfer at a model molecule/metal interface: C6F6/Cu(111). Two photoemission measurement reveals a transient molecular anionic resonance located at 3 eV above the Fermi level. This mol ecular resonance is dispersed parallel to the surface, i.e. resonant quantum well behavior. Both the energetic position and the dispersion of this molecular resonance depend intimately on the interfacial electronic structure and the strength of molecule-s urface interaction. With increasing coverage of pre-adsorbed atomic hydrogen which weakens molecule-surface interaction, the position of molecular resonance in C6F6 increases while the effective electron mass decreases. We conclude that the resonant molecular quantum well is confined to the interface and is a result of both molecule-molecule and molecule-surface interaction.

4:20pm **SS3-WeA8 Dynamics of Photo Excited Carrier Trapping and Recombination at Si(111) Interfaces Probed By Time-Resolved Second Harmonic Generation*, D. Bodlaki*,** *E. Borguet,* University of Pittsburgh

Carrier trapping and recombination is the primary fate of conduction band electrons. Interfaces are known to play an important role in these processes. However, probing the interface is challenging as the interface represents but a small fraction of the total number of atoms in a macroscopic sample. Distinguishing between photoprocesses due to surface states and those from excitation of states in the bulk, resulting from crystal impurities or defects, is difficult especially if one is monitoring a bulk property such as photocurrent. Second Harmonic Generation (SHG) is known to be a versatile in-situ, real time probe of buried interfaces. In this study SHG was used to probe carrier relaxation at various Si interfaces and to asses the passivating nature of the surface. Carriers were created by optical excitation via an interband transition induced by an 800 nm, 4 psec pump pulse. Subsequently, the nonlinear optical response of the interface was probed by SHG of 800 nm light. The SHG dynamics depend strongly on the surface chemistry. Native oxide covered surfaces exhibit an initial increase in SHG response followed by a linear decay on a nanosecond timescale. Surface modification changes the dynamics. RCA cleaned, oxide covered samples also show an initial increase in SHG response, but the subsequent decay appears slower. H terminated surfaces show distinctively different behavior: initially the SHG signal decreases then recovers faster then the oxide covered silicon. The different dynamics probably reflect the degree of interface passivation. Defect sites deplete the conduction band carrier population by trapping or recombination.

4:40pm **SS3-WeA9 Surface Femtochemistry: Observing and Controling Adsorbate Motion on Metal Surfaces on Femtosecond Time Scale*, H. Petek,*** University of Pittsburgh **INVITED**

Electronic and nuclear dynamics of alkali atoms adsorbed on noble metal surfaces are investigated in real time by the interferometric time-resolved two-photon photoemission technique.@footnote 1@ Photoinduced charge transfer with a <20 fs laser pulse turns on repulsive Coulomb force between alkali atoms and the substrate, thereby initiating desorption from the surface. The resulting nuclear wave packet motion is detected through changes in the surface electronic structure. In the extreme case of Cs/Cu(111), the alkali atom desorptive motion can be observed for up to 200 fs, which according to a Newton's law model corresponds to stretching of the Cu-Cs bond by ~0.3 Å.@footnote 2@ Furthermore, the coherent polarization created by the charge-transfer excitation persists for up to 60 fs. Demonstration of quantum control, whereby it is possible to generate displaced ground and excited state wave packets, is accomplished by interference between the pump and probe excited polarization in the sample.@footnote 3@ However, the photodesorption process is frustrated by the wave packet spreading and decay through recoil-induced phonon generation, reverse charge transfer, and electron inelastic scattering, which induce the phase and energy relaxation.@footnote 4@ Prospects of controlling the electronic and nuclear motion of atoms and molecules at surfaces will be discussed. @FootnoteText@ @footnote 1@S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. Lett. 82, 1931 (1999). @footnote 2@H. Petek, H. Nagano, M. J. Weida, and S. Ogawa, Science 288, 1402 (2000). @footnote 3@H. Petek, M. J. Weida, H. Nagano, and S. Ogawa, J. Phys. Chem. A 104, 10234 (2000). @footnote 4@H. Petek, H. Nagano, M. J. Weida, and S. Ogawa, J. Phys. Chem. (Feature Article; in press). .

Applied Surface Analysis
Room 134 - Session AS-ThM

Oxides and Oxidation

Moderators: D.R. Baer, Pacific Northwest National Laboratory, J. Haber, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences

9:00am **AS-ThM3 Atomic Oxygen Irradiation of Polymers: Ground Simulation of LEO Environment***, **G. Lempert**, R. Intrater, I. Gouzman, E. Grossman, Y. Lifshitz,* Soreq NRC, Israel*; A. Hoffman,* Technion Haifa, Israel

External surfaces of spacecraft in low earth orbit (LEO) are exposed to the various constituents of the space environment, including atomic oxygen (AO) and solar UV radiation, which often compromise the material properties. Material degradation by LEO atomic oxygen is simulated in a variety of experimental facilities, each with their respective limitations. RF oxygen plasma is a widely used facility for screening materials for LEO application. In addition to the neutral oxygen atoms, the plasma generates electrons and ions as well as vacuum ultraviolet (VUV) radiation, which may also contribute, either directly or synergistically, to degradation of materials. In the present study, direct and synergistic degradation effects on polymers were investigated by exposing the polymers to various combinations of the different species and the VUV emanating from an RF oxygen plasma. The different exposure conditions, including AO alone, AO+VUV, AO+e@super -@+O@super +@+VUV, AO+e@super -@+VUV, AO+O@super +@+VUV, were separated downstream beyond the RF reactor exit. The samples were characterized by mass loss measurements, changes in surface composition, by XPS, and ATR-FTIR spectroscopy, and changes in surface morphology by AFM. The polymer samples investigated were, Kapton, fluorocarbons such as Teflon FEP, Tefzel and Tedlar, having different C/F ratios, and polyethylene. Fluorine containing polymers were confirmed to be more resistant to AO alone than hydrocarbons. However, fluorocarbon polymers, sensitive to VUV radiation, showed synergistic degradation effects and higher erosion yield under AO+VUV irradiations. The effect may be interpreted by VUV radiation induced scissioning, thereby facilitating the material erosion under AO attack. The results presented demonstrate the synergistic effects on the degradation of different polymer materials and elucidate the limitations of the validity of the common RF plasma for screening materials for LEO applications.

9:20am **AS-ThM4 Surface Oxidation on Pure Liquid InSn Alloy***, **M. Jenko**,* Institute of Metals and Technology, Slovenia

Fluxless vacuum soldering is widely used for hermetical encapsulation of image intensifier tubes and recently for miniature channel photomultiplier. Extremely clean surfaces are required to obtain good wetting at soldering process of this sophisticated sealing technique. An ultra thin oxide film, covering the liquid solder, can often cause leakage of fluxless soldering seals. The model study of pure indium oxidation in the temperature range from 20 to 400°C in a vacuum at 5x10@super -5@ mbar oxygen pressure was performed using in situ AES measurements. The formation of In@sub 2@O@sub 3@ in the temperature range from 20 to 360°C was established. At temperatures higher than 360°C isothermal dissociation of ultra thin In@sub 2@O@sub 3@ film on liquid In surface was found. We also studied the initial phases of surface oxidation on pure liquid InSn alloy (20at.% In, 80at.% Sn). The surface of liquid solder was exposed to pure oxygen at 250°C. On oxidized InSn surface (1,5 x 10 @super 5@L) only In@sub 2@O@sub 3@ was found. Thermodynamic calculations showed that a mixture of SnO, SnO and In@sub 2@O@sub 3@ was formed at these conditions. The mixed oxides appeared to be thermodynamic unstable near the alloy-oxide interface. The only stable oxide formed on the surface of liquid InSn alloy was found to be pure In@sub 2@O@sub 3@ at the temperatures of 250 ° and below 360°C. At higher temperatures (higher than 360°C) isothermal dissociation of ultra thin In@sub 2@O@sub 3@ on liquid InSn surface following by the process In@sub 2@O@sub 3@ (s)+ 4 In(l)= 3 In@sub 2@O (g) was established too.

9:40am **AS-ThM5 Oxidation of Scandium Layers on Tungsten***, **A. Shih**, J.E. Yater, C. Hor, R. Abrams,* Naval Research Laboratory

Scandate cathodes have demonstrated an emission density as high as 400A/cm@super 2@ at 1300 K. In order to develop a reliable fabrication technique for scandate cathodes, a thorough understanding of the surface chemistry involving Sc, Ba, O and W is essential. An initial approach is to investigate the interaction among the elements in subsets separately. In this study, Sc on W is studied by AES and TPD. The study reveals three states of Sc adsorption on W that originate from the first-, second- and multi ple-layer. It is desirable to incorporate metallic Sc in the fabrication because its high mobility is conducive to coating uniformity and to Sc replenishment. However, can metallic Sc survive the cathode activation process, which takes a few hours at 1500 K? The desorption-rate equation for the multiple-layer state has been determined as a function of the substrate temperature. At 1500 K, the evaporation rate is 40 µm/hour. Oxidation increases the binding energy of Sc. At 1500 K the evaporation rate of oxidized Sc is less than 0.04 layers/hour. Consequently Sc in the scandate coating should be in an oxidized form. We studied the oxidation process of Sc films and found that at room temperature oxygen has a very limited diffusion length in Sc films. In a 13-layer film after an exposure of 2000 L, 7 layers of Sc remains unoxidized. However, an elevated substrate temperature accelerates the oxidation process. For a 13-layer film, 3 layers and 1.5 layers of Sc remain un-oxidized after an oxygen exposure 48 L at substrate temperatures of 520K and 720K, respectively. This underlies the need of a thermal treatment of a scandate cathode in an oxidizing environment before activation.

10:00am **AS-ThM6 Mechanism of the Activation of Mg@sub 2@Ni for Hydrogen Up-Take by Surface Treatment With Liquid Water and Water Vapor***, **J.K. Lomness**, L.A. Giannuzzi, M.D. Hampton,* University of Central Florida

Magnesium nickel alloy (Mg@sub 2@Ni) has been considered an excellent hydrogen storage medium because it has a high hydrogen capacity, forms a very stable hydride, is inexpensive, and it presents no environmental hazards. One of the major problems associated with the use of magnesium nickel alloy for hydrogen storage is its activation for initial hydrogen uptake. Traditionally, high temperatures and high pressures are needed for initial activation of this alloy. It has been discovered that treatment of Mg@sub 2@Ni with liquid water and water vapor activates the alloy for hydrogen uptake. The purpose of this paper is to present results obtained from the surface modification of Mg@sub 2@Ni with liquid water and water vapor. The data obtained suggest the presence of a hydroxide on the surface. It is believed that this is the first report of the presence of hydroxides on the surface of an active hydrogen storage alloy. Data obtained from x-ray photoelectron spectroscopy and transmission electron microscopy will be presented.

10:20am **AS-ThM7 The Interaction of Organic Molecules with Oxidised Metal Surfaces: Studies by High Resolution XPS and ToF-SIMS***, J.F. Watts,*** University of Surrey, UK **INVITED**

The interaction of organic molecules with oxide surfaces is important in many areas of endeavor. At the University of Surrey we have been concerned with this phenomenon for more than two decades, and special emphasis has been applied in the arena of adhesion and adhesive bonding. Our work in this area has been concerned, predominantly, with adsorption from the liquid phase, and it will be shown that XPS and SIMS are ideally suited to the study of adsorption characteristics of such systems. This paper will review fundamental studies that have been undertaken with a view to providing guidelines that can be used in studies of organics on oxide surfaces in other spheres of interest. There are two basic parameters that must be addressed if we are to start to develop a model of the manner of interaction of an organic molecule with an oxide surface. The first is the capacity of the solid surface for the adsorbing molecule, the second is the nature of the bond that is formed between adsorbate and substrate. If the concern is of the behavior of very small amounts of adsorbing species, (up to a few monolayers, for example), there is also the concern regarding the conformation of the molecules and the degree of order in the adsorbed layer. In more complex situations the interest will be in the phenomenon of competitive adsorption where the adsorbing solution contains not one, but many potential adsorbates. Adsorption characteristics of substrates are readily deduced by the construction of adsorption isotherms based on XPS or ToF-SIMS data. In essence, once kinetic equilibrium has been found for a particular system, a series of measurements are made on the adsorption of organic molecules, from solution of various concentrations. The uptake curve, in the case of chemisorption, takes the form of a classical adsorption isotherm, and may be treated by procedures that reflect adsorption in accord with Langmuir, Temkin or other model as appropriate.

11:00am **AS-ThM9 Characterization of Rhenium Oxide Using ESCA***, **B. Panda**,* National Aeronautics and Space Administration

High melting point and inherent ductility (toughness) over a wide range of temperature has made Rhenium an engineering material of choice for several thrust chambers in propulsion systems. Although the material remains tough at high temperatures, it still can transform to several oxides. As many as eight different oxides have been reported in literature.@footnote 1,2@ When characterized using ESCA (Electron Spectroscopy for Chemical Analysis) these oxides show large shifts in the

Re 4f line positions. While this unique property could be used as a tool for oxide characterization, literature indicates that only a few of these oxides have been characterized.@footnote 3@ Current work focuses on characterizing oxides of Rhenium using ESCA. Spectral line (Re 4f) shifts have been measured for various oxides and the results have been compared with the line positions of real-time oxidation products from space hardware. @FootnoteText@ @footnote 1@ Druce,J. G. F. in "Rhenium", Cambridge, At The University Press, 1948,pp.29-35 @footnote 2@ Lebedev, K. B. in "The Chemistry of Rhenium", Translated by Ronson, L. and Woolf, A. A., Butterworths, London, 1962, pp. 13 -17. @footnote 3@ Broclawik, E., Haber, J., and Ungier, L. in "Electronic Structure of Rhenium Oxides" J. of Physics and Chemistry of Solids, Vol. 42, 1981, pp. 203 -208.

Biomaterials
Room 102 - Session BI-ThM
Protein Surface Interaction

Moderator: B.D. Ratner, University of Washington

8:20am **BI-ThM1 Physicochemical Properties of Polysaccharide Coatings as Determinants of Protein Adsorption***, P.G. Hartley,* CSIRO Molecular Science, Australia*; **S.L. McArthur,*** University of Washington*; K.M. McLean,* CSIRO Molecular Science, Australia*; S. Oiseth,* Chalmers University of Technology, Sweden*; G. Johnson, H.J. Griesser,* CSIRO Molecular Science, Australia **INVITED**

The use of protein resistant coatings has long been seen as a means of controlling the biological response to implanted materials. Whilst many such surfaces have been produced, the properties which give rise to their protein resistant character are often poorly elucidated. Polysaccharides have been frequently employed as surface modification agents in the biomaterials area by virtue of their ready availability and apparent protein repellancy. The ability to chemically derivatize polysaccharides is a further key feature which suits them to studies of the relationship between surface chemistry and protein adsorption. In our studies we have utilized this ability to produce a range of derivatized dextran coatings with variable physico-chemical properties. These properties have been characterized in detail using both aqueous and high vacuum surface analytical techniques. These results have then been correlated with the protein adsorption behaviour of the surfaces. The results highlight the interplay between surface charge and steric interactions in determining the protein selectivity and/or repellency of the polysaccharide surfaces. In addition, we have further correlated the surface properties with biological responses using in vitro cell adhesion and growth studies. These studies demonstrate that control over cellular responses may be achieved to a large extent by the manipulation of non-specific interactions between polysaccharide surfaces and extracellular matrix proteins.

9:00am **BI-ThM3 Effect of Adsorbate Alkyl Chain Length and Terminal Group Chemistry on the Adsorption of Fibronectin and Albumin on Self-assembled Monolayers***, **C.M.-J. Fauroux,** C.C. Dupont-Gillain, R.W. Manning,* UMIST, U.K.*; G.J. Leggett,* UMIST, U.K., UK

Recent studies of the responses of mammalian cells to self-assembled monolayers (SAMs) have provided important insights into the relationship between surface chemical structure and cell attachment to artificial surfaces. Our hypothesis is that a mechanistic explanation of the correlations we have observed depends upon a detailed knowledge of the composition of the protein layer that coats the SAM prior to cell attachment and the conformations of the molecules of which it is composed. Of particular importance are fibronectin (fn), which interacts with membrane receptors (integrins) involved in cell attachment, and albumin (alb), the must abundant component of serum but thought to inhibit attachment. We have studied the adsorption of these proteins onto a range of SAMs to determine whether there is a correlation between the results of our earlier studies and the kinetics of adsorption of these proteins. The kinetics of adsorption of single proteins (human alb and human fn) have been studied for methyl, hydroxyl and carboxylic acid terminated SAMs with short and long alkyl chains. Two complementary techniques have been used. Using @super 3@H-radiolabelling, the mass of adsorbed molecules per unit area may be determined. Measurement of the amide band intensity in Fourier transform infra-red spectroscopy (FTIR) also provides a measure of the amount of adsorbed protein. Data obtained by the two methods have been found to be in close agreement. It has been found that more alb adsorbed to methyl terminated SAMs than to carboxylic acid terminated SAMs, while the smallest amounts of adsorbed protein were observed for the hydroxyl terminated surfaces.

9:20am **BI-ThM4 Deformation of Proteins Adsorbed on Glass Surfaces as Characterized by XAS***, **H.E. Canavan,*** George Washington University*; J.J. Hickman,* Clemson University*; W.E. O'Grady,* U.S. Naval Research Laboratory*; D.E. Ramaker,* George Washington University

The interaction of proteins with artificial surfaces is of interest to many in the fields of medicine, biotechnology, and surface science. It is known that certain proteins experience considerable conformational deformation upon adsorption onto surfaces. In contrast, some proteins are described as colloidal or "hard," and experience little if any deformation upon adsorption. In the work presented here, the biomolecular interaction is characterized by X-Ray Absorption Spectroscopy (XAS). Sulfur K-edge XAS will be used to analyze the S-S, S-C and S-O bonds to monitor the extent to which the sulfur bond character is changed in both "hard" and "soft" proteins such as BSA, lysozyme, and cytochrome C upon their adsorption onto a glass surface. In addition, X-ray Photoelectron Spectroscopy (XPS) is used to characterize the glass surfaces both prior and subsequent to protein deposition.

10:00am **BI-ThM6 Reversible Adsorption/Desorption of Proteins from a Thermally Switching Polymer Monolayer***, **D.L. Huber,** M.A. Samara, B.C. Bunker, R.A. Manginell, C.M. Matzke, G. Dulleck,* Sandia National Laboratories

The phase transitions of poly(N-isopropyl acrylamide) (poly NIPAM) hydrogels have been studied extensively for a number of years. We have investigated the thermal transitions of the linear polymer bound to silicon oxide surfaces. The poly NIPAM monolayers are grown from a self assembled monolayer of free radical initiators, and their properties towards protein adsorption are studied as a function of temperature using IR and UV-visible spectroscopies, as well as ellipsometry and fluorescence microscopy. At room temperature, the monolayers are swollen with water and are extremely resistant to protein adhesion, but at elevated temperatures (above 35C) the polymer collapses and expels a large portion of the water. The collapsed polymer monolayers are capable of quickly adsorbing a protein monolayer. The layer of adsorbed protein can be completely desorbed by cooling the polymer to below its transition temperature. A well prepared monolayer has been shown to be capable of repeated adsorption and desorption cycles with no degradation of the effect. Poly NIPAM monolayers have been grown onto a microchip based platform containing micron scale resistive heaters capable of precisely controlling the surface temperature, and the adsorption and desorption of fluorescently labelled proteins monitored using flurorescence microscopy. Possible applications of on chip structures, as well as the adsorption/desorption kinetics will be discussed.

10:40am **BI-ThM8 Polyelectrolyte Multilayers : A New Tool to Design Targeted Biofilms***, **P. Schaaf,*** Institut Charles Sadron / Universite Louis Pasteur Strasbourg, France*; L. Szyk,* Unite INSERM U424 Strasbourg, France*; B. Tinland,* Institut Charles Sadron (CNRS) Strasbourg, France*; F. Cuisinier, P. Schwinte, J.C. Voegel,* Unite INSERM U424 Strasbourg, France

The alternate deposition of polycations and polyanions on a solid surface allows to build a polyelectrolyte multilayer film. This method whose driving force is the charge overcompensation at each adsorption step, offers a simple and elegand way to design new types of films with applications ranging from non linear optics to nanoreactors. The buildup procedure also offers the possibility to develop new bioactive films with multiple functionalities. One can, for example, easily embed proteins into these films. We will present results relative to this later aspect and in particular to the structure and the diffusion of proteins embedded in multilayers. It will be shown that proteins embedded in multilayers are not irreversibly fixed but can diffuse along the film. The diffusion coefficient depends upon the polyelectrolytes in contact with the protein. Such films seem also to preserve the secondary structure of the adsorbed and embedded proteins an even to enhance their thermal stability. Polyelectrolyte multilayers appear also to inhibit the formation of intermolecular beta-sheets frequently observed during the heating of protein solutions. Some new perspectives of these films for the coating of biomaterials will finally be presented.

11:00am **BI-ThM9 Design of Bioadhesive Polymers for Use at Mucosal Interfaces***, **A. Hoffman,*** University of Washington **INVITED**

Mucosal surfaces of the body include "wet" surfaces such as the eye, nose, mouth, GI-tract, vagina and lungs. They represent a large surface area of the body and thus may be an attractive route for delivery of drugs. When a drug formulation is applied to those surfaces, it may resist being washed away due to a combination of its own viscosity plus its intermolecular interactions with the mucous polymer coating. Two typical bioadhesive polymers that have been most often applied for mucosal drug delivery are polyacrylic acid and chitosan. This talk will describe drug delivery formulations containing PAA or chitosan or their derivatives that may provide better control over drug release rate and duration.

11:40am **BI-ThM11 The Role of Protein-surface Interactions in Implanted Joints***, M.R. Widmer, M. Heuberger, J. Voros,* ***N.D. Spencer,*** ETH-Zurich, Switzerland

Proteins appear to play an important role in the boundary lubrication of both natural and implanted hip and knee joints. However, the nature of the interaction of proteins in synovial fluid with the prosthetic tribosurface appears to influence the effectiveness of boundary lubrication significantly. Protein adsorption (waveguide and fluorescence experiments) and tribological (pin-on-disk) studies have been carried out on a number of polymer and model surfaces in order to determine the tribological role and nature of such interactions.

Surface Science
Room 121 - Session SS1-ThM
Quasicrystals

Moderator: M.A. van Hove, University of California, Berkeley

8:20am **SS1-ThM1 Peter Mark Memorial Award Lecture - Surface Preparation and Electronic Properties of d-AlNiCo***,* ***E. Rotenberg***[1]*,* Lawrence Berkeley National Laboratory*; W. Theis, K. Franke,* Free University, Germany*; K. Horn,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; P. Gille,* Maximilians-Universitat Munich, Germany **INVITED**

Apart from their striking structural properties, i.e. perfect long range order without translational symmetry, quasicrystals exhibit fascinating physical properties unlike those of ordinary metallic alloys. As the properties of all metals are determined by the valence states near the Fermi level, we have undertaken a program to prepare clean quasicrystalline surfaces and characterize these states by angle-resolved photoemission. The samples were characterized by ESCA, xray photoelectron diffraction (XPD) and LEED. Our k-dependent photoemission intensity maps from the tenfold and two inequivalent twofold surfaces from d-Al@sub 71.8@Ni@sub 14.8@Co@sub 13.4@ shows the existence of dispersing s-p- and d-derived valence states. We use an extension of the concept of the Brillouin zone in order to characterize the observed dispersion. Maps from all three surface orientations yield a consistent picture of free- electron-like constant energy surfaces in 3D k-space. We find the centers of these energy surfaces to be located at the positions of dominant electron diffraction spots as expected from the quasi-Brillouin zone model. Dispersion arises from delocalized quasicrystal valence states, while a large non-dispersing intensity in our spectra could be attributed to either localized states or scattering from the hierarchy of densely spaced Bragg planes in quasicrystals.

