Monday Morning, October 2, 2000

Biomaterial Interfaces
Room 202 - Session BI+SS-MoM

Biological Surface Science

Moderator: D.G. Castner, University of Washington

8:20am **BI+SS-MoM1 Suspended Lipid Bilayers on Porous Alumina Surfaces***, **C. Steinem**, J. Drexler, C. Hennesthal,* WWU Muenster, Germany

The study presents a new class of artificial membrane system "suspended bilayers" closing up the gap between solid supported membranes (SSMs) and black lipid membranes (BLMs). Suspended bilayers were prepared on the basis of porous alumina surfaces which were produced by an anodic etch of neat alumina foils. Gold was evaporated on the upper surface of the porous material. The porous material was characterized by scanning electron microscopy (SEM), scanning force microscopy (SFM) and impedance spectroscopy. As revealed by SEM and SFM pores exhibit a mean diameter of 65 nm. Functionalization of the upper gold surface was achieved by self assembly of 3-mercaptopropionic acid (MPA) rendering the surface negatively charged at pH 8.6. To obtain suspended solid supported we fused unilamellar vesicles of N,N-dimethyl-N,N-dioctadecyl ammonium bromide varying in their sizes on the MPA-covered surface. Bilayer patches spanning the pores were visualized by scanning force microscopy in buffer using contact mode. The bilayer covered nanopores are thought to serve as second aqueous compartments of femtoliter volume providing enough space to incorporate transmembrane proteins and to generate ion gradients across the membrane together with the ability to use sensitive surface analysis tools.

8:40am **BI+SS-MoM2 Formation and Characterization of Stabilized Supported Phospholipid Bilayers***, **S. Saavedra**, E. Ross, J. Conboy, S. Liu, D.F. O'Brien,* University of Arizona

The utility of phospholipid bilayers as non-fouling coatings in molecular device technologies is hampered by the chemical and mechanical instability of these structures relative to (for example) alkylsiloxane self-assembled monolayers. Towards the use of lipid bilayers in applications such as biosensing, we have investigated two-dimensional polymerization as a strategy to stabilize planar supported lipid bilayers. UV-induced and redox-initiated polymerization have been used to prepare air-stable bilayers from phosphatidylcholine monomers containing sorbyl moieties in the acyl chains. Preparation of these structures using Langmuir-Blodgett-Kuhn and vesicle fusion techniques, and characterization of their physical and chemical properties, including nonspecific protein adsorption behavior, will be described.

9:00am **BI+SS-MoM3 Regulating Molecular Recognition and Self-assembly via Mechanical Forces: The Cell Adhesion Protein Fibronectin at Phospholipid Interfaces***, A. Krammer, G. Baneyx, D. Craig,* University of Washington*; K. Schulten,* University of Illinois at Urbana-Champaign*; **V. Vogel**,* University of Washington **INVITED**

While major progress has been made in the past to reveal how chemical factors regulate biorecognition, insight into pathways by which nature utilizes external forces to regulate biorecognition and signaling holds the potential for major new discoveries in biomedicine. Knowledge in this field is rudimentary since high-resolution crystallographic structures of biomolecules have mainly been obtained from equilibrated states. The role played by mechanical forces applied to the terminal ends of domains in regulating exposure of their recognition sites will be discussed here for the multidomain protein fibronectin. One of fibronectins many functions is to promote cell adhesion to surfaces. Starting from the equilibrium structure of fibronectin type III domains (FnIII), steered molecular dynamics simulations were applied to study the pathway by which their tertiary structures unravel under external forces. First we found that the accessibility of the cell recognition site on the FnIII10 domain, i.e. the RGD-loop, to integrins is reduced in an early stage of the forced unfolding pathway. Furthermore, forced unfolding studies of various fibronectin type III modules have shown that FnIII-7, FnIII-8, FnIII-9 and FnIII-10 differ considerably in their mechanical stability, and the simulations predict that FnIII-10 unfolds first. Finally, we have experimentally analyzed the pathway on which fibronectin assembles into fibrillar networks underneath phospholipid monolayers, and find again that mechanical forces are crucial to initiate its spontaneous self-assembly. Thus, spontaneous assembly of fibronectin into fibrils cannot be induced by adsorption to solid surfaces, yet it is the fibrillar state that allows cells to apply the forces needed to partially unfold fibronectin's domains.

9:40am **BI+SS-MoM5 New Methods for Patterning Fluid Lipid Bilayer Membranes on Solid Supports***, **J.S. Hovis**, S.G. Boxer,* Stanford University

Two new methods are introduced for patterning fluid lipid bilayer membranes on solid supports. These methods, called blotting and stamping, rely on the observation that supported lipid bilayers exhibit self-limiting lateral expansion. The consequence is that it is possible to pattern these fluid surfaces without modifying the underlying substrate. Together these methods constitute a simple and powerful approach for preparing patterned fluid lipid bilayers in nearly any geometry. One important application of these methods is the ability to create composition arrays of lipids and membrane associated proteins. These arrays allow the opportunity to study lipid-lipid, lipid-protein, and/or protein-protein interactions in a parallel fashion. Information gained about these important biological interactions will be highlighted.