9:00am **SS1-ThM3 Structure, Morphology and Dynamics of High Symmetry AlNiCo-Surfaces***,* ***W. Theis,*** *H.R. Sharma, K. Franke, A. Riemann, S. Fölsch, K.H. Rieder,* Freie Universität Berlin, Germany*; P. Gille,* Ludwig-Maximilians-Universität München, Germany

Although many aspects of the bulk structure and dynamics of decagonal quasicrystal are well understood, knowledge regarding their surface structure is much more limited. Employing highly surface sensitive elastic He-atom scattering (HAS) and high resolution low energy electron diffraction (SPA-LEED), we have investigated 10- and 2-fold surfaces of Al@sub 71.8@Ni@sub 14.8@Co@sub 13.4@. The observed SPA-LEED and HAS diffraction patterns reveal that the top most surface layer retains the full symmetry extrapolated from the bulk. Both SPA-LEED and HAS show weak superstructure peaks. In the diffraction patterns of the 2-fold surface we observe extremely weak streaks corresponding to a 16 Å periodicity in addition to the strong peaks reflecting the main 8 Å periodicity. The spots in the odd lines of the diffraction pattern are shifted with respect to the even lines by 0.5 Å@sup -1@. He-atom scattering from the 10-fold surface reveals a low corrugation, extremely few defects, an average terrace width in the order of 100 Å, and a predominant step height of 2 Å. Low temperature (5 K) scanning tunneling microscopy (LT-STM) confirms this step morphology showing a high density of rough 2Å-steps without any tendency towards step pairing and revealing regions of two different surface termination and repeating 5-fold symmetric motives. Surface phonons of the 10-fold surface have been investigated by inelastic He-atom scattering. In experiments with cooled and heated samples and He-atom kinetic energies ranging from 8 to 35meV the (acoustic) Rayleigh mode was observed. Strong single phonon signatures are limited to wavevectors q < 0.5 Å@sup -1@ and the phonon linewidths are resolution limited up to q = 0.25 Å@sup -1@, beyond which they increase rapidly, similar to the behavior recently observed in the corresponding bulk phonons. @footnote 1@ @FootnoteText@ @footnote 1@ F. Dugain, et al, Eur. Phys. J. B. 7, 513 (1999).

9:20am **SS1-ThM4 Tribological Properties of Quasicrystals and Quasicrystal Approximants***,* ***C. Mancinelli,*** Carnegie Mellon University*; J.S. Ko,* Merck & Co.*; A.J. Gellman,* Carnegie Mellon University

An experimental comparison has been made between the properties of the surfaces of an Al@sub70@Pd@sub 21@Mn@sub 9@ quasicrystal and its Al@sub 48@Pd@sub 42@Mn@sub 10@ approximant. This investigation has attempted to identify connections between the quasicrystalline structure and bulk properties. The Al@sub70@Pd@sub 21@Mn@sub 9@ sample was a single grain icosahedral quasicrystal cut to expose its five-fold symmetric (000001) surface. The approximant was polycrystalline @beta@-phase Al@sub70@Pd@sub 42@Mn@sub 10@, which has a CsCl-type cubic structure. Surfaces of both were prepared under ultra-high vacuum (UHV) conditions and then used for comparative measurements of their frictional properties and oxidation rates. The aluminum based quasicrystals and their approximants are oxidized by reaction with O@sub 2@ to form a thin film of aluminum oxide that ultimately passivates their surfaces. The oxidation process was studied using Auger Electron Spectroscopy to measure the oxide film thickness following controlled exposures to both O@sub 2@ and H@sub 2@O. The interesting difference between the two samples is that the rate of oxidation of the approximant is significantly higher than that of the quasicrystal in spite of the fact that the bulk Al concentration of the approximant is lower than that of the quasicrystal. Friction measurements were made under UHV conditions between pairs of quasicrystals and pairs of approximants whose surfaces were either clean or oxidized to varying degrees. The friction measurements were made between pairs of clean surfaces and between pairs of surfaces exposed to controlled oxidation. The friction between pairs of the approximant surfaces is roughly twice that measured between the quasicrystal surfaces under all conditions of surface oxidation. The results of this work do suggest that there is a direction connection between the quasicrystalline structure and low friction.

9:40am **SS1-ThM5 Surface Properties of Quasicrystals***,* ***P.A. Thiel,*** Iowa State University **INVITED**

There has been a systematic progression of knowledge, over the past 10 years, concerning the atomic arrangements and compositions at surfaces of bulk quasicrystals. Our group has been particularly involved in studying surfaces of the icosahedral aluminum-rich phases, both in ultrahigh vacuum and in air. The understanding of the surface structure of these materials is currently at a point where, we believe, it can be used as a springboard toward understanding more complex phenomena. Following a review of the picture that has evolved for the native surfaces in vacuum and in air, we will discuss more recent results for friction, wetting, and epitaxy.

10:20am **SS1-ThM7 Auger Spectroscopy and the Electronic Structure of Quasicrystals***,* ***V. Fournèe,*** *J.W. Anderegg, A.R. Ross, T.A. Lograsso, P.A. Thiel,* Iowa State University

So far, the electronic structure of QC has been probed primarily by photoelectron and x-ray spectroscopies. These studies mainly focussed on the existence of a structure induced minimum of the density of states located at the Fermi level, the so-called pseudogap. Auger spectroscopy, on the other hand, can yield unique insight into important aspects of the electronic structure of alloys such as screening and electron correlation effects. Here we will present our experimental work on the transition metals LMM Auger lines in several quasicrystalline phases, the Al-Pd-Mn and Al-Cu-Fe icosahedral QCs and the Al-Ni-Co decagonal QC. This include the core-core-valence and the core-valence-valence Auger spectra. From the line shape, line splitting and energies of the Auger spectra, it is possible to derive empirical parameters correlated with the extent of quasiatomic or bandlike behavior, which depends on the relationship between the local DOS and the value of the on-site correlation energy. Our first results in the i-Al-Pd-Mn clearly shows that the Mn-L3M45M45 has a bandlike behavior and reflects the self-convolution of the Mn-3d valence band. The width of the Mn-3d band is quite narrow in the QC, as compared to pure Mn. We also found a decrease of the 3d-containing Auger transition rates in the QC relative to the metal. This could be due to an increased localization of the

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[1] **Peter Mark Memorial Award Winner**

3d states in the quasicrystals, that will lower the probability for a 3d electron to fill a 2p photohole. This is consistent with the reduction of the intrinsic width of the Mn 2p3/2 core level observed by photoemission spectroscopy.

10:40am **SS1-ThM8 Nucleation and Growth of Al and Ag Thin Films on Five-fold Surface of Icosahedral Quasicrystals***, **T. Cai**, V. Fournee, T.A. Lograsso, A.R. Ross, P.A. Thiel,* Iowa State University

Aluminium and silver are deposited on the five-fold surface of icosahedral Al-Cu-Fe and Al-Pd-Mn quasicrystals. The nucleation and growth of thin metal films on quasicrystalline surface are studied using scanning tunnelling microscopy. Our first results on Al films deposited on Al-Cu-Fe show that, at low coverage, Al atoms form pentagonal stars, all adopting the same orientation, though with no evidence of order between the Al pentagonal stars. As Al coverage is increased, but still within the submonolayer regime, the density of Al pentagonal stars increases. The five-fold symmetry of the quasicrystalline substrate is responsible for arranging deposited atoms with a local five-fold symmetry, which is incompatible with the translation periodicity of the cubic lattice of the individual elements. With scanning tunnelling microscope, we expect to observe directly the transition from a pentagonal symmetry to the face-centred cubic symmetry as the metallic film develops on the quasicrystalline surface.

11:00am **SS1-ThM9 Accessing the Role of Net Planes in Decagonal Al-Ni-Co**, ***C.J. Jenks**, J. Bjergaard, P.A. Thiel, P. Canfield,* Iowa State University*; A. Cervellino, W. Steurer,* ETH-Zurich, Switzerland

Net planes linking the periodic and quasiperiodic directions in decagonal Al-Ni-Co are discussed. These net planes are thought to play a critical role in the stability and growth of decagonal quasicrystals. To explore their potential roles we have studied single grain surfaces of decagonal Al-Ni-Co. We have used surface analytical techniques to study surface morphology which sheds light on the structural stability of these planes.

Surface Science
Room 122 - Session SS2-ThM

Electronic Structure II

Moderator: H. Petek, University of Pittsburgh

8:40am **SS2-ThM2 Fermi Surface Evolution of Ag(111) Films Grown onto Si(111) Surfaces***, V. Perez-Dieste,* LURE, France*; J.F. Sanchez-Royo,* LURE and ICMUV, France*; J. Avila,* LURE and ICMM, France*; M. Izquierdo, L. Roca, A. Tejeda,* LURE, France*;* ***M.C. Asensio,*** LURE and ICMM, France

Growth of metal films on semiconductor substrates has been the subject of extensive experimental and theoretical studies over the last decades. The determination of the metallization onset at the semiconductor interfaces and the obtention of thin single-crystal metal films, only a few atomic layers thick with atomically flat surfaces, are important goals because of their consequences on the manufacture of integrated circuits and nanosized devices. In this work, we investigate the epitaxial growth of silver overlayers on reconstructed Si(111) surfaces studied by LEED and Photoelectron Diffraction (PhD). The electronic properties of these films have been investigated by high energy resolution Angle-Resolved Photoemission (ARPES) with a synchrotron radiation source. Particular attention has been paid to the determination, by ARPES, of the spectral weight at the Fermi level along large extensions of the reciprocal space of the investigated films, from which the Fermi surface (FS) can be extracted. The evolution of the FS and the valence-band structure as a function of the silver coverage could be measured at several metal coverages. In the submonolayer regime, very localized interface-derived spectral features dominate the density of states at the Fermi level, whereas in the intermediate regime, a complex mixture of states from both the interface and the metallic silver film defines the incipient FS contours. A well defined bulk-like silver FS could be identified already at interfaces of a few Ag monolayers. However, the symmetry of these bulk-like FS contours showed sixfold symmetry rather than the threefold symmetry, characteristic of a Ag(111) single crystal. By PhD, it has been demonstrated that is due to the existence of two domains rotated 60Âº silver metallic overlayers.

9:00am **SS2-ThM3 Ultrathin Epitaxial Mg Films on Si(111): Quantum Size Effects***, L. Aballe,* ***C. Rogero****, K. Horn,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

We demonstrate, using angle-resolved photoelectron spectroscopy and LEED, that highly perfect ultrathin epitaxial Mg(0001) films can be grown on Si(111) using low temperature deposition and annealing. This is in contrast to films grown at room temperature which present an interfacial silicide and subsequent growth of a disordered Mg metallic film. The wave-vector dependent electronic structure of the well-ordered films is investigated in detail with photoelectron spectroscopy, as a function of overlayer thickness. The spectra exhibit a number of thickness-dependent discrete peaks in the region of the magnesium s-p band for films up to 40 monolayers thick. These are caused by electron confinement within the Mg overlayer, and can be identified as quantum well resonances derived from the magnesium s-p band. These quantum well resonances (QWR) are interpreted in terms of the phase-accumulation model, and the Mg band structure is found to account for all the main features in the spectra. An estimation of the decay length of the Mg(0001) surface state wave function is obtained from its dependence of binding energy on film thickness. The in-plane dispersion of the QWR for films of different thicknesses is measured and analyzed along the surface Brillouin zone. The data point to a strain-driven thickness-dependent structural transition at a critical thickness of about 20 Mg monolayers. The dependence of spectral intensity on photon energy in the range of the Mg bulk and multipole plasmon energies demonstrates the effect of field enhancement in the Mg film.

9:20am **SS2-ThM4 Resonant Photoemission Investigation of the Electronic Structure of Plutonium***, **J.G. Tobin**, D.A. Arena,* Lawrence Livermore National Laboratory*; J. Terry, R.K. Schulze, J.D. Farr, T. Zocco,* Los Alamos National Laboratory*; K. Heinzelman, E. Rotenberg, D. Shuh,* Lawrence Berkeley National Laboratory*; G. van der Laan,* Daresbury Lab, UK

The valence electronic structures of the actinide metals and alloys in general and plutonium (Pu) in particular remain mired in controversy. Interestingly, the various phases of Pu metal provide a mirocosm of the metallic actinides as a whole. Thus, unravelling the nuances of the interplay of electronic and geometric structures in Pu will illuminate the properties of all transuranic metals. In a sense, the behavior of the Pu 5f electrons is completely counter-intuitive. The dense phase, a, has some semblance of delocalization in the 5f valence bands and can be treated theoretically within single electron models such as the Local Density Approximation (LDA). The a phase is monoclinic, which is a low symmetry ordering. The less dense d-phase is fcc and exhibits evidence of localized and/or correlated electronic behavior. Experimental Resonant Photoemission (ResPes) results for a- Pu and d- Pu bulk samples will be presented and compared to the results of an atomic model calculation. Both Pu samples exhibit limited agreement with the atomic model calculations. As expected, a- Pu appears to have more 5f valence band delocalization than d-Pu. Evidence of an enhanced sensitivity to surface corruption, by using synchrotron radiation as the excitation, will be presented. This work was performed under the auspices of the U.S Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. Los Alamos National Laboratory is operated by the University of California under Contract No. W-7405- ENG-36. Experiments were carried out at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source, built and supported by the U.S. Department of Energy. The Advanced Light Source and DKS are supported by the Director, Office of Science, Office of Basic Energy Sciences, Matl. and Chem. Sciences Divisions, of the U.S. DOE under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

9:40am **SS2-ThM5 Visualization of the Electronic Structure of Metal Surfaces with Scanning Tunneling Spectroscopy***, **J.I. Pascual**,* Fritz-Haber-Institut der Max-Planck Gesellschaft, Germany*; Z. Song,* Dalian Institute of Chemical Physics. China*; J.J. Jackiw,* Pennsylvania State University*; M. Hansmann, G. Ceballos, H. Conrad, K. Horn, H.-P. Rust,* Fritz-Haber-Institut der Max-Planck Gesellschaft, Germany

In this presentation we analyze the electronic structure of several metal surfaces with an in-creasing level of complexity: from the (111) sur-faces of noble metals, with isotropic s-p states, to anisotropic alloy surfaces like NiAl(110), where the influence of Ni d-states dominates its elec-tronic structure in the proximity of the Fermi level. The measurements are done in a low temperature scanning tunneling microscope, where the energy resolution and stability are greatly improved. The spatial dependence of the differential tunnel con-ductance in the proximity of scattering potentials like defect sites or step edges offers a direct way to access structural information on the electronic states of the surface. There, the electron wave phase is fixed at the defect position, producing oscillations in the spatial shape of the density of states in the defect vicinity. The wavelength of these oscillations in real space can be easily transformed to reciprocal space information by means of a Fourier transformation.@footnote 1@ We are going to show the capabilities of this transformation by analyzing surface states on both, the isotropic and anisotropic surface states. Band gap edges also may produce oscillations in the density of states, and therefore, are also ac-cessible. By measuring the differential conduc-tance in a large range of energies we reconstruct the states' topology in the reciprocal space. The energy range is not limited to the proximity of the Fermi energy: we probe states up to the vacuum level. Above this point we also resolve information about the surface density of states by analyzing the shape of the field emission resonances. . @FootnoteText@@footnote 1@L. Petersen et al. Phys. Rev. B 57, R5868 (1998).

10:00am **SS2-ThM6 Temperature-Dependent Fermi Gap Opening in the c(6X4)-C@sub 60@/Ag(100) Two-Dimensional Superstructure***, M. Sancrotti, C. Cepek, I. Vobornik,* Laboratorio Nazionale TASC-INFM, Italy*; A. Goldoni,* Sincrotrone Trieste, Italy*; E. Magnano,* Laboratorio Nazionale TASC-INFM, Italy*; G. Selvaggi,* Universita' di Modena, Italy*; J. Kröger,* Zürich Universität, Switzerland*; G. Panaccione, G. Rossi,* Laboratorio Nazionale TASC-INFM, Italy

The interest in fullerene-based films, their surfaces, and related low-dimensional systems has been recently renewed for example by the discovery that superconductivity persists at surfaces of A@sub 3@C@sub 60@ films@footnote 1@ and by the possibility of achieving a critical temperature as high as 52 K in hole-doped C@sub 60@ single crystals.@footnote 2@ The possibility of controlling at a fine scale the charge state of single C@sub 60@ molecules and the buckyball-buckyball distance makes the fullerene-based films extremely charming for a wide range of applications. In addition, chemical and physical properties of low-dimensional C@sub 60@-based layers may be considered superior to the bulk materials, prepared by means of standard intercalation methods and plagued by the presence of multi-phases. Here we report on a high-resolution angle integrated photoemission study@footnote 3@ of one monolayer of C@sub 60@ chemisorbed on Ag(100). The results show the reversible opening of a gap at the Fermi level at temperatures 25 @<=@ T @<=@ 300 K. The gap reaches a maximum value of 10 meV at T @<=@ 70 K. This finding is a first evidence of an electronic phase transition in C@sub 60@ monolayers and has implications on the ongoing debate about surface superconductivity in C@sub 60@-based bulk materials. @FootnoteText@ @footnote 1@ R. Hesper, L.H. Tjeng, A. Heeres, and G.A. Sawatzky, Phys. Rev. Lett. 85 (2000) 1970 @footnote 2@ J.H. Schön, Ch. Kloc, R.C. Haddon, and B. Batlogg, Science 288 (2000) 656 @footnote 3@ C. Cepek, I. Vobornik, A. Goldoni, E. Magnano, G. Selvaggi, J. Kröger, G. Panaccione, G. Rossi, and M. Sancrotti, Phys. Rev. Lett. 86 (2001) 3100

10:20am **SS2-ThM7 Electronic Transport through Surface-state Bands***, S. Hasegawa,* University of Tokyo, Japan **INVITED**

Surface states that are inherent in surface superstructures, provide unique platforms for studying low-dimensional electron systems, exhibiting some aspects of many-body effects, in phase transitions, for example. Electronic transport is a key for such physics, too. First, I present direct detections of electrical transport through the surface-state bands on silicon, by in-situ measurements in UHV with macroscopic four-point probes,@footnote 1@ microscopic ones,@footnote 2,3@ and four-tip STM.@footnote 4@ The influences of atomic steps and domain boundaries on the conductivity were directly measured. Next, I present characteristic changes in surface conductivity at a surface phase transition.@footnote 5@ A Si(111)-8x2-In surface at 100K is believed to be a charge-density-wave (CDW) phase.@footnote 6@ By adding small amounts of impurity atoms on it, the CDW phase was destroyed, accompanied with steep increases in conductivity. This means that the metalicity of the surface is recovered by this change; the impurity atoms act as electronic disturbers. @FootnoteText@ @footnote 1@ S. Hasegawa, et al., Prog. Surf. Scie. 60 (1999) 89. @footnote 2@ I. Shiraki, et al., Surf. Rev. Lett. 7 (2000) 533. @footnote 3@ C. L. Petersen, et al., Appl. Phys. Lett. 77 (2000) 3782. @footnote 4@ I. Shiraki, et al., Surf. Scie. (2001) in press. @footnote 5@ S. V. Ryjkov, et al., Surf. Scie (2001) in press. @footnote 6@ H.-W. Yeom, et al., Phys. Rev. Lett. 82 (1999) 4898.

11:00am **SS2-ThM9 Electronic Structure of the Alkali Halide-metal Interfaces: LiCl(100)/ Cu(100)***, M. Kiguchi, H. Inoue, K. Saiki, A. Koma,* The University of Tokyo, Japan

When an insulator film is prepared in the close vicinity of a metal surface, a novel phase is formed whose property may differ from the bulk one. It is suggested that the band gap is reduced for an insulating thin film on a metal substrate, due to the presence of the dielectric boundary and the overlayer reduced dimensionally. However, the large difference of chemical bond between metals and insulators makes it difficult to form a well ordered interface. The electronic structure of the insulator-metal interface has been little studied. Recently, we have succeeded in growing a single-crystalline LiCl film on Cu(100) in a layer-by-layer fashion. In the present work, we have studied the electronic structure of LiCl film on Cu(100) using EELS (electron energy loss spectroscopy) and UPS (ultraviolet photoelectron spectroscopy), as a model system of alkali halide-metal interface. The EEL spectrum(Ep=60 eV) shows clear band gap region from 0 eV to 7 eV. The band gap energy did not change for the LiCl thickness from 1 ML to 20 ML. In addition, the 61 eV loss peak observed in the EELS (Ep=200eV) did not change with the thickness. The result of EELS indicates that relative position of the conduction band to the valence band and to the Li 1s core band was unchanged. In the result of UPS, on the other hand, the valence band showed upward shift with decreasing film thickness. The results of EELS and UPS suggest the occurrence of the bend bending in ionic layers.

11:20am **SS2-ThM10 Theoretical Analysis of Field Emission from Atomically Sharp Al Tips***, Y. Gohda,* The University of Tokyo, and CREST, Japan Science and Technology Corp., Japan*; S. Watanabe,* The University of Tokyo, and CREST, Japan Science and Technology Corp.

Well-conditioned tips, which end with a single atom, are of current interest, because they produce self-collimated, coherent electron beams, total energy distribution (TED) of which can have multiple peaks (MP).@footnote 1,2@ However, the origin of the MP in TED has been controversial and thus has not been understood well: Binh et al. claimed that they had observed MP from pure W(111) surface with single-atom protrusion,@footnote 1@ while Yu et al. claimed that carburization was essential in observing MP from metal-carbide protrusions.@footnote 2@ In the present work, field emission from Al(100) surface having single-atom protrusion without any impurity is analyzed employing the method newly developed by Gohda et al.,@footnote 3@ which is based on the self-consistent density functional theory including scattering states. We have found that MP in TED of field emission current becomes remarkable as the local potential barrier in front of the topmost Al atom dissapears with increase in applied field strength. We have also clarified that the peak below the Fermi energy is attributed to localized sates at the topmost Al atom, while the peak at the Fermi energy comes from delocalized states. @FootnoteText@ @footnote 1@ V. T. Binh et al., Phys. Rev. Lett. 69, 2527 (1992). @footnote 2@ M. L. Yu et al., Phys. Rev. Lett. 77, 1636 (1996). @footnote 3@ Y. Gohda et al., Phys. Rev. Lett. 85, 1750 (2000).

Surface Science
Room 121 - Session SS1-ThA
Catalysis on Model Systems

Moderator: J. Wintterlin, Fritz-Haber-Institut, Germany

2:00pm **SS1-ThA1 Thin Ce@sub x@Zr@sub 2-x@O@sub 2@(111) Films as Model Catalytic Converter Oxygen Storage Materials*, C.H.F. Peden,*** *T. He, G.S. Herman,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology*; S. Thevuthasan, V. Shutthanandan, D. McCready, J. Szanyi,* Pacific Northwest National Laboratory

Oxygen storage (OS) materials, usually consisting of ceria (CeO@sub 2@) or modified ceria, are used in automobile catalytic converters to effectively damp deviations in the exhaust air/fuel (A/F) ratio in order to optimize the activity of the precious metal catalyst. We are using thin films of CeO@sub 2@ and ceria-zirconia (Ce@sub x@Zr@sub 2-x@O@sub 2@) as models for fundamental studies of the oxygen uptake, storage, and release properties of these materials. This presentation will emphasize the characterization (by x-ray diffraction, atomic force microscopy, reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoelectron spectroscopy (XPS) and diffraction, and Rutherford backscattering spectrometry and high-energy ion channeling) of model CeO@sub 2@ and Ce@sub x@Zr@sub 2-x@O@sub 2@ (x = 1.0, 0.9, 0.8, 0.7, and 0.6) thin films will be presented. A wide range of growth parameters using oxygen plasma-assisted molecular beam epitaxy have been used, and successful production of pure-phase, single-crystalline epitaxial oxide films has been achieved for x > 0.6. At higher Zr levels, evidence for phase-separation is observed. We will also report results of XPS and carbon monoxide temperature-programmed desorption experiments that provide evidence for markedly enhanced kinetics of oxygen storage and release upon doping of CeO@sub 2@ by Zr.

2:20pm **SS1-ThA2 Metal and Oxide Particles on Oxide Supports: Vanadium and Vanadia Deposits on Alumina*, M. Baeumer,*** *N. Magg, J.B. Giorgi, M. Frank, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Vanadium in its various oxidation states is a catalytically very interesting system. Oxide-supported vanadia deposits are, for example, used as catalysts for the selective oxidation and dehydrogenation of hydrocarbons. In order to study this multivalent system in more detail, we have carried out model catalytic studies by depositing vanadium under various conditions onto a thin alumina film grown on NiAl(110). Under UHV conditions metallic aggregates are formed. This is connected with extensive changes in the phonon spectrum of the support (intensity damping, frequency shifts and peak broadening). A comparison to other metals, such as Pd, Rh, Ir and Al, reveals that, especially in the low coverage regime, chemical effects at the particle-support interface play an important role. This is also corroborated by XPS. At high coverages, on the other hand, metallic screening seems to gain in importance. If the V deposition is carried out in an oxygen ambient, oxide particles are formed. According to photoelectron spectroscopic data, they have an average oxidation state of +3. Nevertheless, infrared spectroscopy points to the presence of vanadyl groups on the surface of the aggregates actually being a structural element of V@sub 2@O@sub 5@. For both situations, metal and oxide deposits, the CO adsorption and reaction behaviour will be discussed. IR spectra show that CO adsorption on the vanadia aggregates leads to a blue shift of the CO stretching frequency as compared to the gas phase. Interestingly, an interaction between CO and the vanadyl groups is observed. By contrast, CO adsorption on the vanadium aggregates is connected with a red shift. A comparison to the corresponding IR data of other metals (Pd, Rh, Ir)@footnote 1@ underscores the strong metal-support interaction. @FootnoteText@ @footnote 1@M. Frank and M. Baeumer, Phys. Chem. Chem. Phys. 2 (2000) 3723.

2:40pm **SS1-ThA3 Atomic-scale STM Study of Model Catalysts for Hydrodesulfurization*, J.V. Lauritsen*[1]*,*** University of Aarhus, Denmark*; S. Helveg, B.S Clausen, H. Topsoe,* Haldor Topsoe Research Laboratories, Denmark*; F. Besenbacher,* University of Aarhus, Denmark

Using scanning tunneling microscopy (STM),@footnote 1@ we have recently attained novel atomic-scale information on model catalysts for hydrodesulfurization (HDS), an area that currently receives world-wide attention due to new environmental legislations regarding the sulfur content in fuel. The HDS activity is related to MoS@sub 2@-like nanoclusters promoted with Co atoms located near the edges. Controversy has, however, prevailed since traditional spectroscopy techniques provide no conclusive information regarding the cluster morphology, catalytically relevant edge structures, active sites or promotional effect of Co. We have successfully synthesized ~30Å wide single-layer MoS@sub 2@ clusters on an inert Au(111) substrate as a model system for HDS catalysts. High resolution STM images display an unprecedented view of the atomic details of the MoS@sub 2@ nanoclusters, which contrary to expectations exhibit a triangular morphology. We have also been able to resolve the structures of the catalytically active edges, and from interplay with DFT theoretical calculations we have determined the detailed atomic-scale structure.@footnote 1,3@ The STM images reveal spectacular electronic features near the edge of the triangles, which with input from theory can be associated with electronic edge states. When the MoS@sub 2@-based catalysts are promoted with Co, the STM images directly show a morphological transition from triangular to hexagonally truncated structures. This is driven by a preference for Co to be located at only one type of MoS@sub 2@ edges.@footnote 2@ We are currently investigating the interaction with thiophene, a typical sulfur containing molecule, and preliminary STM results indicate a strong bonding of the molecules to the cluster edges. @FootnoteText@ @footnote 1@ S. Helveg, J.V. Lauritsen et al., Phys. Rev. Lett. 84, 951 (2000) @footnote 2@ J.V. Lauritsen et al. J. Catal. 197, 1 (2001) @footnote 3@ M. Bollinger, J.K. Norskov, private communication.

3:00pm **SS1-ThA4 A Temperature Programmed Desorption Study of Propene Adsorption on Gold Islands Dispersed on TiO@sub 2@(110)*, H.M. Ajo,*** University of Washington*; V.A. Bondzie,* University of California at Riverside*; C.T. Campbell,* University of Washington

The adsorption of propene on TiO@sub 2@(110) and on gold islands dispersed on TiO@sub 2@(110) [Au/TiO@sub 2@(110)], both at 120 K, has been studied using temperature programmed desorption (TPD), x-ray photoelectron spectroscopy(XPS) and low energy ion scattering spectroscopy (LEIS). Propene adsorbs on both TiO@sub 2@(110) and Au/TiO@sub 2@(110), with desorption peak temperatures of ~190 and ~240 K, respectively, for tiny doses of propene. When only 17% of the TiO@sub 2@(110) surface is covered by gold islands [17% Au/TiO@sub 2@(110)], moderate propene doses populate both the 240 and 190 K TPD peaks, in that order. Since both the dose of propene needed to saturate the 240 K peak and its peak area increase with the gold island coverage, the desorption peak at 240 K is attributed to propene adsorbed at the edges of gold islands. This feature is also seen at about this same temperature even when the gold islands are only one atom thick. Temperature-dependent LEIS results suggest that this propene binds to both a gold island edge and a titanium site. Tiny doses of propene to the 17% Au/TiO@sub 2@(110) surface give the 240 K TPD peak but no 190 K feature. This shows that all of the propene desorbs from these island edge sites. Since some propene molecules must initially physisorb on TiO@sub 2@(110) sites, but no propene molecules desorb from these sites during TPD, the propene must be mobile enough on the TiO@sub 2@(110) surface, either at the dosing temperature or during TPD, to migrate to the gold island edge before desorption (i. e., below 190 K).

3:20pm **SS1-ThA5 Atom-resolved and Nano-scale Structures and Catalyses at TiO@sub 2@ and CeO@sub 2@ Single Crystal Surfaces*, Y. Iwasawa*,** The University of Tokyo, Japan **INVITED**

This paper presents several important topics in surface catalytic chemistry. Atom-resolved and nano-scale structures of TiO@sub x@ on TiO@sub 2@(110) and (001) surfaces have been visualized by STM and NC-AFM. The surfaces and the TiO@sub x@ structures were transformed to new surface structures in a complicated manner induced by heating and adsorption. Structure models are presented. Carboxylic acids were catalytically decomposed on TiO@sub 2@(110), and the reaction sites and reaction kinetics were characterized by in-situ STM observation. Nano-structures of Pt and Au on TiO@sub 2@(110) were produced by using Pt or Au precursor complexes in different ways. A unique clear-cut size regulation of the Pt particles was found. A new mechanism is presented. Very small Au particles with 0.7 nm height were successfully formed by UV irradiation of the Au-complex adsorbed surface or by UV irradiation of TiO@sub 2@(110) before deposition of the Au complex. Very small Au particles are remarkably active for low temperature CO oxidation. Atom-resolved and cluster structures of and around oxygen defects at CeO@sub 2@(111) surface have also been imaged by NC-AFM. The oxygen defects were mobile even at room temperature. The phenomenon was entirely different from that observed with the TiO@sub 2@ surface, which may be relevant to oxygen reservoir

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

and oxidation activities of CeO@sub 2@ in automobile catalysts and oxidation catalysts. These surfaces are dynamic and reactive, depending on temperature and atmosphere, which may be relevant to the origin and mechanism of catalysis.

4:00pm **SS1-ThA7 Investigations of Size-Dependent Surface Chemistry on Metal Nanoparticles: Dimethyl Methylphosphonate Reaction on Cu/TiO@sub2@(110)***, **D.A. Chen**, J.E. Reddic, J. Zhou,* University of South Carolina

We are interested in understanding how metal nanoparticle size affects surface chemistry so that specific particle sizes with the desired reactivity can be identified for catalysis applications. Cu nanoparticles were grown on a TiO@sub 2@(110)-(1x2) surface and characterized by scanning tunneling microscopy under ultrahigh vacuum conditions. The Cu nanoparticles deposited on TiO@sub2@(110)-(1x2) exhibit the same "self-limiting" growth behavior previously observed on the unreconstructed titania surface: the particle density increases with increasing coverage while particle size is relatively constant. At all coverages, the Cu particles have a uniform size distribution, and the particle size can be controlled by annealing the surface to higher temperatures. Deposition at room temperature produces particles that are ~25 Å in diameter and ~5 Å high, while annealing to 700 K increases the particle size to an average diameter of 60-70 Å and height of 15-20 Å. We found that a smaller size regime of Cu nanoparticles can be prepared by depositing on this highly reduced titania surface compared to the more stoichiometric titania (1x1) surface. X-ray photoelectron studies of the thermal chemistry of dimethyl methylphosphonate (DMMP) on the smallest Cu nanoparticles (25 Å diameter) show that DMMP decomposition occurs below room temperature. Specifically, P-OCH@sub 3@ bond scission is nearly complete at room temperature, but all P-CH@sub 3@ bonds are not broken until much higher temperatures (550 K). Both phosphorous and carbon can be removed from the surface by heating to 800 K. Although studies of DMMP reaction on the TiO@sub 2@(110)-(1x2) surface show that decomposition of DMMP on titania itself commences around room temperature, our data also suggest that P-OCH@sub 3@ bond scission occurs more readily on the Cu nanoparticles.

4:20pm **SS1-ThA8 Catalytic Oxidation of Propylene on Stepped Pt(411): In-situ Mechanistic Studies Over an Extended Pressure Range***, **H.D. Lewis**, D.J. Burnett, A.M. Gabelnick,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; J.L. Gland,* University of Michigan

Surface defects play an important role in reactivity by, for example, lowering activation barriers for dissociation and increasing the bonding energy of adsorbed species. In this work the catalytic oxidation of preadsorbed propylene has been studied in oxygen pressures up to 0.01 Torr on the stepped Pt(411) surface. Using a combination of kinetic and spectroscopic in-situ fluorescence yield soft x-ray techniques we have characterized the oxidation of propylene. In pressures of oxygen, propylene is completely oxidized by 475 K with oxydehydrogenation preceding skeletal oxidation. The 280 K initiation temperature for oxydehydrogenation is independent of oxygen pressure. The temperature where skeletal oxidation begins decreases from 315 K in 0.0005 Torr oxygen to 300 K in 0.02 Torr oxygen. In the temperature range between oxydehydrogenation and skeletal oxidation a reaction intermediate has been spectroscopically characterized. In-situ catalytic oxidation studies with both propylene and oxygen in the gas phase were also studied. With increasing oxygen pressure the concentration of carbon containing surface species decreases showing competitive adsorption. In this catalytic environment, the onset temperature for deep oxidation decreases with increasing oxygen pressures. Taken together, these results suggest that the inhibition of oxygen adsorption is important in limiting this complex reaction system. This new molecular understanding provides a basis for elucidating the mechanism of this complex surface reaction network.

4:40pm **SS1-ThA9 A Model Catalyst in Action: A Flow-reactor-STM Study of CO-oxidation on Pt(110)***, **B.L.M. Hendriksen**, J.W.M. Frenken,* Leiden University, The Netherlands

The activity of a (model) catalyst can depend on its surface structure. In turn, the surface structure can depend on the reaction conditions. We have used a novel high-pressure, high-temperature scanning tunneling microscope, which is set up as a flow reactor, to determine simultaneously the surface structure and the activity of a Pt(110) model catalyst at semi-realistic conditions for CO oxidation. By controlled switching from a CO flow to an O2 flow and vice versa, we can reversibly oxidize and reduce the platinum surface while imaging the surface with our STM. By simultaneously monitoring the gas composition, we have observed that the formation of the oxide has a dramatic effect on the CO2 production rate. Our results show that there is a strict one-to-one correspondence between the surface structure and the catalytic activity.

5:00pm **SS1-ThA10 The Structures and Phase Transformations of CO and NO on Rh(111) in the Torr Pressure Range Studied by Scanning Tunneling Microscopy***, **K.S. Hwang**, K.B. Rider,* University of California, Berkeley*; M. Salmeron, G.A. Somorjai,* Lawrence Berkeley National Laboratory

Using scanning tunneling microscopy (STM) in a high-pressure reactor cell, we have studied, for the first time, the molecular structure and reaction of CO and NO on Rh(111) in the Torr pressure range. This is a model system for the automobile catalytic converter, where CO is oxidized to CO@sub 2@ and NO is reduced to N@sub 2@. Numerous reaction studies have been done in various temperature and pressure regimes,@footnote 1@ but they generally do not yield direct information about molecular surface structure. Traditionally, molecular surface structure studies have been done at low temperature and pressure. These structures are kinetically frozen however, and may be different from high-temperature, high-pressure structures that are in equilibrium with the gas phase. At high coverage, CO forms a (2x2)-3CO structure on Rh(111) with one top-site and two hollow-site molecules in the unit cell.@footnote 2@ This structure forms at 300 K from low pressure to at least atmospheric pressure. NO at 300 K forms an analogous structure below 0.03 Torr. Above 0.03 Torr we have discovered a new structure with a (3x3) unit cell. By directly observing the phase transformation between the two structures, we have found the heat of adsorption of the new structure to be 0.9 eV and an energy barrier between the two structures of 0.7 eV. When CO and NO are coadsorbed on Rh(111) at low partial pressures of NO, NO appears to mix randomly among the CO molecules. As the partial pressure of NO increases, the NO segregates into islands. The (3x3)-NO structure nucleates on these islands, though the presence of CO on the surface inhibits the phase transition until the NO partial pressure is three to five times that of CO. At temperatures above 300 K, we have seen evidence of the reaction between CO and NO occurring. @FootnoteText@ @footnote 1@ V. P. Zhdanov and B. Kasemo, Surf. Sci. Rep. 29 (1997) 31. @footnote 2@ M. A. Van Hove, R. J. Koestner, and G. A. Somorjai, Phys. Rev. Lett. 50 (1983) 903.

Surface Science

Room 122 - Session SS2-ThA

Nucleation & Growth

Moderator: P.A. Thiel, Iowa State University

2:00pm **SS2-ThA1 The Use of Instabilities in Epitaxial Growth for Lateral Patterning of Surfaces***, **H.-J. Ernst**,* CEA Saclay, France **INVITED**

The use of intrinsic instabilities in growth processes is currently actively explored as a promising pathway to reach a lateral patterning of surfaces at the nanometerscale. The origin of these instabilities is traced back to the presence of an excess energy barrier for adatom diffusion over descending steps, the Ehrlich-Schwoebel barrier. Structural patterns can be created either by spontaneous self-organization of the material deposited, or by guided growth on prestructured substrates. The deposition of Cu on singular and vicinal Cu surfaces illustrates this approach, using Helium Atom Scattering (HAS), Scanning Tunneling Microscopy (STM) and Low Energy Electron Microscopy (LEEM) as structural probes. Surprisingly, the interaction of green laser light with these surfaces leads as well to atomic scale restructuring. @FootnoteText@ I like to acknowledge the contributions of F. Charra, L. Douillard, R. Gerlach, and T. Maroutian at various stages of this project.

2:40pm **SS2-ThA3 Evolution of Mounds during Ag/Ag(100) Homoepitaxy: Temperature Dependence of Pre-asymptotic Behavior***, **K.J. Caspersen**, A.R. Layson,* Iowa State University*; C.R. Stoldt,* University of California at Berkley*; V. Fournee, P.A. Thiel, J.W. Evans,* Iowa State University

Step edge barriers are known to induce unstable epitaxial growth characterized by "mound" formation, but a detailed understanding of the roughening and coarsening dynamics is lacking. Most theoretical studies aim to elucidate asymptotic behavior for simple models in the regime of (mound) slope selection. We instead perform realistic atomistic modeling of Ag/Ag(100) growth where slope selection is often slow, and the experimentally relevant "pre-asymptotic" behavior is then characterized by slow coarsening and rapid roughening. To describe observed 25ML morphologies from 150-300K ,@footnote 1@ our model includes irreversible island formation (with a 0.40eV barrier for terrace diffusion), distinct step edge barriers for straight and kinked step edges (0.07eV and

~0eV), and a realistic description of periphery diffusion which controls island shapes and coalescence (rapid diffusion along straight steps; 0.41eV barrier for kink rounding). This model then reproduces the key features of mound evolution observed at various temperatures for growth up to 60-100ML, it allows a precise characterization of evolution of the mound distribution (as quantified by a suitable tessellation), and also reveals the crossover to slope selection for thicker films. @FootnoteText@ @footnote 1@K.J. Caspersen et al., Phys. Rev. B 63 (2001) 085401.

3:00pm **SS2-ThA4 Mechanisms for Hole Formation in Surface Alloy Systems: Rh/Ag(001)@footnote 1@**, ***L.D. Roelofs,*** Haverford College*; R.J. Behm,* University of Ulm, Germany*; D.A. Chipkin,* Haverford College

We present a study of mechanisms for surface hole formation during heterogeneous, metal-on-metal epitaxial growth of surface alloy systems. We consider specifically the system Rh/Ag(001) for which a detailed STM study of the structures formed during epitaxy at room temperature is available.@footnote 2@ Three mechanisms are proposed and investigated via a kinetic Monte Carlo simulation based on a simple model for the atomic-level energetics. It is found that the dominant mechanism of hole formation in this system involves the growth of vacancy islands via an upward exchange diffusion move. First principles total energy computations using the VASP suite of programs confirm the plausibility of the explanation. Our simulation also accounts, via the same mechanism, for the observation of the growth of Ag islands on top of deposited material. An alternative mechanism for hole formation, coalescence of point vacancies, is found not to contribute appreciably to formation of vacancy clusters, but point vacancies do catalyze structure formation by other means. The mechanism identified in the present study should be applicable to other soft substrate surface alloy systems. L.D.R. thanks the DOE for supporting a visit to Sandia Livermore in order to carry out the VASP calculations.. @FootnoteText@ @footnote 1@Funded by the NSF via grant DMR - 9974545 @footnote 2@S.-L. Chang, et al., Phys. Rev. B53, 13747 (1996).

3:40pm **SS2-ThA6 Molecular Dynamics Simulations of Thin Film Nucleation through Molecular Cluster Beam Deposition: Effect of Incident Angle***,* ***Y. Hu***[1]*,* The University of Kentucky*; S.B. Sinnott,* The University of Florida

Deposition of organic cluster beams on surfaces leads to the creation of polymeric thin films through rapid chemical reactions. These reactions occur over timescales on the order of a few picoseconds and therefore are suitable for study by molecular dynamics. Besides such factors as incident energy and cluster size, the deposition angle is believed to have important effects on the nucleation of thin films grown through molecular, ionic and cluster beam deposition. In this work, angular effects on molecular organic beam deposition are studied extensively through classical molecular dynamics simulations. The reactive empirical bond potential developed by Brenner et al.@footnote 1@ is used in this simulation. Various organic cluster beams are deposited on the hydrogen terminated diamond (111) surface at room temperature. The beam impacts the surface along different crystallographic orientations at incident angles of 0Â°, 15Â°, 45Â° and 60Â° with respect to the normal to the surface. Two beam energies are considered: one corresponding to 25eV/cluster molecule and one corresponding to 50eV/cluster molecule. As the angle increases from the normal, the amount of energy deposited along the surface normal decreases. Therefore we have also considered cases where the energy normal to the surface is constant while the total energy varies. The results show the dependence of the angle effects on the crystallographic orientations, the incident energies and the reactivity of the impacting species. This work is supported by the National Science Foundation (CHE-9708047). @FootnoteText@ @footnote 1@S.B.Sinnott, L.Qi, O.A.Shenderova, D.W.Brenner, in Chaper 1 Volume 4 of Advances in Classical Trajectory Methods, Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces, Ed. W. Hase(JAI Press, Inc. Stamford, CT, 1999), p. 1-26.

4:00pm **SS2-ThA7 Scanning-tunneling/Atomic-force Microscopy Study of the Growth of KBr Films on InSb(001)***,* ***J.J. Kolodziej,*** *B. Such, P. Czuba, P. Piatkowski, F. Krok, M. Szymonski,* Jagiellonian University, Poland

Thin epitaxial KBr films have been grown on InSb (001) surface. Scanning tunneling and non-contact atomic-force microscopy in ultra-high vacuum has been used to study surface structures generated during growth, for coverages ranging from 0.3 to 120 ML. It is found that in submonolayer coverage regime oval-shaped islands of monatomic thickness are formed. These islands are often cut along crystallographic direction and the distribution of these islands on the substrate surface is anisotropic reflecting anisotropic diffusion of KBr molecules during the growth. The KBr/InSb interface is likely to be stabilized by a bond between the halide ion and AIII atoms arranged in chains on InSb. At 1 - 1.5 ML coverage continuous KBr film is formed and the material in excess of 1 ML forms rectangular islands with edges oriented along and directions on the surface. For multilayer coverages pyramidal structures of rectangular bases are formed indicative of slow diffusion of KBr molecules down across steps. These rough KBr films can be, as a result of thermal annealing, converted to flat films exposing large (> 0.1 micrometer), atomically flat (100) terraces.

4:20pm **SS2-ThA8 In situ Variable Temperature-pressure STM on Selected Nanoparticles: From Nucleation and Growth to High Pressure Stability***,* ***A.A. Kolmakov****, D.W. Goodman,* Texas A&M University

The nucleation and stability of metal nanoparticles on oxides are of great importance in catalysis, gas sensors and microelectronics. Using variable temperature and pressure scanning tunneling microscopy (STM) in conjunction with in-situ deposition techniques, a versatile imaging approach has been developed that allows the nucleation, growth and alloying of individual nanoparticles to be followed in-situ. Selected nanoparticles can be exposed to reactive gas mixtures and the evolution of their morphology followed while spanning a pressure range of over eleven orders of magnitude. Since the size and composition of the particles can be controlled individually, direct comparison of various particles with similar treatments can be carried out in a single experiment. In particular, the stabilities of Au and Ag nanoparticles supported on TiO@sub 2@ (110) have been investigated while carrying out a catalytic reaction (CO oxidization) and while exposing the sample to an aqueous environment.

4:40pm **SS2-ThA9 Characterization by XPS, LEED and STM of Silicon Deposited onto HfB@sub 2@ (0001)***,* ***R. Singh***[2]*,* University of Illinois at Chicago*; W. Hayami, T. Tanaka,* National Institute for Materials Science, Japan*; M.W, Trenary,* University of Illinois at Chicago

In the microelectronics industry, transition metal diborides like TiB@sub 2@ and HfB@sub 2@ have received a great deal of attention as possible diffusion barriers because both diborides are refractory materials that have high melting points, high degrees of hardness, and are chemically very stable. While studies have been done to assess the ability of these materials to prevent the diffusion of copper into silicon, there have not been any studies of the actual bonding, or interface, between silicon and a diboride. Since the structures and composition of the interfacial region necessarily dictate the properties and morphology of the subsequent film, this region is of great importance. Also, while HfB@sub 2@ on Si more closely resembles the actual application of a diffusion barrier, many experimental advantages are gained from studying Si on HfB@sub 2@, while yielding the same results as HfB@sub 2@ on Si. Silicon was deposited onto a clean and well ordered single crystal by the reaction of silane, SiH@sub 4@(g), at 800C. Two phases of hafnium and silicon, were identified on the surface. The Hf@sub 5@Si@sub 3@ phase has a hexagonal unit cell and was found to form hexagonal islands that were more than 100Å in width and scattered over the surface. This surface exhibited a complex (@sr@7x@sr@7)R19.1 LEED pattern and two distinct XPS peaks in the Si2p region at 99.8 and 99.4 eV assigned to silicon and the silicide respectively. The HfSi@sub 2@ phase has an orthorhombic unit cell and formed nanometer-wide lines which, at higher coverages, form a "wagon wheel" structure. STM also shows rows of silicon dimers both before and after the 900C anneal, growing side by side the silicide features. These dimers are "bean-like" protrusions that have a (@sr@7x@sr@3) silicon structure. After annealing the dimer covered surface to 1300C the Si-Si bond was cleaved and the individual silicon atoms relaxed to form a honeycomb-type structure, occupying the three fold hollow sites.

5:00pm **SS2-ThA10 Heteroepitaxy of a Manganese Carbonate on Calcite in Aqueous Solutions***,* ***A.S. Lea,*** *A. El-Azab, D.R. Baer, J.E. Amonette,* Pacific Northwest National Laboratory

Heteroepitaxy of a manganese carbonate phase on the (1014) surface of calcite using an AFM has been observed in solution when the ion activity product of Mn@super 2+@ and CO@sub 3@@super 2-@ exceeds the solubility limit of MnCO@sub 3@. Thermodynamic data indicates that the resulting phase is a Mn@sub 0.5@Ca@sub 0.5@CO@sub 3@ phase and is consistent with our XPS and EPR measurements. These islands, while growing many microns in length along the [221] direction, have a uniform width of 150-220 nm and a uniform height of only 2.5 nm, corresponding

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

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

to eight atomic layers. The islands cease growing when they encounter a step edge and have been observed to dissolve when undercut by a growing etch pit. Comparison of the crystal lattices of calcite and the Mn@sub 0.5@Ca@sub 0.5@CO@sub 3@ phase, indicate the direction of preferred growth is along the direction of greatest lattice mismatch, 3.3% as opposed to a mismatch of 2.2% along the direction of island width, [010]. A 25% decrease in stiffness along the [221] direction compared to the stiffness along the [010] direction is sufficient to account for this discrepancy. We have used a glued wetting layer model with conditions of constant surface chemical potential to model the observed morphology of the heteroepitaxial layer. Although not all the required parameters are accurately known, the model accurately depicts the measured cross-sectional profiles of the islands. This result implies that the models and considerations associated with nano-phase formation on surfaces in vacuum apply to a significant degree to growth in solution. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RL0 1830.