10:00am **BI+SS-MoM6 The Interaction of Phospholipid Vesicles with Binary Alkanethiol/Hydroxythiol Monolayers***, **V. Silin**,* National Institute of Standards and Technology*; H. Wieder,* Max Planck Institute for Polymer Research, Germany*; J. Woodward, A. Plant,* National Institute of Standards and Technology

Surfaces modified by self-assembly have applications in sensors, diagnostics, chemical processing, and biomaterials, where they may incorporate features such as molecular recognition and enzymatic activity. Understanding the forces that direct self-assembly of biologically important molecules in predictable arrangements will aid the development of such applications. The focus of this study is a mimic of biological membranes formed by the interaction between two self-assembled systems: phospholipid amphiphiles that associate into bilayer vesicles in water, and monolayers of alkanethiols on metal surfaces. We have studied the interaction of small (60nm) POPC vesicles with binary thiol monolayers of known surface free energy. The surfaces were prepared on gold by self-assembly from binary solutions of the thiols CH3-(CH2)10-X (X = CH3; OH) in THF. The surface plasmon resonance (SPR) technique was utilized to follow the vesicle fusion kinetics and to characterize the resulting assemblies. A dramatic influence of the surface layer composition on the formation of POPC films was observed. The formation of an additonal POPC monolayer was detected only on the completely hydrophobic (100% CH3) surface. The largest thickness of POPC layer was detected at a CH3/ OH ratio of 50% (in the assembly solution). For the completely hydrophilic surface (100 % OH) the POPC layer thickness was found to be close to the thickness of a phospholipid bilayer. Thus, the increase of hydrophilic component on the surface leads to the formation of an unordered POPC film that seems to contain a mix of fused and unfused vesicles. Most likely the formation of an ordered bilayer of POPC molecules has been observed for the completely hydrophilic surface. The SPR data were supported by AFM, capacitance and contact angle measurements.

10:20am **BI+SS-MoM7 Formation of 2D Crystals of Proteins on Solid Supports, and Their Application for Immobilizing Molecules or Particles***, **A.D.R. Brisson**,* University of Groningen, The Netherlands **INVITED**

The immobilization of molecules or particles on solid supports constitutes a central issue in various fields, eg. the immobilization of enzymes in the biosensor area, or the immobilization of DNA molecules on microarrays in genomics. Existing technologies rely mainly on the chemical modification of solid surfaces and the subsequent immobilization of the molecules of interest via non-specific interactions. The strategy we have selected is based on the use of functionalized 2D crystals of proteins formed on solid-supported lipid bilayers (SPBs) as a matrix for anchoring proteins/particles in a specific manner. Its main potential advantages are the wide panoply of functional groups that could be introduced in proteins, the well-known chemistry of the coupling reactions involved, the well-defined density of anchoring groups, and the specificity of the coupling reactions ensuring an oriented binding of bound molecules. In addition, protein 2D crystals could serve as templates for creating ordered arrays of immobilized particles, at the nanometer scale. The formation of SPBs by fusion of lipid vesicles on mica,@footnote 1@ and the growth of protein 2D crystals on SPBs were extensively studied by AFM and Electron Microscopy (EM) in the case of two protein systems, annexin V@footnote 2@ and streptavidin. Pre-formed 2D arrays of modified annexin molecules were used for immobilizing proteins, liposomes, and membrane fragments containing membrane proteins. An unexpected result was the induced ordering of membrane proteins resulting from their specific binding to an ordered protein matrix. On the other hand, while close-packed assemblies of liposomes could be bound to protein 2D arrays, attempts to fuse them into suspended lipid bilayers have yet been unsuccessful. The immobilization of inorganic particles is under investigation. Results of these studies will be presented. @FootnoteText@@footnote 1@Reviakine et al. Langmuir 16, 2000, 1806. @footnote 2@Reviakine et al. J. Struct. Biol. 121, 1998, 356.