Surface Science
Room 134/135 - Session SS1-ThP
Catalysis on Model Systems Poster Session

SS1-ThP1 A Model Catalyst in Motion: Restructuring of a Pt(110) Surface at Atmospheric Pressure, ***B.L.M. Hendriksen***, *J.W.M. Frenken,* Leiden University, The Netherlands

The surface structure of a catalyst can depend on the reaction conditions. However, most model studies have been performed at well-defined, but strongly non-realistic, conditions such as ultrahigh vacuum or very low pressures. We have used a novel high pressure, high temperature scanning tunneling microscope, which is set up as a micro-flow reactor, to study a platinum (110) surface at semi-realistic conditions for CO oxidation, i.e. high pressure and temperature. Already a low partial pressures of CO induces the lifting of the Pt(110)-(1x2) missing row reconstruction [T. Gritsch et al., Phys. Rev. Lett. 63, 1086 (1989)] to form a tiger-skin like structure consisting of (1x1) patches. As soon we apply an atmospheric pressure of CO at 425 K, this intermediate structure coarsens to form smooth (1x1) terraces, as we have observed in STM-movies.

SS1-ThP3 Lateral Interactions in Elementary Surface Reactions between CO and NO on Rhodium Surfaces, *M.J.P. Hopstaken, A.P. van Bavel,* Eindhoven University of Technology, The Netherlands; ***J.W. Niemantsverdriet,*** Eindhoven University of Technology, The Netherlands, Netherlands

Unraveling catalytic mechanisms in terms of elementary reactions and determining the kinetic parameters of such steps is at the heart of understanding catalytic reactions at the molecular level. Here we report the use of temperature programmed desorption and static secondary ion mass spectrometry to study reactions between NO and CO on Rh(100) and (111). On both surfaces the reaction rates of the different elementary steps depend highly on coverage. At low coverage, dissociation of NO is completed around 250 K and 340 K for the Rh(100) and the Rh(111) surface, respectively. When the surface is saturated with NO, dissociation only starts when some NO desorbs first, i.e. when empty sites become available. However, inhibition of NO dissociation at intermediate coverages cannot be explained by site blocking alone, but is due to lateral interactions with other adsorbates such as N, O, and NO. Studying the effect of coadsorption of these species enables an estimate of the magnitude of these lateral interactions. The combined influence of lateral interactions and site blocking leads to explosive behavior in the CO + NO reaction on saturated surfaces. The explosion is triggered by the desorption of a small amount of CO. The liberated sites enable the dissociation of NO and the subsequent reaction of O-atoms with CO creates even more free sites. The process is autocatalytic in the free sites and becomes explosive. These explosions have been observed in real time with TPD and SIMS.

SS1-ThP4 Molecular Beam Study of the N@sub 2@O + CO Reaction on Rh(111), ***S. Wehner***, *F. Zaera,* University of California, Riverside

Rhodium is well known for its unique ability to reduce NO to N@sub 2@. It is this property that makes it indispensable in the three way catalysts used in cars to clean their exhausts. Former studies in this laboratory using molecular beams have shown that the catalytic reduction of NO by CO takes place at the periphery of surface islands of adsorbed nitrogen atoms, and most likely involves the formation a N-NO intermediate. Here, results from a kinetic study on the conversion of N@sub 2@O + CO mixtures on Rh(111) surfaces are presented. It was found that the overall behaviour is similar to that of the NO + CO reaction. The reaction rate with both nitrogen oxides reaches a maximum near 500 K for stoichiometric beams, but in the case of N@sub 2@O the rate-limiting step is the formation of CO@sub 2@, not the production of N@sub 2@ as when NO is used. These results will be contrasted with our previous work on the NO + CO and CO + O@sub 2@ systems to get an overall picture of the elementary steps involved in the cleaning of car exhausts.

SS1-ThP5 Oxygen Defect Structures and Diffusion of Surface Oxygen Atoms on CeO@sub 2@(111) Surface Studied by Noncontact Atomic Force Microscopy, ***Y. Namai***, *K. Fukui, Y. Iwasawa,* The University of Tokyo, Japan

CeO@sub 2@ is widely used as a component of automobile catalysts, where CeO@sub x@ (x@<=@2) is believed to work as a buffer of active oxygen of the catalysts to the most efficient region for oxidation of CO and hydrocarbons in exhaust gas. Migration of surface oxygen atoms to active sites for the oxidation and surface structural changes in the reduction-oxidation cycles are crucial issues to understand the role of CeO@sub x@ in an atomic scale. Noncontact Atomic Force Microscopy (NC-AFM) is a recently developed technique to visualize surface structures in an atomic scale. We have applied NC-AFM to a CeO@sub 2@(111) surface and succeeded in obtaining atom-resolved images for the first time. By annealing an Ar ion-sputtered CeO@sub 2@(111) surface at 1173 K for 1 min, hexagonally arranged oxygen atoms with a constant separation of 0.38 nm were observed by NC-AFM. Oxygen point vacancies were found on the surface as dark depressions. Further annealing of the surface at 1173 K in vacuum increased the density of point vacancies and multiple defects began to appear from total annealing period of 4 min. Triangular defects which consist of neighboring three oxygen vacancies and line defects which consist of 2-4 oxygen vacancies along the [10-1] direction, the [0-11] direction, and the [1-10] direction were visualized by NC-AFM. Successive NC-AFM observation revealed that oxygen atoms on slightly reduced CeO@sub 2@(111) surfaces are mobile even at room temperature. Mobility of the surface oxygen atoms seems to depend on the density of surface oxygen defects. Such mobile oxygen atoms may be a key species in the oxidation reactions.

SS1-ThP7 Adsorption Geometry of Modifiers in Chiral Catalysis, *J. Kubota,* ***F. Zaera,*** University of California, Riverside

It has been recently determined that heterogeneous hydrogenation catalysts such as platinum can be made enantioselective by the use of molecular modifiers. For instance, alpha-ketoesters such as ethyl pyruvate can be selectively hydrogenated by cinchona-modified platinum catalysts to produce the corresponding optically-pure (R)- or (S)-alpha-hydroxoesters (ethyl lactates from the pyruvate). In these, the adsorption geometry of the modifier appears to be critical to the performance of the catalyst. Here we report on infrared studies on the characterization of the adsorption of those modifiers from the liquid phase onto platinum surfaces. A number of cinchona molecules were probed, and the effects of concentration and solvent on the adsorption were investigated.

SS1-ThP8 Combustion of Hydrogen Over a Palladium Catalyst Studied with Laser Induced Fluorescence Imaging, ***A. Johansson***, *M. Forsth, A. Rosen,* Goteborg University and Chalmers University of Technology, Sweden

Catalysis is of great fundamental, practical and economical interest in today's society. Noble metals, such as palladium, is widely used as heterogeneous catalysts for reduction of emissions of car exhausts. It is therefore important to study the catalytic property of this metal. Combustion of hydrogen with oxygen was chosen as a model system to make it as simple as possible, avoiding hydrocarbons. The oxygen and hydrogen molecules adsorb and react via reaction intermediates to form water. An important intermediate is the OH molecule. The hydroxyl radical OH also has spectroscopic properties which make it convenient to study. Laser Induced Fluorescence (LIF) was used to investigate the gas-phase concentration of the OH molecule. An ICCD camera was used as detector to study the OH concentration profile in two dimensions outside the palladium surface. The polycrystalline palladium foil was resistively heated up to 1300K and nearby temperatures. The chamber was evacuated with roots and turbo pumps. The hydrogen and oxygen gas flow was regulated with two mass flow controllers, one for each gas. The mass flow controllers were calibrated with a quadropole mass spectrometer connected to the chamber. The working pressure in the chamber was varied from 0.1-100 Torr. The hydrogen/oxygen reaction on a hot palladium surface was also modelled using the Chemkin software package. Estimations of important reaction parameters could be achieved by comparing experimentally obtained OH-profiles with modelled profiles. Also, sensitivity analysis of the obtained model indicated which reactions that are rate-limiting and which reactions that are less important from a catalytic point-of-view. These last results should be taken as advises as to where future experimental efforts should be made. The water production rate is measured with micro calorimetry.

SS1-ThP9 Scanning Tunneling Microscopy Studies of the Growth and Morphology of Cu Clusters Deposited on TiO@sub 2@(110), ***J. Zhou***, *J.E. Reddic, D.A. Chen,* University of South Carolina

The growth of metals on oxide surfaces has become an important area due to the variety of applications involving metal-oxide interfaces. We have conducted scanning tunneling microscopy (STM) studies of Cu clusters grown on single-crystal TiO@sub 2@(110) (rutile) surfaces under ultrahigh vacuum conditions as a model for understanding the early stages of metal-on-oxide growth. Previous investigations of Cu deposited on TiO@sub

2@(110)-(1x1) have shown that the Cu clusters exhibit 'self-limiting' growth in the sense that with increasing coverage, the Cu cluster densities increase but the cluster sizes remain approximately constant. Our current studies of Cu grown on a partially reconstructed TiO@sub 2@(110)-(1x2) demonstrate that surface defects play an important role in determining the size and spatial distribution of the Cu clusters. Growth on the (1x2) surface is also 'self-limiting' and produces very uniform size distributions at all Cu coverages. However, the average cluster size at room temperature on the (1x2) surface (25Å diameter, 5Å height) is much smaller than on the (1x1) surface (~40Å diameter, 6-8Å height), and this difference is attributed to the decreased adatom mobility on the more defective (1x2) surface. Furthermore, the Cu clusters show no preference for residing at the titania step edges, which are the highest coordinate sites, even when the surface has been annealed to high temperatures (700-800 K) to increase the diffusion rate of the Cu adatoms. To further investigate this growth behavior, the initial stages of Cu cluster growth will be investigated by depositing Cu at low temperatures (25K-100 K) to prevent Cu adatom diffusion. The surface will then be heated to initiate adatom diffusion, and changes in the Cu clusters will be imaged by STM. We will also explore how the morphology of the Cu clusters is changed by oxidation at various temperatures. Both Cu deposition and oxidation studies can be performed during STM imaging.

SS1-ThP10 LITD-FTMS Study of Dehydrogenation of Cyclohexane on Al@sub 2@O@sub 3@-supported Pt Clusters*, **M.M. Ivey**, M.F. Luo, J.C. Hemminger,* University of California, Irvine

We present a study of the adsorption and subsequent thermally activated dehydrogenation of cyclohexane on oxide-supported Pt clusters by use of Fourier transform mass spectrometry (FTMS) in combination with laser-induced thermal desorption (LITD).@footnote 1@ Pt clusters were generated by thermal evaporation of Pt onto an Al@sub 2@O@sub 3@ ultra thin film of 10 Å thickness that was grown on a NiAl(001) surface through oxygen adsorption at high temperature.@footnote 2@ Both cyclohexane desorption and dehydrogenation are observed. The branching between the desorption and dehydrogenation paths was monitored using a combination of AES, TDS and LITD. The cyclohexane dehydrogenation on Pt clusters behaves in a manner significantly different from that on Pt(111) single crystal surfaces. We will show the reactivity/desorption behaviour for this system for a range of Pt surface loadings. This will be discussed in the light of the dependence on Pt average cluster size which was determined by an AES quantitative analysis of CO chemisorption, assuming hemispherical cluster shapes. @FootnoteText@ @footnote 1@ D.P. Land, C.L. Pettiette-Hall, J.C. Hemminger and R.T. McIver, Acc. Chem. Res. 24 (1991) 42. @footnote 2@ M.M. Ivey, H.C. Allen, A. Avoyan, K.A. Martin and J.C. Hemminger, J. Am. Chem. Soc. 120 (1998) 10980.

Surface Science
Room 134/135 - Session SS2-ThP
Beam Interactions with Surfaces Poster Session

SS2-ThP1 Evaluation of Surface Activity using a Molecular Probe*, **K. Iizumi**, K. Ueno, K. Saiki, A. Koma,* The University of Tokyo, Japan

It is important to investigate activity of various surfaces, since surfaces provide stages where various kinds of phenomena occur. We have examined to evaluate the surface activity through the interaction between C@sub 60@ and the surface. When the surface is active, the interaction between C@sub 60@ and the surface is strong. This strong interaction breaks the high symmetry of C@sub 60@ molecule and modifies its electronic structure. Then the electronic structure of adsorbed C@sub 60@ molecule indicates activity of the surface, onto which C@sub 60@ adsorb. In this sense, a C@sub 60@ molecule can be a good probe to know the degree of activity of the surface. In this paper, we chose three types of surfaces and estimated their activity. These three type of surfaces are as follows; (i) Si(111)-7x7 surface, (ii) dangling bond terminated Si(111) surface: Si(111)-@sr@3x@sr@3-Ag, Si(111)-@sr@3x@sr@3-Ga and Si(111)-1x1-As, (iii) layered material: MoS@sub 2@ cleaved surface. Monolayer C@sub 60@ films were grown on these surfaces and investigated electronic structures of C@sub 60@ by electron-energy-loss (EEL) spectroscopy in the reflection geometry. This is a powerful technique to study surface electronic structures of various materials. EEL spectra of C@sub 60@/Si(111)-7x7 and C@sub 60@/Si(111)-@sr@3x@sr@3-Ga are quite different from that of bulk C@sub 60@. On the other hand, EEL spectra of C@sub 60@/MoS@sub 2@ and C@sub 60@/Si(111)-1x1-As are the same as that of bulk C@sub 60@. The EEL spectrum of C@sub 60@/Si(111)-@sr@3x@sr@3-Ag resembles to that of bulk C@sub 60@. However there is small difference in peak intensities. As a result, we conclude that degrees of activity of above five surface are as follows: Si(111)-7x7, C@sub 60@/Si(111)-@sr@3x@sr@3-Ga >> Si(111)-@sr@3x@sr@3-Ag > C@sub 60@/MoS@sub 2@, C@sub 60@/Si(111)-1x1-As.

SS2-ThP2 Low-Energy Ion Scattering Study of Ag-Al Surface Composition@footnote 1@*, **R. Bastasz**, J.A. Whaley,* Sandia National Laboratories*; W.P. Ellis,* Los Alamos National Laboratory

Diffusion and segregation effects have been examined for the Ag-Al system using the surface-specific technique of low-energy ion scattering (LEIS), which probes the outer atomic layer of materials.@footnote 2,3@ Thin (25 µm) foils of high-purity Ag and Al were placed in contact with each other and mounted on a heater assembly in a UHV chamber with the Al surface exposed. Initially LEIS signals from O and Al atoms were observed on the native oxide surface, but after cleaning by 1 keV He@super +@ bombardment only He@super +@ scattering from surface Al atoms was detected. The surface composition was then measured as a function of temperature up to 575 °C. No Ag was observed on the outer Al surface of Ag-Al foil samples heated to <500 °C. At 500 °C, prolonged heating resulted in the appearance of a LEIS signal from Ag at the Al surface. When the temperature of a fresh sample assembly was increased to near the eutectic (about 555 °C), the solids reacted rapidly to form a two-phase system@footnote 4@ and a LEIS signal from surface Ag immediately appeared. LEIS measurements of the surface composition of the clean binary system in the range 25-550 °C showed the Ag surface coverage to increase with temperature. Above the eutectic temperature, the Ag coverage decreased. Such LEIS measurements make it possible to determine the diffusivity of Ag in Al as well as the segregation enthalpy for Ag on Al surfaces. @FootnoteText@ @footnote 1@ This work was supported by the US Department of Energy under contract DE-AC04-94AL85000. @footnote 2@ E. Taglauer, in: "Surface Analysis- The Principal Techniques", J. C. Vickerman, Ed. (Wiley, 1997) Chap. 6. @footnote 3@ R. Bastasz, J. A. Whaley, and W. P. Ellis, Surf. Rev. Lett. 6 (1999) 605. @footnote 4@ A. J. McAllister and J. J. Murray, Bull. Alloy Phase Diagr. 1 (1983) 36.

SS2-ThP4 New Approaches to Diffusion and Electronic Properties of Surfaces: Spin-Echo Quasielastic Helium Scattering (SE-QHAS) and Metastable Helium Atom Scattering (MHAS)*, **P. Fouquet**,* Cavendish Laboratory, UK and MPI für Strömungsforschung, Germany, United Kingdom*; A.P. Jardine, J. Ellis, W. Allison,* Cavendish Laboratory, UK*; G. Witte,* Ruhr-Universität, Germany

We present current progress of two major new developments in atomic beam surface scattering: QHAS is a uniquely powerful technique for studying diffusion on atomic length and time-scales. Since helium atoms scatter from the diffusing species as they move, QHAS gives a detailed reciprocal space map of the paths the atoms take as they traverse the surface. We demonstrate the way that QHAS data can be used to study potential energy surfaces of diffusing atoms and adatom-adatom potential energies, as illustrated by analyses of experimental data on the CO/Cu(001) and Na/Cu(001) systems.@footnote 1@ Till now, QHAS has been limited to systems showing very high mobilities (D > 5 x 10@super -6@ cm@super 2@ s@super -1@), we show how measurements can be made over a much wider range of mobilities by using spin echo techniques and give details of a new ultra high resolution scattering machine that is being developed in the Cavendish. In contrast to that, metastable, excited He-atoms are highly sensitive to the surface electron density. We have shown experimentally that MHAS is capable of measuring the valence state occupation of alkali metals during growth on Cu(001).@footnote 2@ Our data interpretation has since found support by theoretical work which proved that, for the investigated systems, MHAS exclusively probes the electronic density of states projected onto the He 1s state.@footnote 3@ We have extended our measurements to alkaline earth metals (Ba), semiconductor surfaces (GaAs(100)) and oxygen coadsorption. The data supply novel information about the metallisation transition of ultrathin metal films as well as the catalytic oxidation of semiconductors. @FootnoteText@ @footnote 1@ J. Ellis, A.P. Graham, F. Hofmann, J. P. Toennies, Phys. Rev. B 63, 195408 (2001). @footnote 2@ P. Fouquet, G. Witte, Phys. Rev. Lett. 83, 360 (1999). @footnote 3@ L.N. Kantorovich et al., Surf. Sci. 444, 31 (2000).

SS2-ThP5 A Molecular Beam Study of Helium Absorption and Diffusion in Amorphous and Crystalline Ice*, J.L. Daschbach,* *P. Ayotte, G.A. Kimmel, Z. Dohnalek, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

Molecular beam and thermal desorption techniques are employed to study the absorption and diffusion of He atoms in thin amorphous and crystalline ice films at low temperatures (20-100 K). The He absorption probability increases strongly with increasing translational energy (0.065 - 0.23 eV) and decreases dramatically as the incident angle is moved away from the surface normal (0-60°). These findings are indicative of a large activation barrier and a strong steric effect for the insertion of the He atoms into the bulk. Comparison between crystalline and amorphous ice suggests that absorption into the bulk occurs through hexagonal ring structures existing at the ice surface. Diffusion of He in ice is studied by growing ice films of varying thickness on top of a He impregnated ice substrate, and subsequently measuring the He permeation through the overlayer using temperature programmed desorption (TPD). The resultant He TPD data is analyzed using a coupled diffusion/desorption model to extract the temperature dependent diffusivity. The diffusion exhibits Arrhenius behavior with a diffusion barrier of 0.14 eV. The details of the experimental findings and their implications will be presented. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

Surface Science
Room 134/135 - Session SS3-ThP
Surface Reactions Poster Session

SS3-ThP1 Thermal Behavior of NO on Stepped Pd(112)*, K. Irokawa,* *S. Ito, K. Okada, T. Okuya, H. Miki,* Science University of Tokyo, Japan

The thermal behavior of NO on a stepped Pd(112) surface has been investigated by ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy(XPS) and Auger electron spectroscopy(AES). Ramsier et al. reported that at low coverage NO adsorbed molecularly at terrace sites on Pd(112) with the NO axis perpendicular to the terrace and as increasing the coverage NO adsorbed at step sites with the NO tilted to downstairs.@footnote 1@ It was found that four peaks appeared at 2.7, 9.4, 11.2 and 14.8eV below the Fermi level in a UPS spectrum, when the surface was saturated with NO at 300K.@footnote 2@ The peak appeared at 11.2eV originates from 1@pi@+5@sigma@ orbital of NO molecules adsorbed at the step sites of Pd(112) and the three remaining peaks originate from 2@pi@, 1@pi@+5@sigma@ and 4@sigma@ orbitals of NO molecules adsorbed at the terrace sites. The peak at 11.2eV vanished at 383K with increasing temperature, although the remaining peaks disappeared at 423K. This result indicates that an activity of NO dissociation at the step edge of the Pd(112) surface is much higher than the terrace. The N atoms desorbed from the surface at 700K. This behavior observed by UPS is consistent with results of XPS and AES. @FootnoteText@ @footnote 1@ R.D.Ramsier, K.-W.Lee and J.T.Yates,Jr., Surf. Sci. 322 (1995) 244. @footnote 2@ K.Irokawa, S.Ito, T.Kioka, H.Miki, Surf. Sci 433-435 (1999) 297.

SS3-ThP2 Simulation of Lateral Interactions in the Dissociation of NO on Rh(100) by Dynamic Monte Carlo Simulations*, A.P. van Bavel,* *J.J. Lukkien,* Eindhoven University of Technology, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

The kinetics of the dissociation of NO on Rh(100) is largely determined by lateral interactions as a recent study using Temperature Programmed Desorption (TPD) and Temperature Programmed Static Secondary Ion Mass Spectrometry (TPSSIMS) by Hopstaken et.al.@footnote 1@ clearly shows. At zero coverage limit the NO dissociation is completed around 200 K. At increasing initial NO coverages the dissociation is retarded due to strong repulsions between NO and its decomposition products. At saturation coverage the NO dissociation is even fully retarded until a few NO molecules desorb from the surface, thereby creating the necessary vacancies for dissociation. The created vacancies are immediately filled with the atoms formed. This way an auto-catalytic process is developed, since the atoms cause more stronger repulsions and thereby more desorption. Due to the essential role of interactions and to the possibility of island formation, the kinetics cannot satisfactorily be described using a mean-field approach. Therefore, we have developed a model to describe the dissociation of NO on Rh(100) by means of Dynamic Monte Carlo simulations. We have included pairwise additive interactions between neighbouring species and diffusion of all adsorbates. Repulsion between NO and its decomposition products is larger than the mutual repulsion between NO molecules. This - in combination with the higher mobility of NO - leads to segregation in the adlayer to form mixed N@sub ads@+O@sub ads@ islands and compression of the NO in islands. The Monte Carlo simulations provide a means to estimate the magnitude of the interaction between neighbouring adsorbate species. @FootnoteText@ @footnote 1@ Hopstaken, M.J.P., Niemantsverdriet, J.W.; J. Phys. Chem. 104 (2000) 3058.

SS3-ThP3 Multi-directional N@sub 2@ Desorption in Thermal Dissociation of N@sub 2@O on Pd(110) and Rh(110) at Low Temperatures*, H. Horino,* Environ. Earth Sci. Hokkaido University, Japan*; T. Matsushima,* CRC, Hokkaido University, Japan

Multi-directional N@sub 2@ desorption was found in N@sub 2@O dissociation on Pd(110) and Rh(110) below 170 K by angle-resolved TDS. N@sub 2@ desorption sharply collimates off the surface normal in the (001) plane. Hot-atom-assisted N@sub 2@ desorption is proposed in aligned N@sub 2@O(a) dissociation. N@sub 2@O(a) is mostly dissociated during heating procedures, emitting N@sub 2@(g) and leaving O(a). N@sub 2@ showed four desorption peaks. Pd(110);@beta@@sub 1@-N@sub 2@ peaks around 150 K, @beta@@sub 2@-N@sub 2@ 134 K, @beta@@sub 3@-N@sub 2@ 123 K, and @beta@@sub 4@-N@sub 2@ 110 K. @beta@@sub 4@-N@sub 2@ was clearly seen at low N@sub 2@O exposures. It sharply collimated at ±50° off the surface normal. @beta@@sub 3@-N@sub 2@ was significant and revealed inclined sharp emission centered at ±43° off the surface normal. A similar distribution was also found with @beta@@sub 1@-N@sub 2@ found at high N@sub 2@O exposures, whereas @beta@@sub 2@-N@sub 2@ showed a cosine distribution. The preference of each N@sub 2@ peak was sensitive to pre-adsorbed O(a). Rh(110);@beta@@sub 1@-N@sub 2@ peaks at 165K, @beta@@sub 2@-N@sub 2@ 140 K, @beta@@sub 3@-N@sub 2@ 120 K and @beta@@sub 4@-N@sub 2@ 110 K. @beta@@sub 3@-N@sub 2@ and @beta@@sub 4@-N@sub 2@ collimated at @theta@=±33° and ±75°, respectively. These were seen at small exposures. @beta@@sub 1@-N@sub 2@ showed a cosine distribution. @beta@@sub 2@-N@sub 2@ desorption collimated at @theta@=±30°. Sharp inclined desorption possesses high kinetic energy. Prior to dissociation, N@sub 2@O(a) must lie on the surface. For inclined desorption, a surface parallel momentum must be transferred from nascent hot oxygen atoms to desorbing N@sub 2@. Larger inclined angles and higher kinetic energy may be expected on Rh(110) because higher hot-atom energy comes from the stronger metal-O bonding.