Semiconductors
Room 306 - Session SC1+EL+SS-MoM

Chemistry of Silicon Oxides and Nitrides

Moderator: E. Cartier, IBM

8:20am **SC1+EL+SS-MoM1 Atomic-Order Thermal Nitridation of Si(100) and Subsequent Epitaxial Growth of Si***, **T. Watanabe**, M. Sakuraba, T. Matsuura, J. Murota,* Tohoku University, Japan

Atomic-order nitridation by NH@sub 3@ on Si(100) and subsequent Si growth by SiH@sub 4@ were investigated using an ultraclean low-pressure CVD system with a Xe flash lamp. Thermal nitridation on Si(100) at 400°C in an NH@sub 3@ environment with and without the flash lamp light irradiation is explained by Langmuir-type physical adsorption of NH@sub 3@ and nitridation by the adsorbed NH@sub 3@. The nitridation can be enhanced by Xe flash lamp light irradiation, and the N atom concentration tends to saturate to about 2.7x10@super 15@ cm@super -2@. In the Si deposition on the ultrathin silicon nitride, it is found that N desorption from the Si nitride films hardly occurs, and Si grew on silicon nitride, whose N atom concentrations are from about 2x10@super 14@ cm@super -2@ to about 2.7x10@super 15@ cm@super -2@, at 385°C in an SiH@sub 4@ environment with and without the flash lamp light irradiation. The incubation period of Si growth is observed and increases with increasing N atom concentration of the silicon nitride film. On the silicon nitride of N atom concentration of about 2x10@super 14@ cm@super -2@, the incubation period is hardly observed and it is found by RHEED measurements that Si epitaxially grew. Layer-by-layer growth control of silicon nitride is proposed by combining atomic-order nitridation on Si and atomic-layer growth of Si on the silicon nitride.

8:40am **SC1+EL+SS-MoM2 The Role of Inter-dimer Interactions in NH@sub 3@ Dissociation on Si(100) - (2 x 1)***, K.T. Queeney,* Smith College*; K. Raghavachari, **Y.J. Chabal**,* Bell Laboratories, Lucent Technologies

The chemistry of gas-phase precursors to film growth on the Si(100) surface in ultrahigh vacuum is often well-described by localized interaction of the adsorbate with a single Si-Si dimer.@footnote 1@ However, our combined experimental and theoretical studies of the dissociation of NH@sub 3@ to form NH@sub 2@-Si-Si-H on this surface reveal that this reaction is in fact governed by a complex set of inter-dimer interactions involving both bare and adsorbate-covered Si dimers. External transmission FTIR spectroscopy allows us to probe both the lower-frequency @delta@(NH@sub 3@) modes of metastable, undissociated NH@sub 3@ and the higher-frequency @nu@(SiH) modes resulting from dissociation. By comparing our experimental results with density functional calculations describing two-dimer clusters, we find that the vibrational spectra can only be interpreted when inter-dimer effects are considered. Specifically, while hydrogen bonding between undissociated NH@sub 3@ and dissociated NH@sub 2@ species renders coupling of adjacent nitrogen-containing groups thermodynamically favorable, kinetic control of the dissociation process yields a predominance of the opposite configuration, resulting from the influence of dissociated species on the buckling of neighboring bare dimers during adsorption. We propose that such adsorbate-induced effects on the electronic structure of neighboring dimers may have general implications for controlling the two-dimensional ordering of reactions on the dimerized Si(100) surface. @FootnoteText@ @footnote 1@ See for example: R. Konecny and D. J. Doren, J. Chem. Phys. 1997, 106 (2426); B. B. Stefanov and K. Raghavachari, App. Phys. Lett. 1998, 73 (824).

9:00am **SC1+EL+SS-MoM3 Quantum Chemical Study of Silicon Nitride Deposition Using Ammonia***, **Y. Widjaja**, C.B. Musgrave,* Stanford University

Density functional theory is used to examine the reaction mechanisms of nitridation of the Si(100)-2x1 surface by NH@sub 3@. The surface is modeled using the cluster approximation. A detailed reaction mechanism is investigated including ammonia adsorption and decomposition, insertion of N into Si-Si bonds, and H@sub 2@ desorption. We find that nitrogen prefers to be in the subsurface layer, bonded to three Si atoms. The energy barriers leading to the nitridation of the Si(100) surface are also calculated. The activation barrier of the rate limiting step is found to be higher than the activation barrier for NH@sub 3@ desorption. This confirms the experimental observation that a large fraction of the NH@sub 3@ that dissociates on adsorption will recombine and desorb. Furthermore, we have also calculated the vibrational frequencies of various surface nitride structures. The computed frequencies are then compared with the experimental HREELS spectra. The comparison further allows the unambiguous characterization of the surface species. Using the calculated barriers and frequencies we use transition state theory to estimate a rate for nitridation of the (100) silicon surface. We investigate the validity of the cluster approximation and find that bigger cluster models are necessary to describe the nonlocal electronic effects.