SS3-ThP4 Adsorption and Reaction of SO@sub 2@ with Cu(110) and Cu(110)-p(2x1)-O*, A.R. Alemozafar,* *X.-C. Guo, R.J. Madix,* Stanford University

Sulfur dioxide (SO@sub 2@) is infamous for its role as an environmental pollutant and in most circumstances a catalyst poison. Over the past twenty years SO@sub 2@ has been investigated on a number of single crystal metal surfaces, yet there is little SO@sub 2@/Cu(110) work. The results of our study which combines STM and TPRS to advance the understanding of the reactions of SO@sub 2@ on Cu(110) are reported. STM images reveal the formation of c(2x2), p(2x2) and c(4x2) surface structures when SO@sub 2@ interacts with the clean Cu(110) surface. The p(2x2) and c(4x2) structures form small domains, approximately 3-4 lattice units across, while the c(2x2) structures are considerably larger. The LEED pattern resulting from this reaction is a diffuse c(2x2), consistent with the domain sizes revealed by STM. STM studies of the dissociative adsorption of D@sub 2@S on Cu(110) reveal a c(2x2) sulfur structure on the surface with a corrugation identical to that observed upon SO@sub 2@ interaction with the Cu(110) surface, indicating that the c(2x2) moieties are due to sulfur adsorption. The p(2x2) and c(4x2) moieties are distributed randomly throughout the scan area in equal proportions, and STM shows similar corrugations of these two phases suggesting that they are the same SO@sub x@ species, stable up to 450 K (determined) by separate TPRS experiments. With the use of isotopic labeling the TPRS work suggests that the SO@sub x@ species is SO@sub 3@, with SO@sub 3@ bound to the surface via one of its oxygen atoms. This stoichiometry is consistent with the 1:2 ratio of the fraction of the surface covered by S and SO@sub x@ when the clean surface is exposed to SO@sub 2@. Further, from our STM images the binding site for the SO@sub 3@ can be determined to be a four-fold hollow. With our STM we have also probed the mobility of surface species. The real-time movie reveals the mobility of both SO@sub 3@ and oxygen rows along the [001] and [110] azimuths, respectively.

SS3-ThP5 NEXAFS Investigation of SO@sub 2@ Reactions on Oxygen-modified Ni (100) Surfaces*, **C.M. Kim,*** Kyungpook National University, Korea

The surface reaction of SO@sub 2@ and O on a Ni (100) surface has been investigated using a Near Edge X-ray Absorption Fine Structure (NEXAFS) technique and X-ray Photoelectron Spectroscopy (XPS). Four different surfaces were studied; clean Ni(100), p(2x2)_O/Ni(100), c(2x2)_O/Ni(100), and NiO(111)/Ni(100). Chemisorbed SO@sub 2@ was formed at 160 K on all four surfaces. Upon heating, SO@sub 2@ was decomposed to SO and atomic sulfur on clean Ni(100). On p(2x2)_O/Ni(100) and c(2x2)_O/Ni(100), however, SO@sub 3@ was formed in the temperature range of 200 to 400 K. Sulfur K-edge NEXAFS results showed that SO@sub 3@ was adsorbed with C3-axis perpendicular to the surface. On the NiO(111)/Ni(100) surface, both SO@sub 3@ and SO@sub 4@ were formed.

SS3-ThP6 Mechanism of O@sub 2@ Ejection from Pt(111) at 100K Induced by Gas-phase D Atom*, J.-Y. Kim, J.S. Choi, S.J. Lee, **J. Lee,*** Seoul National University, Korea

Rettner and Lee@footnote 1@ have shown that the gas-phase H(D) atom incident on an O2-adsorbed Pt(111) surface at 85K induces prompt desorption of O2 with a translational energy well in excess of the surface temperature. To elucidate the mechanism of this nonthermal desorption of O2, we have performed detailed kinetic studies using a D atom beam generated in a hot tungsten capillary tube at 1900K. Real-time monitoring of the gas-phase desorption products and post-reaction TPD measurements have been made with a QMS to find out 1) O2 and D2O desorb simultaneously with different kinetics, 2) the initial desorption rate of O2 is proportional to the O2 coverage, 3) at submonolayer O2 coverages, the O2 desorption rate increases with time following a step-like initial jump, which is more pronounced at a lower coverage, and 4) post-reaction TPD spectra show multiple D2O desorption peaks with increasing D atom exposure. Based on these observations, we conclude that O2 desorption occurs by site displacement of primary as well as secondary hot D atoms, which competes with D2O formation reaction. @FootnoteText@@footnote 1@ C. T. Rettner and J. Lee, J. Chem. Phys. 101 (1994) 10185.

SS3-ThP7 CO Adsorption on the c(2x2)-Mn/Cu(100) Surface Alloy: Magnetically Driven Restructuring*, **M. Grüne,*** Universität Bonn, Germany*; G. Boishin,* Universität Linz, Austria*; C. Becker, J. Breitbach, A. Frey, T. Pelster, K. Wandelt,* Universität Bonn, Germany

The c(2x2)-Mn/Cu(100) surface alloy is stabilized by the large magnetic moment of the Mn atoms yielding a substantial exchange energy.@footnote 1@ We have investigated the adsorption of CO on this alloy at 100 K by means of HREELS, UPS, LEED, and work function measurements. CO chemisorption passes through two subsequent stages. In no stage a CO-induced superstructure LEED pattern is seen. Initial adsorption of mainly side-on-CO, accompanied by adsorption at defects, leaves the substrate order intact. Subsequent adsorption of CO ontop Mn irreversibly destroys the long-range order of the substrate. This takes place by lateral interdiffusion, as can be shown by the application of UPS symmetry selection rules. We propose that the loss of the translational symmetry is related to a suppression of the local magnetic moment by ontop-CO adsorption. The reduction of the mnagnetic energy contribution causes a lifting of the energetic exclusion of Mn nearest neighbours, leading to a considerable entropy gain by lateral intermixing. @FootnoteText@ @footnote 1@see e.g.: M. Wuttig, Y. Gauthier, S. Blügel, Phys. Rev. Lett. 23 (1993) 3619-3622.

SS3-ThP8 The Adsorption and Dehydrogenation of Cyclohexane and Benzene on Pt Islands on ZnO(0001)-O*, A.W. Grant, **L.T. Ngo,** C.T. Campbell,* University of Washington

The dehydrogenation of perdeuterated cyclohexane and benzene on Pt/ZnO(0001)-O model catalysts were studied with temperature programmed desorption (TPD), ion scattering spectroscopy (ISS), and X-ray photoelectron spectroscopy (XPS). Pt grows as 2-dimensional (2D) islands on ZnO(0001)-O until they cover ~50% of the surface, and then 3D islands form. Thus, the reactivity of these Pt islands can be studied as a function of their thickness and lateral dimensions. On Pt(111), most of the adsorbed cyclohexane converts to benzene (> 300 K) decomposing to H@sub 2@ and adsorbed carbon. Two H@sub 2@ TPD peaks, at ~360K and ~540 K, are due to desorption of H lost in producing adsorbed benzene and C-H bond scission in benzene, respectively.@footnote 1@ Perdeuterated cyclohexane desorbs molecularly at ~200 K from Pt-free ZnO(0001)-O, and ~240 K from the Pt islands, where decomposition also occurs. The Pt island thickness affects the decomposition reaction of the resulting adsorbed hydrocarbons dramatically. @FootnoteText@ @footnote 1@ J. A. Rodriguez and C. T. Campbell, J. Phys. Chem. 1989, 93, 826-835.

SS3-ThP9 Acetylene on Cu(110): Trimerization and Chemical Bonding*, **H. Öström,** L. Triguero, K. Weiss, D. Nordlund, H. Ogasawara,* Uppsala University, Sweden*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Uppsala University, Sweden and Stanford University, Sweden

We have studied the chemical bonding of acetylene on Cu(110) and the well known trimerisation reaction to benzene by high resolution X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray emission spectroscopy (XES). At liquid nitrogen temperature the XP spectra show two different C 1s peaks which correspond to two nonequivalent acetylene species adsorbed in different sites. By heating the sample, one species transforms into the other. This species disappears above room temperature due to the trimerisation of acetylene to benzene. We monitored the reaction with time resolved XPS, finding that benzene leaves the surface as soon as it is formed, in agreement with previous results. The adsorption geometry of the different adsorbate species have been determined by polarization dependent NEXAFS spectra, which shows that both species lie down on the surface, with different molecular alignment. XES shows that both species are chemisorbed on the surface with their electronic structure significantly distorted from the gas phase. The experimental results are completed by ab-initio cluster model calculations performed in the framework of density functional theory (DFT).

SS3-ThP10 Thermal Chemistry of cis-1,2-Dichloroethene on Pd(111)*, **D.M. Jaramillo**, D.E. Hunka, D.P. Land,* University of California, Davis

The decomposition of halogenated compounds on metal surfaces has generated significant interest due to the facile remediation of halocarbons by metal particles. Of particular importance are the reactions of toxic and/or carcinogenic compounds, such as chloroethenes. We have elucidated some mechanistic information about the decomposition of cis-1,2-dichloroethene on palladium. After adsorption on Pd(111) at 100 K, cis-1,2-dichloroethene thermally decomposed by 400 K to yield chlorine and hydrocarbon fragments. The only decomposition products observed by temperature programmed desorption (TPD) and laser-induced thermal desorption (LITD) were hydrogen chloride and hydrogen. Very little HCl was formed on the surface and only for exposures above 0.3 L. However, the presence of chlorine, observed by Auger electron spectroscopy (AES), on the surface above 650 K for exposures below 0.4 L indicates that decomposition occurred even though no HCl was observed. Possible surface intermediates were identified using Fourier transform reflection-adsorption infrared spectroscopy (FT-RAIRS).

SS3-ThP11 Adsorption of Cyclopentene and Cyclohexene on Ordered Sn/Pt(111) Surface Alloys*, **J. Breitbach,** D. Franke, G. Hamm, F. Jaeger, C. Becker, K. Wandelt,* University of Bonn, Germany

The adsorption of cyclopentene (C@sub 5@H@sub 8@) and cyclohexene (C@sub 6@H@sub 10@) on Pt(111) and two Sn/Pt(111) surface alloys has been investigated using HREELS, UPS, LEED and TPD. The two ordered Sn/Pt(111) alloys were prepared by annealing a Sn film deposited onto Pt(111). Depending on the temperature of annealing the surface exhibited a (2x2) or (@sr@3x@sr@3)R30° LEED pattern corresponding to a surface composition of Pt@sub 3@Sn and Pt@sub 2@Sn, respectively.@footnote 1@ At temperatures below 250K C@sub 5@H@sub 8@ and C@sub 6@H@sub 10@ adsorb intact on the pure Pt(111) surface. The di-@sigma@-bonding of the molecules is signified by the absence of the olefinic CH-stretching mode that is identified for the undisturbed molecules in the multilayer. Upon heating part of the C@sub 5@H@sub 8@ and C@sub 6@H@sub 10@ desorb and the remaining amounts are converted to C@sub 5@H@sub 5@ and C@sub 6@H@sub 6@, respectively. On the alloy surfaces the decomposition of C@sub 5@H@sub 8@ and C@sub 6@H@sub 10@ is completely suppressed. As the Sn concentration is increased, there is a marked decrease in the C@sub 5@H@sub 8@ desorption temperature from 278K on Pt(111) to 243K on the (2x2) alloy and to 192K on the (@sr@3x@sr@3)R30° alloy. This behaviour is in close analogy to the behaviour of ethylene on Sn/Pt(111)@footnote 2@ and hints to similar adsorption geometries of cyclopentene and ethylene on the pure Pt(111) surface. The adsorption of C@sub 6@H@sub 10@ is more dramatically influenced by alloying: On the (2x2) surface C@sub 6@H@sub 10@ is still di-@sigma@ bonded, while on the (@sr@3x@sr@3)R30° surface C@sub 6@H@sub 10@ is physisorbed. It can be concluded that C@sub 6@H@sub 10@ adsorbs on Pt-threefold hollow sites on Pt(111), which are not present on the (@sr@3x@sr@3)R30° surface. @FootnoteText@ @footnote 1@ M.T. Paffett, R.G. Windham Surf. Sci. 208

(1989) 34 @footnote 2@ Y.-L. Tsai, C. Xu and B.E. Koel Surf. Sci. 385 (1997) 37.

SS3-ThP12 Adsorption and Reaction of s-Triazine on Al(111)*, **V.J. Bellitto**, B. Bartlett, J.M. Valdisera, J.N. Russell, Jr.,* Naval Research Laboratory

Polycyanurates, cyanate ester resins with low-k-dielectric properties, are useful for the fabrication of microelectronic devices. Formed by the trimerization of monomers with cyanate functionalities, the polymer linkage in polycyanurates is a triazine ring. To understand how this linkage interacts with aluminum, a material used as interconnects in microelectronics, we examined the chemical interaction of 1,3,5-Triazine (C@sub 3@H@sub 3@N@sub 3@) and its isotopomer (C@sub 3@D@sub 3@N@sub 3@) on Al(111) using infrared reflection absorption spectroscopy (IRRAS), x-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). A multilayer of triazine was produced by dosing the Al(111) surface while held at 140 K. Based on IRRAS measurements, triazine was randomly oriented in the multilayer. The multilayer desorption peak temperature occurred at 173 K, leaving a monolayer of triazine on the surface. At surface temperatures between 205 K and 300 K, similar IRRAS spectra were observed, showing modes at 1564 and 1341 cm@super -1@ and the absence of a mode at 737 cm@super -1@. Symmetry analysis of the IRRAS spectrum indicates the triazine molecular plane is tilted with respect to the Al(111) surface in the adsorbed monolayer, bonding through one of the nitrogen lone pairs. Thermal decomposition product desorption began around 425 K. HCN and H@sub 2@ desorption were observed, but surprisingly CH@sub 4@ and C@sub 2@H@sub 4@ desorption were also detected. Monitoring the decomposition products of C@sub 3@D@sub 3@N@sub 3@ confirmed the product assignments. Consistent with the desorption results, around 425 K the beginning of carbide and nitride formation was observed with XPS. Above 750 K, decomposition product desorption ceased. A broad phonon mode was observed at ~800 cm@super -1@ due to the formation of AlC@sub x@N@sub y@.

SS3-ThP13 The Chemistry of 1,1-Dichloroethene on Pd(111) Investigated by TDS, LITD-FTMS, STM and FTRAIRS*, **D.E. Hunka**,* University of California, Davis*; D.C. Herman,* University of North Carolina, Chapel Hill*; K.D. Lormand, A. Loui, S. Chiang, D.P. Land,* University of California, Davis

Chloroethene contamination in ground water is a concern from both an environmental and health standpoint. All six chloroethenes are contained in over half of the sites listed on the EPAâ€™s National Priorities List as well as possible carcinogens. One promising method of remediating these pollutants is using zero valent metals to degrade these halocarbons. Both iron and iron palladium bimetallic clusters have been shown to effectively decompose several small chlorocarbons, including dichloroethenes (DCEs). However, no systematic studies on palladium alone have been performed to date. In this study, the chemistry of 1,1-dichloroethene on clean Pd(111) has been investigated using thermal desorption spectrometry (TDS), laser induced thermal desorption Fourier transform mass spectrometry (LITD/FTMS), scanning tunneling microscopy (STM) and Fourier transform reflection absorption infrared spectroscopy (FTRAIRS). TDS and LITD-FTMS results indicate a coverage dependent decomposition mechanism. Coverages above 0.32 L show a stepwise decomposition initiated by C-Cl bond scission in which two successive stable surface intermediates are produced. These intermediates are proposed to be monochloroethylidyne and chlorovinylidene, respectively. The decomposition of 1,1-DCE in coverages below 0.32 L are initiated by C-H bond cleavage, and produce one stable surface intermediate, proposed to be dichloroethylidyne. All surface intermeidiates will be investigated and confirmed by FTRAIRS. Finally, STM reveals that adsorption and decomposition of 1,1-DCE happens preferentially at step edges.

SS3-ThP14 Structural Study on (CH@sub 3@)@sub 2@S/Cu(100) by Near Edge X-ray Absorption Fine Structure and X-ray Photoelectron Spectroscopy*, **S. Yagi**,* Nagoya University, Japan

Adsorption behavior of a molecule on metal surface has been interested in a catalytic and surface reaction fields. In this study, we have studied an adsorption structure of the (CH@sub 3@)@sub 2@S on Cu(100) surface by use of polarization dependent S K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) and S 1s X-ray Photoelectron Spectroscopy (XPS) techniques. The Cu(100) crystal was cleaned by means of the Ar@super +@ bombardment and annealing up to 800 K. The cleanliness and order of the surface were verified by XPS and LEED. Research grade (CH@sub 3@)@sub 2@S molecule was introduced with an exposure of 0.4 L to the Cu(100) at 90 K, in order to obtain a submonolayer phase. S K-edge NEXAFS and XPS measurements were carried out at the soft X-ray double crystal monochromator beamline BL-3 on Hiroshima Synchrotron Radiation Center. By comparing the edge-jump ratio between the submonolayer phase and the S atomic adsorption phase, the S amount was estimated to be 0.2 ML. Noticeable polarization dependence can be seen in the NEXAFS spectra, first feature (1s-@sigma@@super *@(S-C)) is enhanced at normal incidence (electric vector is parallel to the surface). This result imply that the (CH@sub 3@)@sub 2@S molecule is lying on the Cu(100) surface without the cleavage of the S-C bonds. A significant chemical shifts of the S 1s XPS peak were observed to a lower binding energy side in the submonolayer phase compared to that of the multilayer. It found that the charge transfer occurs from the substrate to the S atom of the molecule.

SS3-ThP16 Reactions of Perchlorate on Titanium/Titanium Oxide Surfaces Studied by LITD/FTMS.*, **K.D. Lormand**, D.E. Hunka, D.P. Land,* University of California, Davis

Organic contaminants in water supplies have been a concern for decades, due to possible deadly health effects. Perchlorates, in particular, have posed a major concern as of late due to their irreversible and damaging affects on the human thyroid,@footnote 1@ long residence time in water sheds, and resistance to existing catalysts used in water treatment.@footnote 2@ Catalysts, such as palladium, iron, and platinum, have been found to be quite effective in reducing the concentration levels of most halocarbon residues, but are ineffective on perchlorates. However, preliminary studies of oxidized surfaces of titanium exposed to ultraviolet radiation have been seen to reduce perchlorates in aqueous solutions effectively. Reaction mechanisms of many halocarbon residues on palladium and platinum catalysts have already been elucidated using laser induced thermal desorption and conventional thermal desorption with FT mass spectrometry (LITD/FTMS) on clean surfaces in ultra high vacuum (UHV). Though these studies reveal accurate reaction mechanisms, they are done in an ultra clean environment and do not fully incorporate atmospheric gases into the equation. We have recently designed a new LITD/FTMS chamber to allow the rapid introduction of samples from reaction in aqueous solution into UHV for analysis. This allows for more inclusive reaction mechanisms to be determined due to the incorporation of atmospheric water and oxygen. The reaction of perchlorate is investigated on both titanium metal as well as titanium oxide using LITD/FTMS. While titanium itself is less reactive, the oxides show increased activity and studies of varying oxide layers are presented. @FootnoteText@ @footnote 1@ Siglin, J.C.; Mattie, D.R.; Dodd, D.E.; Hildebrandt, P.K.; Baker, W.H. Toxicol. Sci. 2000, 57(1), 61-74. @footnote 2@ http:/www.epa.gov/ogwdw000/ccl/perchlor/perchlo.html .

SS3-ThP17 Surface-Termination-Dependence of the Reactivity of Single Crystal Hematite with Carbon Tetrachloride*, N. Camillone III, K. Adib, K.T. Rim, J.P. Fitts, G.W. Flynn,* Columbia University*; S.A. Joyce,* Pacific Northwest National Laboratory*; **R.M. Osgood, Jr.**,* Columbia University

We describe ultrahigh vacuum Auger electron spectrometric measurements of the uptake of chlorine following the exposure of single crystal hematite to CCl@sub 4@ at room temperature. We compare the surface chemistry of two distinct terminations of @alpha@-Fe@sub 2@O@sub 3@: the Fe@sub 3@O@sub 4@ "selvedge" and the @alpha@-Fe@sub 2@O@sub 3@ / FeO "biphase." For Fe@sub 3@O@sub 4@ (111)-2x2 we estimate that saturation levels of Cl of at least ~ 27 % of a monolayer are attained at relatively low exposures of on the order of 0.1 L. No significant amount of carbon uptake is detected. Low energy electron diffraction measurements suggest that, dependent upon preparation procedures, at least two types of @alpha@-Fe@sub 2@O@sub 3@ / FeO biphase structures can be formed. Interestingly, no significant Cl or C adsorption is detected for either of these biphases, revealing a marked difference in the reactivity of the terminations. Comparison of these results with the surface structure of these terminations suggests that the active site for the dissociative adsorption of CCl@sub 4@ on Fe@sub 3@O@sub 4@ (111)-2x2 must comprise both an iron cation and an oxygen anion that is uncapped by iron cations. Modification of the biphase termination by thermal treatment, as well as the electron-stimulated and thermal desorption of Cl from the saturated Fe@sub 3@O@sub 4@ (111)-2x2 selvedge will be discussed. Finally, the relationship between these results and our recent STM measurements on this system will be presented.

SS3-ThP18 Optical and STM-based Excitation of Adsorbed Molecules*, **L. Bartels**,* University of California at Riverside*; D. Moeller, T.F. Heinz,* Columbia University*; E. Knoesel,* Rowan University*; G. Meyer, S.W. Hla,* Free University Berlin, Germany*; A. Liu,* University of California at Riverside*; K.H. Rieder,* Free University Berlin, Germany

Optical and STM-based excitation of adsorbed molecules Photodesorption and other photochemical reactions have been studied for a long time. Using femtosecond lasers, lately minute details of such surface reactions could be revealed that result in desorbing species. Simultaneously, scanning tunneling microscopy has matured from a pure imaging technique to a highly precise and powerful adsorbate and surface manipulation tool. Here experiments are shown, in which the diffusion of individual adsorbed molecules is induced by electron attachment from an STM tip and by optical excitation. In both cases the resultant diffusive motion on the surface is measured by STM. In both cases diffusion pattern are found, which do not occur under equilibrium thermal conditions.

SS3-ThP19 A Comparative Study of the Adsorption of Acetylene, Ethylene and Benzene on the Pure Pd(111) Surface and the Ordered Pd@sub 2@Sn Surface Alloy on Pd(111)*, **G. Hamm**, T. Schmidt, J. Breitbach, D. Franke, C. Becker, K. Wandelt,* University of Bonn, Germany

The adsorption of acetylene, ethylene and benzene on the pure Pd(111) surface and the ordered Pd@sub2@Sn surface alloy on Pd(111) has been investigated with TPD, LEED, UPS and HREELS. The surface alloy with (@sr@3 x @sr@3)R30° periodicity corresponding to the Pd@sub 2@Sn composition was produced by annealing of multilayer amounts of Sn vapor deposited onto Pd(111).@footnote 1@ Below 300K benzene chemisorbs intact on the pure Pd(111) surface, bonding via its @pi@-electron system. In the range 300-500K most of the adsorbed benzene desorbs while a small part is dehydrogenated leaving a CCH species on the surface. For the first time an ordered superstructure of benzene has been found at room temperature. On the alloy, benzene can only be physisorbed. Ethylene is most probably di-@sigma@ bound on the pure Pd(111) surface below 250K, whereas ethylidyne is the dominant species after the adsorption of ethylene at 350K. In the temperature range from 150 to 300K most of the ethylene desorbs. At the same time part of the molecules undergo a three step conversion into ethylidyne above 250K. Due to the absence of appropriate conversion sites and the weak adsorption, this reaction is totally suppressed on the alloy. Acetylene chemisorbs on both surfaces. While the electronic structure of the adsorbed molecule is nearly identical on the pure Pd(111) surface and the alloy, vibrational spectroscopy reveals marked differences. Benzene is reactively formed from adsorbed acetylene on pure Pd(111), exhibiting two desorption peaks at 200K and 500K, which are ascribed to tilted and flat lying benzene. The majority of the acetylene is, however, converted to ethylidyne near room temperature via a vinylidene intermediate. In contrast to Pd(111), both reactions are suppressed on the alloy surface resulting in a single acetylene desorption peak at about 160K. @FootnoteText@ @footnote 1@ A. F. Lee, C. J. Baddeley, M. S. Tikhov, R. M. Lambert, Surf. Sci. 373 (1997) 195.