9:20am **SC1+EL+SS-MoM4 Thermal Nitridation of Ultrathin Silicon Dioxide Films Using NH@sub 3@ Gas***, **O. Jintsugawa**, M. Sakuraba, T. Matsuura, J. Murota,* Tohoku University, Japan

Nitrided ultrathin SiO@sub 2@ film is attractive as the gate insulator of future MOS devices. In this work, thermal nitridation of thin SiO@sub 2@ films and transport of nitrogen species into SiO@sub 2@ films were investigated. A 30Å-thick SiO@sub 2@ film on Si(100) was formed by wet oxidation at 700°C , and was thermally nitrided for 90min at 750-850°C in NH@sub 3@ gas at 100Pa using an ultraclean low-pressure CVD system. The depth profile of N atom was obtained by the repetition of etching by a 1%-diluted HF solution and XPS measurements. By the thermal nitridation, most of the N atoms were present near the SiO@sub 2@ surface and the N atom concentration was remarkably lower (1/2 and 1/10 at 850 and 750°C, respectively) than that of the nitrided Si surface without the SiO@sub 2@ film. By 850°C nitridation, N atom diffused into the SiO@sub 2@ film and Si substrate nitridation were observed. The N atom concentration was estimated to be 4x 10@super 15@cm@super -2@ on the SiO@sub 2@ surface, 1x10@super 21@cm@super -3@ in the SiO@sub 2@ film, and 8x10@super 13@cm@super -2@ at the SiO@sub 2@/Si interface. Binding energy of N 1s at the SiO@sub 2@ surface and in the SiO@sub 2@ film was shifted 2eV-higher than that at the SiO@sub 2@/Si interface. By 750°C nitridation, the N atom concentration on the SiO@sub 2@ surface was 3x10@super 14@ cm@super -2@ and, in the SiO@sub 2@ film and at the SiO@sub 2@/Si interface, the N atom concentration was less than the detection limit (about 3x10@super 20@cm@super -3@ and 4x10@super 12@cm@super -2@, respectively). This result indicates that the existence of surface oxygen more greatly suppresses the reaction of NH@sub 3@ at the lower temperature. Pressure and time dependence of nitridation on the SiO@sub 2@ surface, in the SiO@sub 2@ and at the SiO@sub 2@/Si interface will be also presented.

9:40am **SC1+EL+SS-MoM5 Probing the Chemistry of Dielectric Thin Film Growth on Si Surfaces***, L.D. Flores, **J.E. Crowell**,* University of California, San Diego **INVITED**

The surface and gas phase chemistry involved during dielectric thin film growth of doped and undoped silicon dioxide has been studied using the atmospheric pressure reaction between tetraethoxysilane (TEOS) and ozone. The studies involve low temperature deposition of dielectric thin films using a new atmospheric-pressure chemical vapor deposition (APCVD) reactor utilizing a commercial injector / vent assembly. The APCVD reactor is coupled to a N@sub 2@-purged glovebox and a UHV surface analysis facility equipped with XPS, AES, TPD, and IR spectroscopy capabilities. Gas-phase transmission FTIR spectroscopy measurements were performed in-situ during deposition at 400°C by probing the variable gap region between the 400°C heated Si wafer and the injector. The primary products produced upon reaction of TEOS and ozone are acetic acid, formic acid, formaldehyde, carbon monoxide, carbon dioxide, and water. Reaction of TEOS and oxygen in the gas phase is negligible compared to reactions involving ozone at identical temperatures under these conditions. Potential TEOS / O@sub 3@ reaction products and their reaction with boron and phosphorus containing dopant sources has been investigated in order to clarify their role in the oxidation process and to clarify the chemical mechanism. This was accomplished by following the reaction with ozone of some possible and observed ozonation products in a flow reactor / gas cell using transmission FTIR spectroscopy. The products of acetaldehyde ozonation are shown to be different from pathways leading to acetic acid production during TEOS ozonation. Mechanistic pathways unique to Si-O-C containing species will be presented. The products formed upon introduction of boron and/or phosphorus containing precursors to the process flow will also be discussed.

10:20am **SC1+EL+SS-MoM7 Thickness Control of an Ultrathin Oxide Film on Si(100)2x1 Synthesized by Ozone: A Kinetic Study on Initial Oxidation***, **K. Nakamura**, A. Kurokawa, H. Itoh, S. Ichimura,* Electrotechnical Laboratory, Japan

One of the alternative oxidants for the fabrication of an ultrathin silicon oxide film is ozone. Using highly concentrated ozone, we have succeeded so far in synthesizing an oxide film of 2nm on Si(100) at lower substrate temperature (for example, at 350°C). This oxide film has high density equivalent to that of a thermally grown oxide, much smaller thickness of structural transition layers, and can be obtained also by modifying and upgrading an already existing native oxide film.@footnote 1,2@ Moreover, the oxide thickness must be precisely and accurately controlled because of its practical use as a gate oxide film in MOSFET. In this paper, therefore, we will study growth kinetics of initial oxidation by ozone on silicon surfaces in detail. To fabricate an ultrathin silicon oxide film by ozone, clean Si(100)2x1 surfaces at between room temperature and 700°C were exposed to highly concentrated (>80%) ozone. Initial oxide growth was mainly monitored by x-ray photoelectron spectroscopy (XPS). The results indicate different kinetics on each oxide layer. Following to an adsorption on the surface investigated also by second harmonic generation (SHG), oxide growth on each of the first three oxide layers proceeded in accordance with Langmuir kinetics, indicating random adsorption on the active sites on each layer. Within this thickness, oxidation rates on the second and third layers possessed positive values of activation energy, while the growth rate on the first layer showed no activation barrier. Above this thickness, an oxide film by ozone grew in proportion to exposure time instead above the critical substrate temperature of 550°C. These suggest that control of film thickness should be optimized in the first three layers and above the fourth, respectively, due to different growth mechanisms. @FootnoteText@ @footnote 1@ K. Nakamura, S. Ichimura, A. Kurokawa, K. Koike, G. Inoue, and T. Fukuda, J. Vac. Sci. Technol. A 17 (1999) 1275. @footnote 2@ A. Kurokawa, K. Nakamura, S. Ichimura, and D. W. Moon, Appl. Phys. Lett. 76 (2000) 493.

10:40am **SC1+EL+SS-MoM8 FTIR at Liquid/Solid Interfaces: In-situ Studies of HF Etching of SiO@sub 2@ on Si(100)***, **K.T. Queeney**,* Smith College Department of Chemistry*; E.E. Chaban, Y.J. Chabal,* Bell Laboratories, Lucent Technologies

While much important semiconductor surface chemistry--cleaning, passivating and etching--takes place at the liquid/solid interface, the inherent difficulty of probing such interfaces has limited mechanistic understanding of these processes. We have developed a novel experimental setup that allows us to probe semiconductor/liquid interfaces with FTIR spectroscopy, circumventing the limitations of conventional multiple internal reflection spectroscopy to access the full frequency range of interest (850-4000 cm@super -1@), in particular the Si-O vibrational modes between 900 and 1250 cm@super -1@. We have used this capability to study in detail the etching in dilute hydrofluoric acid of SiO@sub 2@ on Si(100), lending new and valuable insight into the details not only of the chemical nature of the Si/SiO@sub 2@ interface, but also of structural aspects of the remainder of the film, including the SiO@sub 2@/air (water) interface. By analyzing spectra acquired sequentially during the etching process, we derive a layer-by-layer picture of the oxide spectral response; correlation of those spectra with changes in film structure are made via optical modeling. Varying the dielectric constant of the overlying medium (i.e. air versus water) allows quantification of spectral sensitivity to effects such as surface roughness. In addition, the in-situ nature of these studies allows us to evaluate the kinetics of the etching process and provides strong evidence for a structurally distinct layer near the Si(100) substrate, characterized by a marked change in vibrational signature, that is resistant to etching.

Surface Science

Room 208 - Session SS1-MoM

Atomic-Scale Studies of Model Catalysts

Moderator: S.H. Overbury, Oak Ridge National Laboratory

8:20am **SS1-MoM1 STM Study of H - Al (111): From Alane-Formation Reactions to Absorption-Induced Roughening***, **M. Noh**, J.E. Reutt-Robey,* University of Maryland

We investigated the reaction of atomic hydrogen with Al (111) with STM under UHV conditions. We show that hydrogen reacts strongly with the substrate to form aluminum hydride oligomers (alanes) which are stable up to ~350K. At lower reaction temperatures (T< ~230K), the distribution of surface alanes is highly nonuniform, with one dimensional strings of alanes extending for thousands of Å. These strings act as mass barriers that direct the distribution of later-form alanes. The alane strings run roughly parallel to crystallographic steps and exhibit a terrace-width-dependent nucleation. We discuss the physical origin of these intriguing reaction patterns. These surface reactions are accompanied by hydrogen absorption. Subsurface hydrogen is sensed indirectly by regions of increased surface roughness that can eventually leads to delamination. * Supported under NSF contract DMR-9632521 and CHE-9800470.

8:40am **SS1-MoM2 Dynamic Imaging and Chemical Probing on the Atomic Scale: NO/H@sub 2@ and NO@sub 2@/H@sub 2@ on Pt***, T. Visart de Bocarm@aa e@, T. Baer, C. Voss, **N. Kruse**,* Universit@aa e@ Libre de Bruxelles, Belgium

The reaction of NO and NO@sub 2@ with hydrogen has been studied on a Pt single crystal using field ion microscopy (FIM) and atom-probe field ion mass spectrometry (APFIMS) under conditions of applied temperatures (395-530 K), pressures (10@super -4@ - 10@super -2@ Pa) and field strength (8.7 V/nm). The 3D-Pt sample ("field emitter tip") has been found to undergo a transformation from a nearly hemispherical shape into a top- and edge-truncated pyramid. Kinetic instabilities, including rapid ignition and oscillations, were found for both reactions on this reshaped crystal. Video-FIM (time resolution: 20ms) revealed the rough areas lying between the (001) top plane and the (111) slopes of the pyramid to be catalytically most active. Catalytic ignition to water production was seen to occur in (012) areas with subsequent wave propagation either predominantly along the (for NO/H@sub 2@) or along the zone lines (for NO@sub 2@/H@sub 2@). Thus in either case a strongly anisotropic reaction behavior was observed. Under oscillatory conditions the catalytic cycles lasted for several 100ms only. The local chemical analysis of (012) and (133) planes (comprising several ten Pt atoms) demonstrated the formation of water product (desorption as H@sub 2@O@super +@ and H@sub 3@O@super +@) during the catalytic cycles. Major amounts of NO@sub x@@super +@ were registered due to surface diffusion of either NO or NO@sub 2@ into sites emptied by either reaction. Moreover, the mass spectrometric results strongly suggest NO@sub x@@super +@ to be the imaging species at otherwise rather low field strengths.