Surface Science
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Semiconductor Morphology Poster Session

SS4-ThP1 Surface Stress of Thin Epitaxial CaF@sub 2@ Films on Si(111)*, P. Zahl, A. Klust, **M. Bierkandt**, J. Wollschläger,* Universität Hannover, Germany*; M. Horn- von Hoegen,* Universität GH Essen, Germany

In this paper we present the first elastic properties characterisation of ultrathin epitaxial grown calcium fluoride films (thickness up to five molecular layers) using SSIOD (Surface Stress Induced Optical Defection@footnote 1@). This experimental technique will be explained and demonstrated by Hydrogen ad-/desorption on Si(111). From the large difference in thermal expansion coefficients@footnote 2@ between CaF@sub 2@ and Si a change in volume misfit from 0.5% at room temperature up to 2.5% at 1000 K takes place. The analysis of stress increase during growth at different temperatures (e.g. misfits) allows estimating the stress at the Si/CaF@sub 2@ interface. A change of the surface reconstruction at approx. 900K between 1 and 3 TL is detectable by SSIOD. Furthermore, the measurements are showing, that although at 600K a relaxed and stress free thin films can be grown, a volume lattice misfit of approx 1.5% exists. @FootnoteText@ @footnote 1@ P. Zahl, "Oberflächenspannung auf Si(111): Heteroepitaxie von Ge und CaF@sub 2@, Adsorption von H und Sb", Logos Verlag Berlin 2000, ISBN 3-89722-571-9 @footnote 2@ M. A. Olmstead, in: Thin Films: Heteroepitaxial Systems, Chapter: "Heteroepitaxy of Strongly Disparate Materials: From Chemisorption to Epitaxy in CaF@sub 2@/Si(111)", pp. 211-266. World Scientific Publishing, Singapore, 1999 @footnote 3@ Ohmi, S. K. Tsutsui, S. Furukawa; Jpn. J. Appl. Phys., 33:1121, 1994 @footnote 4@ J. Wollschläger, A. Klust, H. Pietsch; Appl.Surf.Sci., 123/124:496-500, 1998.

SS4-ThP2 STM Investigation of Sn,Pb/Si(111)-(3x3) Phase at RT and LT*, **H. Morikawa**, K. Horikoshi, S. Hasegawa,* University of Tokyo, Japan

Pb,Sn/Ge(111) surfaces are well known systems for their 'phase transitions' from room-tenperature(RT) @sr@3x@sr@3 phases to low-temperature(LT) 3x3 phases. However, relatively few investigations have been made for the Pb, Sn/Si(111) systems.@footnote 1@ We have made STM studies for these surfaces both at RT and LT (70K). Although a long-range ordered 3x3 phase does not appear in STM images at LT in the Sn/Si system, we could see an apparent 3x3 domains for the Pb/Si system around defects. Only in the case of Pb/Si, defects aligns to form the 3x3 periodicity. In these systems, defects are important for inducing the 3x3 order. We investigated the defect-defect correlation for both sytems, in relation with the 'Defect Density Wave'on the Sn/Si(111).@footnote 2@ Furthermore we found @sr@3x@sr@3(RT) and 3x3(LT) islands for Pb/Si, which was not seen in the Sn case. @FootnoteText@ @footnote 1@K Horikoshi, et al,Phys.Rev.B 60,13287 (1999) @footnote 2@L Ottaviano,et al,Phys.Rev.Lett.86,1809(2001).

SS4-ThP3 High-Temperature Phase Transitions on the Si(111) Surface*, **C. Jeon**,* Sung Kyun Kwan University, Korea*; C.C. Hwang, K.-J. Kim, T.-H. Kang, B. Kim,* Pohang Accelerator Laboratory, Korea*; C.Y. Park,* Sung Kyun Kwan University, Korea

Surface melting of semiconductors has been widely studied up to now. Recent theoretical@footnote 1@and experimental@footnote 2@ results suggest that the Si(111) surface undergoes an incomplete melting at high temperature below the bulk melting point (1680 K). In this work, angle resolved ultra-violet photoemission spectroscopy was performed to investigate the phase transitions on the Si(111) surface with rising temperature from room temperature (RT) up to 1600 K. By analyzing of the integrated emission intensity at the Fermi level, we observed a change of metallic character as a function of temperature.@footnote 3@ As previously reported, the Si(111) 7x7 surface has metallic nature at RT. A linear increase with temperature and an abrupt rise of the intensity at the critical temperature (Tc=1100K) is observed. At the same time, the Si(111) surface structure transforms from the (7x7)-DAS to the high temperature 1x1 structure. At 1470 K, the decrease in its metallicity shows the presence of another phase transition taking place at about 200 K below the bulk melting point. Based on these results, we'll discuss the origin of the two phase transitions on the Si(111) surface at elevated temperatures. @FootnoteText@ @footnote 1@ A. Natori, T. Suzuki, and H. Yasunaga, Suf. Sci. 367, 56 (1996) @footnote 2@ Y. Fukaya and Y. Shigeta, Phys. Rev. Lett. 85, 5150 (2000) @footnote 3@ I. Stich, R. Car, and M. Parrinello, Phys. Rev. Lett. 63, 2240 (1989)

SS4-ThP4 Thermal Decay of Isolated Single Silicon Mounds on the Si(100)-(2x1) Surface*, **S. Nishida**, A. Ichimiya,* Nagoya University, Japan

We have studied the decay process of a silicon mound on the Si(100)-(2x1) surface at 500°C. The mound has been fabricated by an STM tip. The shape of the mound is a quadrangular pyramid with facets of regular array of steps that have double layer height. For the all step, the dimer rows are perpendicular to the step edges, so called the D@sub B@ step. Just after fabrication, the pyramid begins to decay layer-by-layer. During the decay, area of the bottom single layer of the pyramid is grown toward the dimer row direction. The layer width does not change toward perpendicular to the dimer rows. The area of the topmost layer of the pyramid decreases toward perpendicular to the dimer rows, because the both S@sub B@ step edges are pinned by the step edges of the lower ones. Therefore the D@sub B@ step edges remain at the each step edge, and move scarcely. But only the S@sub B@ steps at the bottom layer move due to attachment and detachment of atoms which are detached from the upper layers. The decay process of a single layer mound on the Si(100) surface is very different from that of the topmost layer of the pyramid. The S@sub B@ steps fluctuate greatly. Roughness of the S@sub B@ steps changes periodically. The aspect ratio of the mound oscillates between about 2.5 and 1.5. The decay rate of a single layer mound varies with each mound. The rate is affected by the defect of the surface. The increase of the defect ratio causes the decrease of the decay rate.

SS4-ThP5 Growth of Cu on Si(5 5 12)

***P.H. Woodworth**, J.C. Moore, J.L. Skrobiszewski, A.A. Baski,* Virginia Commonwealth University

We have used scanning tunneling microscopy (STM) to study the growth behavior of Cu on the row-like surface of Si(5 5 12). Our prior work concerning noble metal growth (Au, Ag) on this surface has shown a variety of row-like overlayer structures and Au-stabilized facet planes.@footnote 1@ This study compares and contrasts the growth behavior of Cu to its counterparts. At very low coverage (<0.1 ML) and moderate annealing temperatures (600°C), Cu induces faceting of the (5 5 12) surface to the nearby (337) and (5 5 13) planes, neither of which is a stable clean Si surface. Faceting to (337) has also been observed for low-coverage Au deposition, indicating a similarity between these two metals. In contrast to both Au and Ag growth, however, Cu is not seen to form row-like overlayer structures on the basal Si(5 5 12) surface. At higher coverages up to one monolayer, Cu causes the surface to form sawtooth facets comprised of (113) and (111) planes, where an ordered (113)2x2 reconstruction is observed. Interestingly, a large number of domain boundaries form between the 2x2 regions, resulting in a "weave-like" pattern of short rows. The stabilization of the (113) plane by metal deposition on (5 5 12) has also been observed for Au, Ag, and Sn deposition, but the 2x2 reconstruction is unique to Cu. Results for Cu deposition on (113) to produce the 2x2 phase will also be presented. @FootnoteText@ @footnote 1@ A.A. Baski, K.M. Jones, K.M. Saoud, Ultramicroscopy 86 23 (2001).

SS4-ThP6 LEED I-V Curve Analysis of Adsorption Structures of Ba on Si(001) Surface

***T. Urano**, Y. Takeda, S. Hongo,* Kobe University, Japan

Ba atoms adsorbed Si(001) surfaces show 2x3, c(2x6), 2x1 and 2x4 superstructures at submonolayer coverage, successively.@footnote 1,2@ These structures have been examined by LEED I-V curve analysis. The genetic search algorithm proposed by Doll and Van Hove@footnote 3@ has been operated to find a global optimum structure efficiently. After that the automated Tensor LEED analysis is carried out to refine the structure more precisely. Several structure models have been proposed by other researchers.@footnote 4@ In our previous LEED observation using a single domain Si(001)2x1 substrate, the direction of the two-fold periodicity of the 2x4 and 2x3 structures was determined to be parallel to the Si dimer.@footnote 1@ For the 2x3 structure, several models having Ba atoms of 1/6 monolayer(ML) and 1/3 ML, which is consistent with the UPS results showing the existence of dangling bond and dimer bond states, have been considered. The results of STM observations@footnote 5@ have been also considered. At the moment, though the R-factor value is not small enough, the model in which Ba atoms sit on the 3rd layer substrate Si atoms is most suitable. For the 2x1 and 2x4 structures, an amount of Ba atoms in the models are 1/2 and 1 ML, respectively. These results will be shown in the conference. @FootnoteText@ @footnote 1@Y.Takeda et.al.,Surf.Sci.402-404(1998)692. @footnote 2@X.Hu et.al.,Surf.Sci.426(1999)69. @footnote 3@R.Doll and M.A.Van Hove, Surf.Sci.355(1996)L393. @footnote 4@W.C.Fan and A.Ignatiev, Surf.Sci.253(1991)297. @footnote 5@K.Ojima, submitted to Surf.Sci.

SS4-ThP7 High Resolution AES Mapping and TEM Study of Cu(In,Ga)Se@sub 2@ Thin Film Growth

***C.L. Perkins**, Y. Yan, K.M. Jones, R. Noufi,* National Renewable Energy Laboratory

The chalcopyrite Cu(In,Ga)Se@sub 2@ (CIGS) shows promise as an absorber layer in thin polycrystalline solar cells, however, many details of this complicated material's growth processes remain unclear. At one point during the so called "three stage" CIGS growth process used at the National Renewable Energy Laboratory (NREL) and elsewhere, the growing film is subjected to a copper rich flux in a selenium ambient. Previous workers have postulated that during this stage there exists a thin film of liquid Cu@sub x@Se at the outermost portion of the CIGS, and that this layer acts as a reservoir of copper as well as a layer in which rapid mass transport is possible. In this paper we present TEM and high resolution AES mapping data taken on samples that had their growth interrupted at a stage when Cu@sub x@Se was expected to be present. The AES maps show CIGS grains which are highly enriched in copper relative to the rest of the CIGS film, and that these same areas contain almost no indium, results consistent with the presence of Cu@sub x@Se. Small area diffraction analysis and energy dispersive spectroscopy (EDS) performed on these same samples independently confirm the presence of Cu@sub x@Se at the surface of growing CIGS films. The implications of these results are discussed in terms of the efficiencies of CIGS photovoltaic devices.

SS4-ThP8 Surface Structures of SiC(0001) Surfaces and Oxygen Adsorption Effects

***T. Aoyama**, A. Ichimiya,* Nagoya University, Japan*; Y. Hisada, S. Mukainakano,* Denso Corporation, Japan

Surface structures of SiC(0001) @sr@3x@sr@3 R30° and 3x3 surfaces have been studied by rocking curves of reflection high energy electron diffraction (RHEED) intensities and auger electron spectroscopy (AES). The @sr@3x@sr@3 reconstruction is observed by annealing the Si pre-deposited specimen in a Si flux at 1000°C for 5 min. The 3x3 reconstruction is observed by successive annealing the @sr@3x@sr@3 surface in a Si flux at 940°C for 5 min. It is obserbed on the auger spectrums of @sr@3x@sr@3 and 3x3 surfaces that Si LVV peak of the @sr@3x@sr@3 is located at kinetic energy of 87 eV and that of the 3x3 surface is located at 91 eV. From the peak to peak ratio of Si LVV to C KLL of these surfaces, it is considered that the 3x3 is Si-rich surface (the ratio: 3) and the @sr@3x@sr@3 surface is Si-poor (the ratio: 0.6). From the structural analysis with RHEED dynamical calculations, it is concluded that the @sr@3x@sr@3 surface is terminated with C trimers on T@sub 4@ or H@sub 3@ sites and the 3x3 surface is terminated with Si pyramidal clusters. Oxygen adsorption effects on the 3x3 surface have been also studied by RHEED and AES. After 10@super 5@ L (1.5x10@super -4@ Torr, 15 min) oxygen exposure at 1000°C on the 3x3 surface, the RHEED pattern changes to 1x1 periodicity and the peak to peak ratio of Si LVV to C KLL and Si LVV to O KLL becomes 0.5 and 0.8, respectively. It is estimated that about 1/3 ML of oxygen atoms are adsorbed on the surface. From the AES results, it is considered that the oxygen atoms are located on embedded sites.

SS4-ThP9 Surface Morphology of CuInS@sub 2@ Thin Films

***A. Azuma**, Y. Akaki, H. Komaki, T. Ikari,* Miyazaki University, Japan

Solar cell techniques using I-III-VI@sub 2@ chalcopyrite semiconductors have made rapid progress for the solution of environmental and resources problems. Among chalcopyrite semiconductors, CuInS@sub 2@ may be the most promising material for photovoltaic applications due to the bandgap energy of 1.5 eV which perfectly matches the solar spectrum for energy conversion. However, the physical properties of CuInS@sub 2@ are almost unknown.In this work, the CuInS@sub 2@ thin films were grown by vacuum evaporation method. The source material was CuInS@sub 2@ compound material grown by Hot-Press method. Using substrate was glass and growth temperature is room temperature. After the vacuum evaporation, the sample was annealing under Ar or air atmospheres from 200 to 500 °C. The samples were examined by X-ray diffraction (XRD), electron probe microanalysis (EPMA), scanning electron microscopy (SEM) and optical absorption measurements.The XRD spectra indicate that poly CuInS@sub 2@ films are successful grown on glass substrate until 300 °C. CuIn@sub 5@S@sub 8@ and Cu@sub 2@S are grown with increasing the annealing temperatures. The EPMA results are in good agreement with the stoichiometry compositions of the CuInS@sub 2@, CuIn@sub 5@S@sub 8@ and Cu@sub 2@S films. Surface Morphology of the samples is drastically changed. A number of the spots increase with increasing the annealing temperatures. Furthermore, absorption coefficients decrease with increasing the temperatures.

SS4-ThP10 Atomic Resolution Imaging of Si(100)1x1:2H Dihydride Surface with Non-contact AFM

***S. Araragi**, Y. Sugawara, S. Morita,* Osaka University, Japan

Noncontact atomic force microscopy (NC-AFM) is a useful tool which has an atomic resolution applicable to many fields such as surface science. It is very important to understand the interaction on hydrogen atoms and silicon surface, when we deepen the knowledge as the surface treatment and semiconductor materials of a nano scale. Therefore, the hydrogen terminated silicon surfaces have been actively studied as the most important fields of surface physics. In the previous experiment, we succeeded in the NC-AFM imaging of individual hydrogen atom on the Si(100)2x1:H monohydride surface. Thus, the NC-AFM is suitable for the observation of the hydrogen terminated silicon surface. In this paper, we investigate how the NC-AFM images the Si(100)1x1:2H dihydride surface. As a force sensor, we used a clean silicon tip. The image with the 1x1 structure was observed when the tip was relatively far from the sample. When the distance between the tip and the sample became closer, the 2x1 structure where the bright line and the dark line were alternately located was observed. Furthermore, when the tip became closer, the 1x1 structure was again appeared. It is considered that the attractive interactions between the tip and the sample changed with the change of the distance between the tip and the sample. When the tip is relatively far from the sample, the 1x1 structure of the original dihydride surface is imaged because of less the attractive interaction. However, when the tip approaches the sample, the attractive interaction between the tip and the sample becomes stronger and hence the structure of dihydride surface changes. It turns out that the Si(100)1x1:2H dihydride surface changes by the attractive interaction between the tip and the sample in NC-AFM.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+SS-FrM
Magnetic Thin Films and Surfaces II

8:20am **MI+SS-FrM1 Novel Spin Structures in Fe@sub 3@O@sub 4@/CoO and Fe@sub 3@O@sub 4@/NiO Superlattices**, ***Y. Ijiri,*** Oberlin College*; J.A. Borchers, R.W. Erwin, S.H. Lee, K.V. O'Donovan,* National Institute of Standards and Technology*; P.J. van der Zaag, L.F. Feiner, R.M. Wolf,* Philips Research Laboratories*; D.M. Lind, P.G. Ivanov,* Florida State University **INVITED**

Using polarized neutron scattering methods, we have probed the magnetic ordering in MBE-grown Fe@sub 3@O@sub 4@/CoO and Fe@sub 3@O@sub 4@/NiO superlattices. Despite significant differences between the spinel ferrite and the rock salt monoxides, it is possible to grow high-quality epitaxial structures for these materials as a result of good oxygen sublattice matching. We have observed for these superlattices substantial changes in the spin structures for both the ferrimagnetic Fe@sub 3@O@sub 4@ and the antiferromagnetic monoxide (CoO or NiO). In particular, we have found new magnetic easy axes along with significant differences in the polarization characteristics for these thin films. The unusual structures are discussed in terms of the role of strain and exchange coupling between disparate magnetic materials.

9:00am **MI+SS-FrM3 Surface Structure and Phase/Orientation Control of Manganese Nitride Grown by Molecular Beam Epitaxy***, **H. Yang**, H.A.H. Al-Brithen, A.R. Smith,* Ohio University*; R.L. Cappelletti, J.A. Borchers, M.D. Vaudin,* National Institute of Standards and Technology

We have investigated the growth of manganese nitride on MgO(001) substrates using molecular beam epitaxy (MBE) and have studied the surfaces using scanning tunneling microscopy (STM). Manganese nitride has many bulk phases (labeled @theta@, @eta@, @zeta@, and @epsilon@). Using MBE, we can individually select these phases by controlling the growth parameters. For example, at low Mn flux, we obtain the N-rich @theta@ phase (MnN), which has fct structure;@footnote 1@ but at increased Mn flux, we obtain the less N-rich @eta@-phase (Mn3N2) which is also fct but includes ordered arrays of N vacancies, according to a model proposed by Kreiner and Jacobs.@footnote 2@ Neutron scattering confirms that the Mn moments are aligned in a layered antiferromagnetic arrangement. By adjusting the growth parameters, we are able to control not only the phase, but also the crystalline orientation. At low Mn flux, the @eta@-phase has its c-axis perpendicular to the growth surface (@eta@1). But at yet higher Mn flux, the c-axis is oriented parallel to the surface (@eta@2), a consequence being two equivalent domains, D1 and D2, at 90° to each other. These domains are evident during growth via RHEED, which shows two closely spaced 1st-order streaks due to the fct structure. Also, 1/3-order lines are observed due to the periodic vacancy planes which are normal to the surface. STM images following growth clearly reveal the two domains at the @eta@2 surface. Row structures corresponding to the vacancy planes are clearly observed. Atomic resolution images show enhancement for the Mn atoms at the intersections of the surface and vacancy planes. This is likely related to the fact that these Mn have fewer N neighbors compared to other surface Mn atoms. This work is supported by NSF. @FootnoteText@ @footnote 1@ Suzuki et al., J. Alloys and Compounds 306, 66 (2000), @footnote 2@ Kreiner and Jacobs, J. Alloys and Compounds 183, 345 (1992).

9:20am **MI+SS-FrM4 Mesoscopic Magnetic Structures Grown by Self-organization***, **J. Kirschner,*** Max-Planck-Institut fuer Mikrostrukturphysik, Germany **INVITED**

Mesoscopic magnetic structures play an increasingly important role in magnetic storage technology, magnetic sensors, non-volatile random access memories, and "magneto-electronics" in general. Lithography-type processes for making such structures, though having been quite successful, will not be addressed in this talk. Rather, typical surface science approaches, involving adsorption, surface diffusion, epitaxial growth phenomena, and self-organisation will be exploited to produce and characterize mesoscopic magnetic structures. For example, magnetic wires may be made by step edge decoration on stepped single crystal surfaces by tuning surface diffusion. They form chains of long segments, connected by weak links. These structures resemble Ising chains, with magnetic properties determined by a gradual approach to thermodynamic equilibrium. Magnetic dots may be created by exploiting localized adsorption on reconstructed surfaces. It will be demonstrated, how magnetic pillars with a height-to-diameter ration of 2:1 can be grown on such a template and that such structures may perhaps overcome the "superparamagnetic barrier" in magnetic storage technology.

10:00am **MI+SS-FrM6 Direct Observation of Orbital Kondo Resonance on the Cr(001) Surface***, O.Yu. Kolesnychenko, R. de Kort, M.I. Katsnelson, A.I. Lichtenstein, **H. van Kempen**,* University of Nijmegen, The Netherlands

Scanning Tunneling Microscopy (STM) is an excellent tool to explore many-body phenomena, such as the formation of the Kondo resonance@footnote 1@. In addition to``classical'' Kondo effect, many-electron resonances have been theoretically predicted for scattering centers with non-spin degrees of freedom. Here, we will present the first direct evidences for the existence of orbital Kondo resonance on a transition metal surface. Low-Temperature STM and STS investigations were performed on the atomically clean Cr(001). The Cr(001) surface was produced by cleavage of a 99.99% Cr single crystal in situ at 4K. As we found out, the cleavage of Cr single crystals produce atomically flat and clean (001) surfaces. The STS investigations of the Cr(001) surfaces showed a very narrow resonance at 26 meV above the Fermi level. We found that at bias voltages corresponding to the resonance energy a cross-like depressions centered around impurities appears. This cross-like feature is a fingerprint of the orbital symmetry of the resonance analogous, for example, to the visualization of a superconducting gap near a zinc atom@footnote 2@. Although the resonance in the Cr(001) surface density of states has been observed previously at room temperature@footnote 3@ and was interpreted as a one-electron surface state, we are going to present additional experimental data which strongly indicate that the observed state on the Cr(001) surface is a many-electron orbital Kondo resonance which is formed by two degenerate spin-split d@sub xz@, d@sub yz@ surface states. We also carried out calculations for the periodic degenerated Anderson model which confirm the existence of the orbital Kondo resonance on the Cr(001) surface. @FootnoteText@ @footnote 1@ H.C. Madhaven, et.al., Nature 403, 512 (2000). @footnote 2@ S.H. Pan. et.al., Nature 403, 746 (2000). @footnote 3@ J.A. Stroscio, et.al., Phys. Rev. Lett. 75, 2960 (1996).

10:20am **MI+SS-FrM7 High Dipolar Magnetic Moment Observed on Ni/Cu(111) Nanostructures by Magnetic Circular X-ray Dichroism***, **C. Boeglin**, S. Stanescu, S. Cherifi,* IPCMS-CNRS, France*; A. Barbier,* CEA/DRFMC, France*; N.B. Brookes,* ESRF, France*; P. Ohresser,* LURE-CNRS, France*; J.P. Deville,* IPCMS-CNRS, France

The correlation between ultrathin film growth, structure and morphology and the induced magnetic properties is of fundamental interest in order to improve the theoretical understanding of magnetic properties in ultra-thin films. We report here growth and morphology studies at the first stages of growth of Ni on a Cu(111) single crystal substrate. This work has been performed by in-situ Auger, RHEED and STM at room temperature. The morphology shows in the early stages of the growth that nickel induces 10-30 nm large triangular islands monolayer in height. In addition stripes are formed at the step edges via a step flow growth mode. The particular shape of the oriented triangular islands has been examined by STM and segregation of Cu atoms could be evidenced on top of the Ni islands after 0.5 ML deposition. It is shown that the Ni morphology and the Cu diffusion both have a strong influence on the magnetic properties. Correlations have be evidenced by performing in-situ Magnetic Circular X-ray Dichroism studies on Ni/Cu(111) ultra-thin films. The evolution of the island size during the growth can be correlated with the evolution of the orbital magnetic moment whereas strong dipolar magnetic moments are related to the formation of a second Cu/Ni interface. Moreover, the in-plane orbital magnetic moment anisotropy has been measured and related to magnetocrystalline effects in the film.

10:40am **MI+SS-FrM8 Relating Magnetic and Structural Changes of Thin FeNi Alloy Films on Cu(100)***, **M. Hochstrasser**, J.G. Tobin,* Lawrence Livermore National Laboratory*; S.A. Morton, G.D. Waddill,* University of Missouri-Rolla*; F.O. Schumann,* Freie Universität Berlin, Germany*; N.A.R. Gilmann, R.F. Willis,* The Pennsylvania State University

At a concentration of around 65% Fe, bulk FeNi alloys exhibit the "Invar effect", a sudden arresting of the Wigner-Seitz cell volume and a zero expansion coefficient. Simultaneously, the crystal structure changes from face-centered cubic to body-centered cubic while the Curie temperature goes to zero. This structural transformation can be arrested in ultrathin alloys films grown epitaxially on a Cu(001) substrate. Theoretical work predicts that the fcc phase can exist in two possible states: a ferromagnetic high volume state or a antiferromagnetic low volume state (2@gamma@ state model) and a volume change between the paramagnetic and the high spin state of ~7%, and 1% change between a non-collinear equilibrium state and the high spin state. Experimental work shows a lattice expansion increasing linearly up to 3% at 65% Fe content followed by a sudden relaxation of 2% with increasing Fe content. The initial volume increase is associated with increasing magnetization/magnetic moment & spin alignment in the Ni-rich alloys. As the alloy is cooled below T@sub C@ (or a strong external magnetic field is applied), an increasing alignment of the magnetic moments causes the nearest-neighbor spins to push apart producing an internal pressure which expands the lattice. With increasing Fe content, this effect increases due to the increasing number of Fe nearest neighbors with the larger atomic magnetic moments. Eventually, a critical limit is reached (~65% Fe), when a magnetic/lattice volume instability develops. W ith x-ray magnetic dichroism the changes in the elemental magnetic moments were tracked. Spin polarized photoemission studies record a sudden decrease in the "mean-field" exchange splitting of the d-states with increasing Fe content through the critical "Invar transition". Angle-resolved photoemission imaging of states at the Fermi level reveal a much smaller splitting of the sp-states, which also tracks the changing magnetization with changing composition.

11:00am **MI+SS-FrM9 The Structure of Ferromagnetic Ultrathin Fe Films on Cu(100) is not fcc**, *A. Biedermann, R. Tscheliessnig, M. Schmid,* ***P. Varga,*** TU Vienna, Austria

Ultrathin Fe films on Cu(100) are an ideal model system to study martensitic fcc-bcc phase transitions in Fe.@footnote 1@ Ultrathin Fe films on Cu are also distinguished by the appearance of a novel ferromagnetic phase which showed distinct fcc-like features in p revious electron diffraction experiments. By means of scanning tunneling microscopy we were able to reveal this phase as a novel "nanomartensitic" phase with the Fe atoms forming localy a bcc like structure @footnote 2@. This shows that the assumption of a ferromagnetic fcc phase is not necessary to explain the ferromagnetism observed in these films. @FootnoteText@ @footnote 1@ A. Biedermann, M. Schmid, and P. Varga, Phys. Rev. Lett. 86 (2001) 464-67 @footnote 2@ A. Biedermann, Rupert TschelieÃŸnig,M. Schmid, and P. Varga, Phys. Rev. Lett., submitted

11:20am **MI+SS-FrM10 Angle Resolved Auger Spectra of Ultrathin Fe on Gd (0001)***,* ***J.P. Nibarger,*** *D.P. Pappas,* National Institute of Standards and Technology

The in-plane to out-of-plane spin-reorientation phase transition of ultrathin Fe on Gd (0001) has been measured recently.@footnote 1@ Theoretical work has indicated the need for six-fold symmetry of the ultrathin Fe film in order to fit existing data on the spin-reorientation phase transition.@footnote 2@ Fe films consisting of 1.5 atomic layers on bulk Gd do no exhibit any long range ordering as determined by low energy electron diffraction. Angle resolved Auger electron spectroscopy (ARAES) will be used because it is sensitive to local order on the atomic scale and will determine the local symmetry of the Fe atoms. ARAES spectra will be shown that demonstrate the extent of six-fold symmetry in these films. @FootnoteText@ @footnote 1@ C.S. Arnold et al., Phys. Rev. Lett. 83, 3305 (1999). @footnote 2@ A.P. Popov, private communication.

11:40am **MI+SS-FrM11 Transverse Magneto-optical Kerr-effect in the Soft X-ray Regime at Iron and Cobalt Films on W(110)***,* ***J. Bansmann,*** *V. Senz, A. Kleibert,* University of Rostock, Germany

Tunable soft X-ray radiation opens the possibility for investigating element-specifically the magnetic properties of thin films, islands, and nanoparticles on surfaces. Well-known techniques are magnetic dichroism in photoemission (MDAD) and X-ray magnetic circular dichroism in photoabsorption (XMCD). However, magnetic phenomena can also be studied using the transverse Magneto-optical Kerr effect (T-MOKE) at the core levels of ferromagnetic materials using linearly polarized radiation. We will present new data using T-MOKE at iron and cobalt films and self-organized islands on W(110). For recording hysteresis curves an external electromagnet has been applied to the setup. Close to the core levels of e.g., iron and cobalt, the reflectivity and the Kerr rotation is strongly enhanced by resonant forward scattering. We could observe huge intensities in reflexion and intensity asymmetries of 50% at Fe and Co films of less than 6ML. The experimental results will be compared to recent calculations. When annealing Fe(110) films on W(110) a well oriented Fe island structure can be created. Our experimental data clearly show a rotation of the easy axis with respect to thin films which depends on the original coverage before annealing and on the temperature during thermal treatment. In the case of cobalt on W(110) we have investigated the magnetic properties of fcc- and hcp-cobalt films on clean and modified W(110) surfaces. Although the direction of the easy magnetization axis does not change using different cobalt structures, the remanent magnetization and coercive forces have clearly changed.

Surface Science
Room 120 - Session SS1-FrM

Dynamics of Metal Surfaces

Moderator: N.C. Bartelt, Sandia National Laboratories

8:20am **SS1-FrM1 Crossover from Surface- to Bulk-Diffusion-Limited Surface Dynamics on Pt(111)@footnote 1@***, B. Poelsema,* University of Twente, The Netherlands*; J.B. Hannon,* IBM T.J. Watson Research Center*; N.C. Bartelt,* ***G.L. Kellogg,*** Sandia National Laboratories

Microscopic measurements of changes in surface morphology due to the motion of single-atom high steps provide detailed information on atomistic processes occurring at a crystal surface. In this study, we use low energy electron microscopy (LEEM) to measure the time-dependent changes in area of two-dimensional Pt islands on Pt(111) as a function of temperature. We find evidence for a crossover from step motion caused by surface diffusion to step motion caused by the flow of material to and from the bulk crystal as the temperature is raised. At temperatures in the range from 1100-1500 K, circular islands residing at the top of three-dimensional stacks exhibit a linear decay, as long as the stack diameter exceeds approximately 1.5 microns. The temperature dependence of the decay rate yields an activation energy of 1.7 eV. On the other hand, for stacks with smaller diameters and temperatures below 1350 K, the decay is non-linear, having a form more closely resembling surface diffusion-limited kinetics. The high-T behavior is similar to that recently observed for NiAl(110), where it was shown that bulk vacancy transport controls step motion on the surface.@footnote 2@ In support of the same interpretation for Pt(111), we observe that the islands grow upon increasing the temperature and shrink upon lowering the temperature in non-equilibrium experiments. The dynamics for Pt(111) are more complicated than NiAl(110), involving a competition between the diffusion of surface adatoms and bulk vacancies. However, preliminary modeling studies indicate that processes involving bulk vacancies can simultaneously explain the temperature dependence of island decay at fixed temperature and the non-equilibrium behavior of islands on Pt(111) as the temperature is varied. @FootnoteText@ @footnote 1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. DOE under Contract DE-AC04-94AL85000. @footnote 2@ K. McCarty, J.A. Nobel, and N.C. Bartelt, preprint.

8:40am **SS1-FrM2 Dimensionality Investigation of an Alloy-dealloy Phase Transition on Ag/Cu(110)***, O. Kizilkaya, D.A. Hite, J. Choi,* ***P.T. Sprunger,*** Louisiana State University

An alloy-dealloy phase transition as a result of 0.4-1 ML deposition of Ag on Cu(110) has been studied by use of angle resolved photoemission spectroscopy (ARUPS). The ARUPS measurements were performed at 3m. TGM beamline at Center for Advanced Microstructure and Devices synchrotron facility. Previous scanning tunneling microscopy studies showed that a surface alloy phase seen at submonolayer coverages of Ag (<0.4 ML) evolves into well ordered Ag chains at higher coverages. These chains consist of Ag dimers and trimers directed on [001] of the substrate and located on monomer and dimer [001] directed vacancies.The ARUPS results for 1 ML coverage of Ag revealed that this unique chain geometry has near 1-dimensional electronic structure showing dispersion along the Ag-chains with no dispersion perpendicular to chains and no dispersion as a function of varying photon energy. The ARUPS were measured in two different geometries, specifically, the vector potential, A, was parallel and perpendicular to [001] plane of Cu(110) in which chain structure was directed. The energy distrubition curves (EDC) as a function of photon energy show the lack of dispersion which imply that Ag chains are not incorporated into Cu(110) substrate. Although no perpendicular dispersion is observed, ARUPS data confirms, by changing the emission angle in surface Brillouin zone along the two high symmetry lines, that the Ag bands in-plane (parallel to the surface) anisotropically disperse. In the experimental geometry probing electronic geometry parallel to the Ag structural chains, that is along the [001] direction of the substrate, the Ag bands disperse as a function of parallel momentum. In contrast, with the experimental geometry probing electronic structure perpendicular to the [001] direction, there is little to no dispersion of the Ag d-bands.These results signify reduced dimensional electronic structure of Ag chains. Research was supported by U.S. DOE contract No. DE-FG02-98ER45712.

9:00am **SS1-FrM3 Vacancies in Solids and the Stability of Surface Morphology***, **K.F. McCarty**, J.A. Nobel, N.C. Bartelt,* Sandia National Laboratories **INVITED**

We have examined the kinetics of island decay on the NiAl (110) surface using low-energy electron microscopy (LEEM). Remarkably, the decay rates are constant in time and totally independent of the local environment (e.g., the width of the immediately adja cent terraces and degree of island curvature). Given the lack of surface current between islands of different curvature, we conclude that surface diffusion is not important to the smoothing process. Instead, we find unambiguous evidence that bulk vacancie s are responsible -- we visibly observe exchange between bulk vacancies and the surface when the sample temperature is changed. For a temperature increase, the surface steps advance. For a temperature decrease, the surface steps recess. These changes result from the increase (decrease) in bulk vacancy concentration for a temperature increase (decrease). Remarkably, the size change accompanying a temperature change is strictly proportional to the perimeter (step length) of the island, and again is totally independent of the local environment. Thus, we conclude that the atoms at surface steps undergo direct exchange with bulk vacancies. We will present simple mathematical models showing how this mechanism quantitatively describes the constant-rate kinetics as well as the bulk-derived flux associated with a temperature change. The complete independence of the surface dynamics on the local environment results from the fact that the steps are interacting directly with the bulk, and thus, the local step density and curvature are largely irrelevant. We will also present results illustrating how the bulk/surface exchange affects NiAl oxidation. This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported by the Office of Basic Energy Sciences-Division of Materials Sciences.

9:40am **SS1-FrM5 Surface Freezing in Binary Metallic Melts***, **A. Turchanin**, W. Freyland, D. Nattland,* University of Karlsruhe, Germany

We report on a new phenomena of surface freezing, whereby an ordered solid film forms on top of the bulk liquid at temperatures above the bulk crystallisation. Recently this phenomenon has been observed in dilute Ga-Pb@footnote 1@ and Ga-Bi@footnote 2@ liquid alloys. Here we present new results on the investigation of surface freezing in the entire composition range of the Ga-Bi system. Second Harmonic Generation and Plasma Generation methods were applied to distinguish between the solid and liquid states of the alloy surfaces as a function of temperature and composition. The surface freezing was detected for all investigated alloys with composition between the eutectic (x(Bi)=0.0022, T(eut)=29.48°C) and monotectic point (x(Bi)=0.085, T(mono)=222 °C). On cooling of such alloys a Bi-rich solid-like film forms on top of the bulk liquid phase at temperatures well above the liquidus line. This film disappears on heating at higher temperatures, which characterizes this transition as a first-order phase transition. The maximum difference between the liquidus temperature and the temperature of the surface freezing transition was detected for the eutectic alloy (T(tr)-T(eut)=20 K). The lines of surface freezing and respective melting merge with the liquidus line approaching the monotectic point. The thickness of the forming Bi-rich solid-like films estimated from our measurements lies in the ranges from 0.5-1 nm to 100 nm. We have indications that it has a tendency to increase approaching the monotectic point. The relation of the surface freezing and wetting transitions occurring in Ga-Bi will be discussed. The surface freezing in Ga-Bi system will be compared with the two-dimensional freezing in dilute Ga-Pb alloy detected by x-ray reflectivity and grazing incidence diffraction methods.@footnote 1@ @FootnoteText@ @footnote 1@B. Yang, D. Gidalevitz, D. Li, Z. Huang, S.A. Rice, Proc. Nat. Acad. Svi USA, 96 (1999) 13009 @footnote 2@A. Turchanin, D. Nattland, W. Freyland, Chem. Phys. Lett. 337 (2001) 5.

10:00am **SS1-FrM6 Submonolayer Growth of Ag on Pt(100): Competition between Alloying and Surface Reconstruction***, **M. Batzill**, B.E. Koel,* University of Southern California

The growth of Ag on Pt(111) and the formation of a nanophasic alloy, has been thoroughly studied. On the Pt(100) surface, the presence of the energy-minimizing, hex-reconstruction gives rise to phenomena different to that on the (111) face. We present STM, AES, and TPD studies of the Ag/Pt(100) interface for submonolayer Ag coverages in a temperature regime between 300 and 900 K. We observe strongly anisotropic growth of Ag islands governed by the anisotropy of the reconstructed surface at 300 K. Adsorption of Ag lifts the reconstruction, resulting in a kinetically trapped Ag80Pt20 alloy formed by using the excess Pt from the reconstruction ejected into the growing Ag-islands. Annealing causes diffusion of Ag from the Ag80Pt20 adislands to the pure Pt(100) reconstructed regions, lifting its reconstruction and forming a nanophasic Ag-Pt alloy. For surfaces with less than 0.3 ML Ag, domains of Pt(100)-hex reconstruction and a Ag30Pt70 alloy coexist in thermodynamic equilibrium. This phase segregation is a result of energy minimization, and can be explained by the presence of two minima in the Ag-Pt surface phase diagram associated with the pure Pt reconstruction and a strain stabilized alloy phase. Deposition of more than 0.3 ML increases the Ag content in the alloyphase until no Pt remains in the monolayer and an abrupt Pt/Ag interface forms.

10:20am **SS1-FrM7 Direct Observation of Surface Alloying and Interface Roughening: Growth of Au on Fe(001)***, M.M.J. Bischoff, T. Yamada, A.J. Quinn, R.G.P. van der Kraan, **H. van Kempen**,* University of Nijmegen, The Netherlands

Iron and gold belong to the family of elements which do not form alloys because of the large size difference of the Fe and Au atoms. Nevertheless, it has been predicted by Tersoff@footnote 1@ that for those elements surface confined mixing may generally occur. In the low coverage limit, this might lead to surface alloying. Because of the immiscibility of these elements, an interesting question is what will happen when this surface alloy becomes saturated, i.e. more Au is deposited than allowed for a surface confined alloy. The Au/Fe combination is especially suitable for the detailed study of possible interface processes like segregation and interface diffusion. The reason is that, while the in-plane lattice match is nearly perfect, there is a large difference in the out-of plane distance between the bcc Fe and the fcc Au (0.14 nm compared to 0.20 nm). This allows to discriminate between interface and surface features. In this paper, we report a scanning tunneling microscopy study on the growth of Au on Fe(001) at 500K. Deposition of 0.5 monolayer (ML) leads to complete coverage by a homogeneous alloyed monolayer and simultaneous formation of islands covering 50% of the terraces. Consecutive deposition of more Au leads to demixing: in this process Au islands embedded in the original Fe(001) terrace are created while Fe islands stick out in the Au covering layers. By using suitable chosen growth and anneal temperatures, the processes at the interface can be followed even for thicker coverages of 5 ML. Scanning tunneling spectroscopy studies on this system will be presented: a new surface state around 0.6-0.7 eV is detected on the homogeneous alloyed surface layer. @FootnoteText@ @footnote 1@J. Tersoff, Phys. Rev. Lett. 74, 434 (1995).

10:40am **SS1-FrM8 Surface Reconstruction STM Studies of Clean and Oxidized Low Index FeAl Surfaces***, **O. Kizilkaya**, D.A. Hite,* Louisiana State University*; D.M. Zehner,* Oak Ridge National Laboratory*; P.T. Sprunger,* Louisiana State University

Details of the atomic reconstruction behavior of clean and oxidized (110), (210) and (310) surfaces of the ordered bimetallic alloy FeAl has been studied with STM. Prefentially sputtering impedes the aluminum concentration on the surfaces. Aluminum preferentially segregates to the surface layer upon sequential annealing of these low index surfaces. Depending on the annealing temperature, there are a sequence of differing surface reconstructions on FeAl(110). At 400 C, a bulk terminated surface is observed. Between the temperatures range of 400-600 C and 800-1000 C an incommensurate FeAl2 overlayer is obtained. At annealing temperatures of 600-800 C, STM images reveal a long-range missing row reconstruction parallel to the [001] direction. For a wide range of annealing temperatures, FeAl(210) reconstructs to a (1x3) structure. The surface has alternating (100) and (110) facets. A similar type of reconstruction is observed for FeAl(310); however, the surface is not stable but facets. The crystal miscuts and kinetic effects are the main reason for instability. In the case of oxidized FeAl(110), STM reveals the formation of a thin-film gamma-alumina at low coverages. This structure is characterized as a hexagonal moir@aa e@ pattern with a spot-spot distance of 1.8 nm. Research conducted at Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy, under contract DE-AC05-00OR22725. Research was supported by U.S. DOE contract No. DE-FG02-98ER45712.

11:00am **SS1-FrM9 Self-Assembly of Nanoscale Hexagons in S/Cu/Ru(0001)@footnote 1@***, **A.P. Baddorf**,* Oak Ridge National Laboratory*; H. Zajonz, D. Gibbs,* Brookhaven National Laboratory

Periodic structures on a nanometer length scale exhibit unique dynamics and forces, and offer a template for ordering of quantum dots. Recently, Hrbek, et al.,@footnote 2@ have shown that small quantities of S adsorbed on the two layer Cu/Ru stripe phase react at dislocations, shorten stripes, and produce a quasi-hexagonal structure. We have examined the growth of this structure and its dependence on temperature with synchrotron x-ray diffraction. Deposition rates were determined by monitoring the intensity at the specular anti-Bragg position (similar to RHEED oscillations). After S deposition of up to 0.2 ML at room temperature, no new diffraction was observed, even after annealing. This is consistent with the results of Hrbek, et al., who found poor order in STM images. For deposition between 100 and 200°C, additional reflections were observed corresponding to a quasi-hexagonal lattice with a periodicity of approximately 44 Å. This structure persisted when the sample was cooled to room temperature. Long range order was indicated by narrow peak widths, 0.009 Å@super -1@ FWHM, corresponding to a correlation length of over 700 Å. Heating above 200°C reduced and broadened the diffraction wavevector, indicating a larger, less ordered lattice. Above 300°C, the quasi-hexagonal diffraction pattern disappeared leaving only diffraction from the linear Cu/Ru stripe phase. This process was reversible, so that cooling below 300°C returned the hexagonal pattern. We interpret this as a melting of the S induced structure. @FootnoteText@ @footnote 1@ORNL is managed by UT-Battelle, LLC under US DOE contract DE-AC05-00OR22725. BNL is supported by US DOE DE-AC02-98CH10886. @footnote 2@J. Hrbek, J. de la Figuera, K. Pohl, T. Jirsak, J. A. Rodriguez, A. K. Schmid, N. C. Bartelt, and R. Q. Hwang, J. Phys. Chem. B 103, 10557 (1999).

11:20am **SS1-FrM10 Application of EELFS Spectroscopy to Local Atomic Structure Study***, **Yu.V. Ruts**, A.N. Maratkanova, D.V. Surnin, D.E. Guy,* Physical-Technical Institute of Ural Branch of RAS, Russia

Fine structures above ionisation edges studied in the EELFS (Extended Energy Loss Fine Structure) technique are similar to those measured in X-ray absorption spectra (EXAFS). A possibility to measure extended structures using both transmission and reflection modes allows to obtain not only bulk parameters of the local atomic structure (partial interatomic distances, coordination numbers, backscattering amplitudes, phase shifts, etc.) but also the surface ones. Surface sensitivity makes the EELFS technique competitive with diffraction techniques especially for studying systems without long-range order. Moreover the EELFS spectroscopy is available in most surface and material physics laboratories having standard equipment with the electron exitation. In contrast to EXAFS the EELFS technique makes possible to study local domains, for example individual blocks or grains, owing to using an electron beam as an exciting source. The essential peculiarity of this method is its high sensitivity to light elements. This is very important for studying surface and bulk oxides, carbides and so on as well as the processes of their formation including gas adsorption. EELFS technique has been proved to be a powerful tool for local structural investigations of clean surfaces and chemisorbed species. Numerous papers have been published to demonstrate the applicability of the EELFS technique in the determination of the structure of different compounds and different metals deposited on clean surfaces. Application of the EELFS technique provides great progress to materials science in regards to atomic structure study. In this paper we give some examples of studying different materials by the EELFS both in transmission and reflection mode using the results obtained by different authors including our own ones. This work was sponsored in part by the Russian Foundation for Basic Research (grants 00-03-33049a and 00-15-97419).

Surface Science
Room 121 - Session SS2-FrM

Gas-Solid Dynamics: Theory and Experiment

Moderator: A.W. Kleyn, Leiden University

8:40am **SS2-FrM2 Chemisorption of O@sub2@ on Al(111): Non-Adiabatic Pathway to Abstraction, and Simulation of STM Data***, **J.Z. Sexton**, A.J. Komrowski, A.C. Kummel,* University of California, San Diego*; M. Binetti, O. Weisse, E. Hasselbrink,* Universitat Essen, Germany

There exists controversy in the literature surrounding the initial oxidation of the Al(111) surface. (1) DFT calculations show the activated reaction of O@sub2@ with Al(111) cannot be modeled using a single potential energy surface and consistency with the observed reaction barrier requires a non-adiabatic charge transfer process.@footnote 1@ The calculations show that the initial charge transfer is most favorable for end-on collisions with Al(111) which is consistent with an abstraction mechanism.@footnote 1@ (2) Abstractive chemisorption in the oxidation of aluminum is a process in which an oxygen molecule reacts with the surface producing one atom bound to the surface and one atom ejected into the gas phase. We have experimentally verified this mechanism using supersonic molecular beams to dose the clean Al(111) surface with variable incident energy O@sub2@. The evidence is as follows: (a) STM images show a transition between exclusively single O-adatom reaction products to more pairs of O-adatom reaction products as the O@sub2@ translational energy is raised from 0.025 eV (thermal) to 0.8 eV. (b) The ejected O-atoms have been detected in the gas phase with REMPI laser spectroscopy. This is consistent with an end-on, non-adiabatic reaction. (3) Interpretation of O-Al(111) reacted sites in STM images can be interpreted in terms of long range dissociation, abstraction, or diffusion.@footnote 2@ The main issue of the controversy is the assignment of single O-Al(111) reacted sites on the room temperature surface. We are performing cluster and slab calculations to simulate the appearance of O - Al(111) features in STM images. The existence of nearly degenerate adsorption sites for oxygen adatoms and local relaxation of the Al surface complicates the interpretation of the STM images. @FootnoteText@ @footnote 1@Y. Yourdshahyan, et al, Sol. St. Comm. 117, 531 (2001). @footnote 2@M. Schmid and P. Varga, in AVS Symposium Abstracts, SS-TuP4, Seattle, WA, (1999) p. 109.