9:00am **SS1-MoM3 STM Studies on Model Systems Relevant for Catalysis***, **F. Besenbacher**,* University of Aarhus, Denmark **INVITED**

Scanning tunneling microscopy (STM) has proven to be a fascinating and powerful technique in the field of surface science. The fact that sets STM apart from most other surface sensitive techniques is its ability to resolve single atoms and molecules on surfaces and furthermore to reveal the dynamics of surface processes by recording many sequential STM images with a fast-scanning, variable-temperature STM.@footnote1@ In this talk I will show how STM can be used in the design of new catalysts. More specifically, I will show how STM studies have lead to the design of new alloy catalysts for the steam reforming reaction,@footnote 2@ to atomic-scale information on the sintering of Pt nanoclusters promoted by hydrogen,@footnote 3@ and to a new insight into the morphology and edge structures of MoS@sub 2@ nanoclusters, which are of interest as model systems for hydrodesulfurization catalysts.@footnote 4@ @FootnoteText@ @footnote 1@ F. Besenbacher, Scanning Tunneling Microscopy studies of metal surfaces, Reports on Progress in Physics 59 (1996)1737 @footnote 2@ F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A. Molenbroek, J.K. Norskov and I. Stensgaard, Design of a surface alloy catalyst for steam reforming, Science 279 (1998) 1913 @footnote 3@ S. Horch, H.T. Lorensen, S. Helveg, E. Lagsgaard, I. Stensgaard, K.W. Jacobsen, J.K. Norskov and F. Besenbacher, Enhancement of surface self-diffusion of platinum atoms by adsorbed hydrogen, Nature (1999) 134 @footnote 4@ S. Helveg J.V. Lauritsen, E. Lagsgaard, I Stensgaard, J.K. Norskov, B.S. Clausen, H. Topsoe and F. Besenbacher, The atomic-scale structure of single-layer MoS@sub 2@ nanoclusters, Phys.Rev. Lett. 84 (2000) 95.

9:40am **SS1-MoM5 Reactivity of Carbonate and Chemisorption of Carbon Dioxide on Ag(110):A Combined STM, LEED, and TPRS Study***, X.-C. Guo, **R.J. Madix**,* Stanford University

Twenty years have passed since we first indentified the surface carbonate species formed by the reaction of carbon dioxide with preadsorbed oxygen on Ag(110) by isotope-labeled TPRS (temperature programmed reaction spectroscopy) studies. In the intervening years the same system has been extensively investigated by many groups with various surface techniques including LEED, HREELS, XPS, UPS, NEXAFS, and STM. The carbonate species was confirmed and a bonding configuration proposed. However the stoichiometry of this basic reaction has recently come into question as a result of STM studies by three independent research groups - each believing to image the carbonate structure on Ag(110). Here we present new results of a combined STM, LEED, and TPRS study in this laboratory. Carbonate is shown to form at modest exposures of preadsorbed oxygen to carbon dioxide, and its structure is readily imaged. However, a high reactivity of the carbonate toward CO is observed, which leads to a stable chemisorbed state of CO2 chemisorption on a Ag(110)-(1x2) reconstructed surface, in dramatic contrast to the weakly adsorbed physisorbed state of CO2 on Ag(110)-(1x1). Thus high exposures of preadsorbed oxygen to carbon dioxide in ultrahigh vacuum are expected to lead to the formation of this species, since one expects there to be a background CO partial pressure accompanying the carbon dioxide dose. Indeed we have duplicated this result with high CO2 exposures. The STM images of the chemisorbed CO2 we obtain agree precisely with those previously attributed to carbonate by other groups, and they are distinctly different from those of carbonate. The carbonate species was correctly imaged with STM and its formation was followed in situ at 300 K. We also report here on the structure and surface mobility of the chemisorbed CO2 species.