9:00am **SS2-FrM3 Surface Temperature Effects in Molecular Beam Scattering: Inelastic State-to-state Scattering and the Dissociation of Hydrogen and Deuterium***, Z. Wang,* University of Texax, Austin*; G.R. Darling, **S. Holloway**,* University of Liverpool, UK

We have carried out quantum mechanical wavepacket calculations on a parameterized LDA potential energy surface for the surface temperature dependence of the inelastic scattering of hydrogen and deuterium molecules from Cu(111). We find, in agreement with experimental data, that the surface temperature dependence of each cross-section invariably has an Arrhenius form with an 'activation energy' that depends upon the translational energy of the molecules. Additional calculations for the dissociation probability reveal very similar results. On the basis of the wavepacket calculations, it has been possible to develop a simple model to explain the results. The model is quite general, robust and results will be presented for vibrationally inelastic scattering and dissociative adsorption. We shall discuss exactly the origins of the Arrhenius form for a system where thermal equilibrium is never established, and the meaning of the derived "activation energy" in terms of the parameters entering into the dynamical model.

9:20am **SS2-FrM4 Monte Carlo Simulation of the Adsorbate Assisted Adsorption in the Case of CO/ZnO***, **U. Burghaus**,* Ruhr-Universitaet Bochum, Germany

Very recently and for the first time the adsorption dynamics of a prototype molecule has been studied in detail on a metal oxide surface [Becker, Kunat, Boas, Burghaus, Woell, JCP 113 (2000) 6334], namely for the systems CO/O-ZnO and CO/Zn-ZnO, which both show a distinct increase in the adsorption probability with increasing CO coverage. This phenomenon (referred as adsorbate assisted adsorption) is in contrast to traditional precursor models. The presented Monte Carlo algorithm [submitted to Surf. Rev. and Lett.], which predicts the enhancement of adsorption by pre-adsorbates, assumes different adsorption probabilities for molecules scattered on bare and already occupied sites. Additionally, the effect of the mass-mismatch of the adsorbate and the surface atoms is considered. Thus, presented is an MC version of the analytical so-called modified Kisliuk model [e.g., R.J. Madix, et al., Surf. Sci. 470 (2001) 226]. In contrast to most of the analytic models, the MCS scheme includes lateral interaction energies, the influence of defects, and the effect of cooperative precursor dynamics. Although adsorbate assisted adsorption has also been observed on metal surfaces, the polar surfaces of ZnO are especially well suited to test the algorithm and the influence of the mass-mismatch on the energy transfer processes involved, since O-ZnO and Zn-ZnO differ solely by the mass of the atoms in the first surface layer. MC simulations will be presented which explain the main effects observed experimentally for both polar surfaces of ZnO.

9:40am **SS2-FrM5 Ultrafast Energy Flow Studied by Femtosecond Vibrational Spectroscopy***, S. Roke, A.W. Kleyn,* Leiden University, The Netherlands*; **M. Bonn**,* Leiden University, The Netherlands, Netherlands

We present a simple model describing femtosecond surface vibrational spectroscopy as a tool to study ultrafast surface chemical dynamics. We compare our calculations to recent experiments in which the interaction between CO and the Ru(0001) surface is studied using the femtosecond surface vibrational spectroscopy: sum frequency generation (fs-SFG). After short-pulsed excitation of the metal leading to desorption of CO, a transient red-shift and broadening in the infrared spectrum of the C-O stretch vibration on a picosecond time-scale are observed. The data are successfully modeled by considering the response of adsorbed CO to heating of the system by a femtosecond laser pulse. The calculations match the experimental data very well and demonstrate that fs-SFG is a very powerful tool to study the dynamics of molecules at surfaces. Detailed analysis shows that this method will enable us to detect transition states and reaction intermediates in chemical reactions at surfaces and determine the transition state lifetime. Results of first experiments on energy flow in a reacting system will be shown at the meeting.

10:20am **SS2-FrM7 Vibrational Energy Transfer and Energy "Pooling" in Adsorbate Layers: CO on NaCl***, S.A. Corcelli,* ***J.C. Tully,*** Yale University **INVITED**

Adsorbate vibrational excitations on insulator surfaces can be very long-lived if the adsorbate frequency is much greater than the Debye frequency of the solid. This allows time for vibrational excitations to resonantly hop among neighbors a great many times before de-excitation. Sometimes this will result in two adjacent adsorbate molecules both excited to v=1. As a result of anharmonicity, the state with one molecule in v=2 and one in v=0 has a slightly lower energy than both molecules in v=1. Similarly, 3 quanta of vibration shared by two neighboring adsorbate molecules produce a lower total energy if all 3 quanta reside on one of the neighbors. This produces a driving force for "pooling" of energy into highly excited molecules. This effect has been demonstrated dramatically by George Ewing and coworkers@footnote 1@ who observed population of vibrational levels as high as v=15 for CO on NaCl. We have developed a perturbation theory approach to calculate all of the operative rate processes; vibrational relaxation, resonant hopping, pooling, and radiation. We have used these rates in a kinetic Monte Carlo simulation of the energy pooling process. Our results are in qualitative agreement with experiment, and reveal interesting phenomena such as self-trapping and Ostwald ripening. In addition, we predict an enormous C-12/C-13 isotope effect. @FootnoteText@ @footnote 1@ H.-C. Chang and G. E. Ewing, Phys. Rev. Lett. 65, 2125 (1990).

11:00am **SS2-FrM9 HD Scattering on Cu (001): Rotationally Mediated Bound State Resonances and Evidence for Interaction of the Bound States with the Surface Phonons***,* ***L.V. Goncharova****, A.V. Ermakov, B.J. Hinch,* Rutgers University

Seeded HD molecular beams have been used to study the laterally averaged HD - Cu (001) physisorption potential by measurements of rotationally mediated bound state resonances (BSR). The physisorption well depth of 30.5 meV was confirmed using a Le Roy plot by combining our HD data with existing H@sub 2@ and D@sub 2@ data. The positions of all rotationally mediated bound state resonance energies are determined well by the results of calculations using different potentials. BSR energies from isotropic potential calculations are considerably higher than the experimentally determined energies, as well as those of the values calculated with an anisotropic potential. So the anisotropic part of the potential cannot be neglected. Calculations predict lower energy for m@sub J@ = 0, indicating that the molecule prefers to have its molecular axis perpendicular to the surface (cartwheel rotation). A considerable shift of the bound state levels in the presence of an adsorbate (chemisorbed hydrogen) is also observed. Resonance energies do not change with the surface temperature. The Debye-Waller analysis of the intensities and the widths of the resonance features show a coupling between the resonant states and surface phonons. The strongest coupling is for the states lower in the potential well.

Surface Science
Room 122 - Session SS3-FrM
Clean and Adsorbed Surfaces

Moderator: J.A. Yarmoff, University of California, Riverside

8:20am **SS3-FrM1 Structure and Electronic Properties of Planar and Faceted Ir(210)***,* ***I. Ermanoski,*** *M. Gladys, G.J. Jackson, T.E. Madey,* Rutgers, The State University of New Jersey*; J.E. Rowe,* U.S. Army Research Office

The atomically rough Ir(210) surface is morphologically unstable: When Ir(210) is covered with more than 0.6 ML of oxygen and annealed, pyramidal facets develop on the initially planar surface. We have used a variety of methods to investigate the structure and electronic properties of planar and faceted Ir(210), including LEED, STM and high resolution soft X-ray photoelectron spectroscopy (SXPS) using synchrotron radiation. To prepare an oxygen-free faceted surface, we use catalytic CO oxidation at ~500 K to react the oxygen off the pre-prepared faceted surface. Cleanliness is verified both by AES and TPD. LEED and STM experiments show that the faceted surface is entirely covered with 3-sided pyramidal facets with dimensions of several nanometers. HRSXPS has been employed to investigate core-level features of all the surfaces mentioned. The Ir 4f7/2 core levels are fitted with Doniach-Sunjic lineshapes. Surface and bulk peak identifications are supported by measurements at different photon energies (different electron escape depths) and variable photoemission angles. All of the surface components (first, second and third layer peaks) are identified with core-level shifts positioned at higher binding energies with respect to the bulk. This result is in contrast to previous reports of binding energy inversion on Ir(100) and Ir(111) surfaces. The adsorption of oxygen onto the planar Ir(210) surface causes a suppression and shifting of the surface features. A comparison of planar and faceted surfaces reveals only minor differences in the SXPS core-level spectra. The effect of metallic overlayers on the morphological stability of Ir(210) will also be discussed. Supported by US DOE and ARO.

8:40am **SS3-FrM2 Linking Stress to Surface Structure Using STM***,* ***G.E. Thayer***[1]*,* UC Davis and Sandia National Labs*; N.C. Bartelt, V. Ozolins,* Sandia National Laboratories*; A.K. Schmid,* Lawrence Berkeley National Lab*; S. Chiang,* University of California, Davis*; R.Q. Hwang,* Sandia National Laboratories

Understanding the role of stress at solid surfaces is necessary to determine why surfaces have particular structures. While significant progress has been achieved in considering how local elastic interactions might contribute to the total surface energy a nd structure, it had not been possible to explicitly confirm this experimentally. The main reason for this is the difficulty in measuring stress fields on surfaces. Here, our approach has been to directly measure strain fields on a surface arising from l attice mismatch. Studying the phase diagram of CoAg/Ru(0001) single-monolayer films using STM, we found that annealed Co-rich films form an alloy with a structure that is not atomically mixed but instead consists of Ag droplets (15-30 atoms in si ze) with in a Co matrix. To quantitatively answer the question of how surface stress contributes to the formation of this structure, we have directly probed the stress fields on the surface. Analysis of atomically resolved images of the CoAg alloy has allowed us t o perform strain measurements over the surface. In our analysis we have compared strain measurements of about 800 Co atoms in a wide variety of Co-Ag neighborhoods with calculations of strain resulting from the Frenkel-Kontorova (FK) model and first-princ iples local spin density approximation (LSDA) calculations. The close agreement between the measurements and the calculations explicitly shows how stress due to lattice mismatch contributes to the formation of the droplet structure of the alloy. Within th e framework of the FK model we determine the relative forces acting on the surface by the measurement of strain fields and we are able to provide a direct link between surface stress and surface structure. We find the agreement even allows for the determination of details such as elastic spring constants from experimental measurements. Our success firmly demonstrates the possibility of using atomically resolved STM data to investigate surface stress.

9:00am **SS3-FrM3 In-Situ STM Study of the Au(111) Herringbone Reconstruction Under Applied Stress***, O. Schaff,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*;* ***A.K. Schmid,*** Lawrence Berkeley National Laboratory*; N.C. Bartelt, J. de la Figuera, R.Q. Hwang,* Sandia National Laboratories

Surface stress is generally invoked as the driving force for the remarkably well-ordered and stable dislocation networks or reconstructions found in the surface layers of many epitaxial thin films, as well as in many metal single-crystal surfaces. To test this conjecture, the effect of uniaxial applied stress on dislocation networks present in the atomic surface layer of Au(111) was studied. The measurements were made using a novel instrument combining ultrahigh vacuum scanned-probe microscopy with an in-situ stress-strain testing machine. The technique provides microscopic information, up to atomic resolution, about the large-scale plasticity of surface layers under applied loads. The herringbone reconstruction of the Au(111) surface is a classic example of a strain stabilized dislocation network. We find that under 0.5% uniaxially applied compressive strain a dramatic restructuring of the network takes place. The three-fold orientational degeneracy of the system is removed and threading edge dislocations are annihilated. By considering the energetics of the herringbone reconstruction in the context of the Frenkel-Kontorova model, we are able to explain why these changes take place at this value of the applied strain.

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

9:20am **SS3-FrM4 Core Level Shifts and Stress at the Ni/W(110) Interface@footnote *@,** ***R.T. Franckowiak,*** Utah State University*; N.D. Shinn,* Sandia National Laboratories*; B. Kim, K.J. Kim, T.-H. Kang,* Pohang Light Source, South Korea*; D.M. Riffe,* Utah State University

Stress can play an important role in determining the structure and stability of heterogeneous interfaces. A recent STM and strain study@footnote 1@ of Ni overlayers on W(110) identified a pseudomorphic (1x1), and incommensurate (8x1) and (7x1) phases that exhibit compressive, tensile, and compressive stress, respectively. Interfacial electronic structure was suggested as the origin of the unexpected compressive stress in the (1x1) phase, rather than simple lattice mismatch in the adsorbed Ni film. This hypothesis was tested by measuring the W(4f) core-level binding energy shifts of interfacial W atoms during Ni overlayer growth. Photoemission spectra were obtained at the National Synchrotron Light Source, Brookhaven National Laboratory, using photon energies between 60 at 110 eV at a resolution of 150 meV. For the compressive pseudomorphic phase, interface W atoms exhibit a shift (compared to the bulk W) of -210 meV, whereas the 8x1 and 7x1 phases induce much smaller shifts of -90 and -120 meV, respectively. These shifts, which cannot be interpreted in terms of simple W-Ni coordination arguments, suggest that the interface tungsten electronic structure is very different in the pseudomorphic phase compared to the denser phases, and thus may be the source of the stress observed in the pseudomorphic phase. The similar W(4f) shifts in the 8x1 and 7x1 phases, which exhibit tensile and compressive stress, indicate that these stresses result from the Ni adlayer, as is expected from simple strain arguments based on the bulk Ni lattice constant. @FootnoteText@ @footnote 1@D. Sander, C. Schmidthals, A. Enders, and J. Kirschner, Phys. Rev. B 57, 1406 (1998). @footnote *@Supported by the DOE-BES Division of Materials Sciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

9:40am **SS3-FrM5 Metal Nucleation and Adhesion on Ionic-Oxide Terraces*,** ***D.R. Jennison,*** Sandia National Laboratories*; A. Bogicevic,* Ford Research Laboratory*; A.E. Mattsson,* Sandia National Laboratories

We present two topics: First, it has recently been proposed@footnote 1@ that oxide surfaces with a substantial number of oxygen vacancies may show greatly increased adhesion. It has also been observed that metal islands nucleate not only at line defects, but also on oxide terraces. Using first-principles DFT, we previously@footnote 2@ studied the Pt dimer on MgO(100), and found that neither the O nor the Mg vacancy increased its stability, and in fact the dimers were only marginally stable at room temperature. We have now extended this study to include the dimers of eight different metals, both on the clean surface and at the O vacancy. We find that not all metals behave similarly! In fact, the dimers of Ag and Au are much more tightly bound on the clean surface than are those of Pd or Pt, and actually increase their stability at the defect. We understand these results based on dimer electronic structure. The second topic concerns the accuracy of DFT for studies of metal/oxide interfaces where the metal binds mostly by polarization, i.e. where there are no significant chemical bonds. This bonding is much stronger than van der Waals and it is measurable by analysis of the Wulff shapes of metal nanoparticles.@footnote 3@ In the cases of Pd and Cu on alumina films, DFT in the LDA predicts a work of adhesion close to experiment,@footnote 3@ while the GGA fails badly (and differs by about 50%). We have now understood this unusual failure of GGA in terms of the surface self-exchange error in DFT, as evidenced recently for another metal.@footnote 4@ In fact, the experimental result, vs. the computational numbers, supports our previous assertion@footnote 5@ that the interfacial binding of most metals on ionic oxides is mainly due to polarization. @FootnoteText@@footnote 1@Y. F. Zhukovskii, et al., PRL 84 (2000) 1256. @footnote 2@A. Bogicevic and D. R. Jennison, Surf. Sci. 437 (1999) L741. @footnote 3@K. H. Hansen, et al., PRL 83 (1999) 4120; T. Worren et al., Surf. Sci. 477 (2001) 8. @footnote 4@K. Carling, et al., PRL 85 (2000) 3862. @Footnote 5@C. Verdozzi, et al., PRL 82 (1999) 4050; A. Bogicevic and D. R. Jennison, PRL 82 (1999) 799. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000; www.sandia.gov/surface_science/drj/.Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000; www.sandia.gov/surface_science/drj/.

10:00am **SS3-FrM6 Structure Analysis of Oxygen-adsorbed and Annealed W(001) Surface at Liquid Nitrogen Temperature***, S. Kamimizu, K. Hara, T. Kokubun, T. Haga, K. Sakamoto,* ***H. Yamazaki,*** The University of Electro-Communications, Japan

The structure of oxygen-adsorbed and annealed W (001) surface was investigated at the liquid nitrogen temperature. We have already reported the structure of this system at the room temperature (H. Yamazaki, et al., Surf. Sci. 447 (2001) 174). The result obtained previously is that the 2x1 LEED pattern was observed, and the most probable calculated structure consists of missing rows of W and double rows of oxygen atoms adsorbed on one of two three-hold hollow sites of W (011) facet which was appeared by losing the W-atoms. The Pendry R-factor for this structure is 0.25. As the energy difference between those two three-hold hollow sites is so small as 12 meV by a rough calculation, the adsorbed oxygen atoms should occupy those two sites by a certain ratio. It is considered that the oxygen atoms fall into the more stabilized adsorption site when the sample is cooled down to the liquid nitrogen temperature. Then the experiment was performed on the same sample at the liquid nitrogen temperature, and the most probable structure was determined with the Pendry R-factor of 0.20. The structure agrees well with that at the room temperature within an error. We will present the experimental and calculating procedure, and the most probable structure compared with that at the room temperature.

10:20am **SS3-FrM7 The Local Adsorption Structure of CH@sub 3@- on Cu(111)***, M. Pascal, C.L.A. Lamont,* University of Huddersfield, UK*;* ***J. Robinson****, R.L. Toomes, J.-H. Kang, D.P. Woodruff,* University of Warwick, UK*; L. Constant, S. Bao, M. Kittel, J.-T. Hoeft, M. Polcik,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Methyl is an important intermediate in many surface reactions, but there is a dearth of information on its local adsorption geometry. We present the results of both experimental and theoretical studies of the structure of CH@sub 3@- on Cu(111). The experiments were based on C 1s scanned-energy mode photoelectron diffraction (PhD) from a surface formed either by exposure to CH@sub 3@- ions from a Bent-type azomethane (CH@sub 3@-N-N-CH@sub 3@) cracking source, or from surface dissociation of methyl iodide (CH@sub 3@I) on the surface. The coadsorbed I , which occupies the fcc hollow sites (directly above a third layer Cu atom) appears to have little effect on the geometry of the methyl which also occupies an fcc hollow site but shows a marginally (0.04±0.03 Å) smaller layer spacing relative to the substrate in the presence of the coadsorbate. In the pure methyl layer the C-Cu outermost layer spacing is 1.66±0.02Å. Density-functional theory results (using the CASTEP code in GGA with ultrasoft pseudopotentials) reproduce the preference for hollow site adsorption (albeit with a very small preference for the hcp hollow) but also reveal a strong preference for an azimuthal orientation in which the C-H bonds are oriented along the Cu-Cu close packed directions, placing the H atoms closer to near-neighbour Cu atoms.

10:40am **SS3-FrM8 Cu(100)c(2x2)-N: a New Type of Adsorbate-Induced Surface Reconstruction***, S.M. Driver,* University of Warwick, UK*; J.-T. Hoeft, M. Polcik, M. Kittel, R. Terborg,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; R.L. Toomes, J.-H. Kang,* ***D.P. Woodruff,*** University of Warwick, UK

Using a combination of N 1s scanned-energy mode photoelectron diffraction and scanning tunnelling microscopy the Cu(100)c(2x2)-N surface is shown to undergo a symmetry-lowering reconstruction with a large amplitude (0.34 Å) periodic distortion of the outermost Cu layer perpendicular to the surface. This contrasts with the more usual surface layer density changes or parallel distortions which are the primary characteristic of other metal surface reconstructions. Atomic resolution imaging under varying tip conditions shows that in the c(2x2) phase STM appears to always image as asperities the Cu atoms, and not the N atoms, and that the N induces the unusual rumpling of the outermost Cu layer. This structural modification is quantified by the PhD data. Our STM images also provide a clear demonstration of the dangers of an over-simplistic interpretation of such data in terms of adsorbate atomic coordinates. The presence of the rumpling reconstruction, which we attribute to N-induced compressive surface stress, allows one to understand many detailed aspects of the mesoscopic c(2x2) island structures observed in this system (and reported in earlier STM investigations). Not only can the general self-organisation be attributed to the minimisation of the long-range elastic strain field energy, but similar elastic strain arguments arising from local rumpling can account for the N-N attraction needed for the island formation. In addition, the symmetry-lowering nature of the reconstruction provides a simple explanation for the systematic width variations of the inter-island boundaries.

11:00am **SS3-FrM9 Phases of Oxygen on Cu(100) Imaged by Low Energy Electron Microscopy**, ***C.L.H. Devlin,*** Air Force Research Laboratory, U.S.*; Y. Sato, S. Chiang,* University of California, Davis

Low energy electron microscopy (LEEM) was used to perform a detailed study of three phases of oxygen on the Cu(100) surface, including two new phases. These phases occurred when the sample was heated above 600°C. Dark field imaging was used to identify regions corresponding to particular low energy electron diffraction (LEED) patterns. The structure of the steps was also examined in the LEEM images of the different phases. At low coverage, the familiar (@sr@2x2@sr@2)R45° structure was observed. When annealed to 600°C, the steps changed from being gently curving to being highly bunched and completely straight with 90° kinks, resulting from a disorder-order transition. At higher oxygen coverage, <1.8ML, a new, complicated LEED pattern emerged, consisting of the (@sr@2x2@sr@2)R45° pattern plus a centered rectangular structure. Images of this surface included decoration of step edges and bright, sometimes hatched, areas on the terraces. Distinct bunching of steps, which curved gently over many microns, occurred. At higher coverage, <3.2ML, another new LEED pattern occurred. The "12-spot" hexagonal pattern corresponds to a hexagonal phase with two domains. The lattice constant of this structure agrees well with that for Cu@sub 2@O, suggesting that this phase corresponds to multilayers of cuprous oxide. LEEM imaging was used to follow structural transitions among the three phases.

11:20am **SS3-FrM10 Temperature Dependence of Oxides on Titanium Surface in UHV**, ***Y. Mizuno,*** Chiba Institute of Technology, Japan*; A. Tanaka,* ULVAC-PHI, Inc.*; Y. Takakuwa,* Tohoku University, Japan*; T. Momose,* Miyagi National College of Technology, Japan*; Y. Yamauchi,* Chiba Institute of Technology, Japan*; T. Homma,* Chiba Institute of Technology

It is well known that titanium has a good ability to passivate a surface, and as a result to exhibit a high degree of immunity against attack by acids and chlorides, although the titanium surface is very active such as a gettering property. Titanium has stable oxides which are Ti@sub 2@O, TiO, Ti@sub 2@O@sub 3@, Ti@sub 2@O@sub 5@, Ti@sub n@O@sub 2n-1@(4<n<38) and TiO@sub 2@. The temperature dependence of titanium oxides was investigated in-situ with using Auger electron spectroscopy (AES) with quadrupole mass spectrometer (QMS) and X-ray photoelectron spectroscopy (XPS) at a temperature range RT-500 °C. The surface of specimen was prepared by electro-polishing, and on the surface thin titanium oxide layer was formed, although the oxide was mainly TiO@sub 2@. As the temperature of titanium surface increases, over 300 °C, O@sub KLL@ Auger intensity decreases in a drastic way, and in contrast Ti@sub LMM@ Auger intensity increases. Over 450 °C, no oxygen was detected on titanium surface in UHV. However, outgassing rates of O@sub 2@, CO, and CO@sub 2@ from the titanium surface did not show large changes in QMS measurements below 450 °C. This behavior is explained such as a gettering property, which is an enhancement diffusion of oxygen from a surface to bulk. In order to investigate temperature dependence on the chemical states of titanium, XPS analysis was performed in-situ at a temperature range between RT - 500 °C. The results showed drastic changes of titanium oxides which the suboxides began to decrease at 150 °C, even the amount of TiO@sub 2@ decreasing over 200 °C. Titanium has a very sensitive oxide surface depending on temperature in UHV.

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