10:00am **SS1-MoM6 Surface Structure and Chemical Properties of a MnO/Rh(100) Model Catalyst***, **J. Nakamura**, H. Nishimura, J. Ogawa,* University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan

The atomic structure of a MnO-deposited Rh(100) surface was studied using STM and LEED. The STM image of MnO/Rh(100) at a Mn coverage of 0.80 showed two hexagonal MnO domains rotated by 90 degree with respect to each other. One of the unit vectors for these hexagonal domains had same direction as the unit vector of the Rh(100) substrate. An averaged spacing of 0.31 nm was obtained by the STM for the nearest neighbor atoms of the hexagonal layer. The LEED pattern showed two hexagonal domains, which were consistent with the atomic structure observed by STM. The structure of hexagonal monolayer was very similar to MnO(111) in terms of lattice constant and symmetry. Adsorption of CO on the MnO/Rh(100) was studied using in-situ IRAS. Linear and bridge CO was observed on the clean Rh(100) and MnO/Rh(100) surfaces. New peaks or peak shifts were not observed on the MnO/Rh(100) in disagreement with the powder catalyst results of a Mn-promoted Rh catalyst. No IRAS peaks of CO were observed on the MnO/Rh(100) above the MnO coverage of unity, indicating that a monolayer MnO species grew on the Rh(100). The ratio of linear and bridged CO species varied with MnO coverage, suggesting that the surface area of bare Rh(100) planes on the MnO/Rh(100) controlled the ratio. The oxygen of MnO/Rh(100) is readily reacted with CO to form CO@sub 2@ at 300-400 K in UHV. The reaction probability at 373 K is close to unity.

10:20am **SS1-MoM7 Adsorption and Reaction on Oxide-supported Pd, Rh and Ir Particles***, **M. Baeumer**, M. Frank, S. Shaikhutdinov, H.-J. Freund,* Fritz-Haber-Institut, Germany

Supported metal clusters and nanoparticles are of fundamental and technical interest. One important area of application is heterogeneous catalysis, for example. On a microscopic level, however, there is only limited knowledge about the dependence of adsorption behaviour and catalytic activity on particle size and morphology. In order to contribute to an understanding of these relationships, we have studied oxide-supported Pd, Rh and Ir particles and their interaction with adsorbates. As a support, a thin alumina film grown on NiAl(110) was employed so that scanning tunneling microscopy and electron spectroscopies could be applied without charging problems. The STM results show that particle sizes ranging from a few atoms up to several thousand atoms are accessible via growth under vacuum conditions. By changing the temperature during deposition, disordered as well as crystalline aggregates are obtainable. After having dealt with the structure, we discuss the adsorption and reaction of ethene on these systems. The studies, which have been carried out using infrared and photoelectron spectroscopy, shed light on the formation of differently co-ordinated species and their thermal dehydrogenation. Gradual changes depending on the metal and the particle size are observed. Finally, we turn to the hydrogenation of ethene with hydrogen which has been investigated by thermal desorption spectroscopy.

10:40am **SS1-MoM8 Reactive Intermediate Species on WO@sub 3@ Resolved at the Atomic Scale during Alcohol Dehydration***, **R.E. Tanner**, P. Meethunkij, E.I. Altman,* Yale University

In order to better relate structure and reactivity on monoclinic @gamma@-WO@sub 3@(001), we have studied reactions on the surface using scanning tunneling microscopy (STM), temperature-programmed desorption (TPD), Auger electron spectroscopy and low-energy electron diffraction. The ordered c(2 x 2) reconstruction may be reproducibly generated by heating in O@sub 2@. The termination of the bulk structure is seen in LEED and STM to correspond to a WO@sub 2@ plane in which half the W@super 6+@ cations are covered by terminal O. The catalytic activity was probed by exposure of the c(2 x 2) surface to a series of alcohols. Methanol, 1-propanol, 2-propanol, and 2-methyl-propan-2-ol (t-butanol) all adsorbed on the surface. The sticking coefficient is similar for all alcohols indicating the ease of deprotonation and formation of alkoxide. TPD showed desorption of water and unreacted alcohol at temperatures less than 600 K, independent of the alcohol. The alkoxide all desorbed as alkenes at higher temperatures, so the c(2 x 2) surface displays only dehydration activity. The peak of the alkene desorption trace decreases from primary to tertiary alcohol (1-propanol --> t-butanol), indicating that desorption is limited by the rate of C-O bond scission of the adsorbed alkoxide, and is independent of the deprotonation rate. STM images revealed terraces covered with adsorbates that have no preference for attachment at steps or other defect sites. Further images are presented where the WO@sub 3@(001)-c(2 x 2) substrate atomic periodicity is seen simultaneously with the alkoxide intermediates. The sites for oxidative dehydration of the alcohol molecules are identified as the exposed five-fold coordinated W@super 6+@ ions on clean terraces, in agreement with the theory of enhanced activity at coordinatively unsaturated sites. The STM tip can be used to remove the alkoxide adsorbates from the surface to reveal the structure of the underlying, reactive adsorption sites.

Surface Science
Room 209 - Session SS2+NS+TF-MoM
Nucleation and Growth

Moderator: G.L. Kellogg, Sandia National Laboratories

8:40am **SS2+NS+TF-MoM2 Homoepitaxial Growth of Ni on Ni(110) : Surface with Anisotropic Diffusivity and Energy Barriers***, **B.-Y. Choi**,* Seoul National University, Korea*; S.-J. Kahng,* University of Illinois at Urbana-Champaign*; J.-Y. Park, Y. Kuk,* Seoul National University, Korea

The homoepitaxial growth of Ni was studied on Ni(110) surface with scanning tunneling microscopy. The Ni(110) surface does not reveal surface reconstruction, but it has corrugated channels along the [1 -1 0] direction and the resultant surface diffusion anisotropy. Homoepitaxial islands grow with high aspect ratio, as large as 1:1000, due to i) the diffusion anisotropy and ii) the energy barrier from an [1 -1 0] side wall to an [001] side wall around the adatom islands. The aspect ratio of the islands decreases with increasing temperature. The competition between these two mechanism will be discussed. At the high coverage (@>=@10ML), the aspect ratio decreases substantially and the growth structure transforms to 3D islands without asymmetry. At these coverage, the surface roughness saturates. Although the microscopic origin is unclear, the phenomenon can be explained with a KPZ type equation with some modifications.

9:00am **SS2+NS+TF-MoM3 Thermodynamics of Thin Film Alloys: Experimental and Theoretical Study of Ag and Co on Ru(0001)***, **G.E. Thayer**,* University of California, Davis*; A.K. Schmid, V. Ozolins, N.C. Bartelt,* Sandia National Laboratories*; S. Chiang,* University of California, Davis*; R.Q. Hwang,* Sandia National Laboratories

It has long been known that the structure of materials in thin film configurations can differ significantly from their bulk phase. This is particularly true of alloy films. It has recently been shown that strain induced by the lattice mismatch between substrate and film can lead to the formation of novel alloys that do not exist in the bulk. One prototypical example is the system of one monolayer Ag/Co films grown on Ru(0001). In the bulk, Ag and Co are immiscible. However, on the Ru surface alloy phases of distinct stoichiometries are formed. We have investigated the phase diagram of 1ML AgCo/Ru(0001) films using scanning tunneling microscopy (STM) and first principles calculations. For Ag rich films, segregation between a pure Ag phase containing dislocations and a pseudomorphically strained alloy of stoichiometry Co@sub 0.6@Ag@sub 0.4@ is found. The driving force for the phase segregation is the competition between two strain relief mechanisms: dislocation formation and alloying. In the Ag saturated Co@sub 0.6@Ag@sub 0.4@ alloy, atomic resolution STM images show that the alloy consists of a Co film containing disordered, elongated Ag droplets with an average size of 30 atoms separated by an average distance of 10 Co atoms. As the composition of Ag in the film is decreased, the Ag droplets become more uniform in size and decrease to an average minimum size of 10 atoms. Simultaneously, the distribution of the droplets becomes uniform and dilute. This behavior has been predicted using first principles, local density approximation (LDA) calculations. These calculations, together with atomically resolved STM images, have quantified configuration energies for various stoichiometries of this system. This investigation has led to a quantitative interpretation of the competition between the chemically repulsive interaction of Ag and Co (also seen in their bulk miscibility gap) and the strain fields in the thin film alloy that they form.

9:20am **SS2+NS+TF-MoM4 Theory of the Nucleation and Growth of Iron on GaAs***, **S.C. Erwin,*** Naval Research Laboratory*; M. Scheffler,* Fritz Haber Institute, Germany

By growing ultrathin films of ferromagnetic metals on semiconductor substrates, it is possible to create a partially spin-polarized electrical current in the semiconductor. This phenomenon is the starting point for a wide variety of magnetoelectronic devices based on the "spin-valve" effect, whereby an externally applied magnetic field can switch the current on and off. Considerable experimental effort has focused on ultrathin films of Fe grown by MBE on GaAs, in part because their small lattice mismatch results in nearly epitaxial films. Although a number of experiments have contributed to a detailed description of the phenomenology of magnetism in these films, little is known about the microscopic physics of magnetism at an intimate metal-semiconductor interface. We use spin-polarized density-functional total-energy methods to investigate the nucleation and initial growth phases of Fe on GaAs(001), focusing on the roles played by diffusion, magnetism, and defect chemistry. Our findings include the following results: (1) magnetism develops in the very first monolayer, and is in fact enhanced by the presence of the interface; (2) surface diffusion is strongly suppressed in the submonolayer regime by the tendency of Fe adatoms to form very stable Fe-As bonds. Finally, we discuss the influence of the initial GaAs reconstruction on the structure and magnetic properties of the Fe film.

9:40am **SS2+NS+TF-MoM5 Nucleation and Growth in Metal-on-Metal Epitaxy - Complications beyond Simple Systems***, **R.J. Behm,*** University of Ulm, Germany **INVITED**

The quantitative atomic scale understanding of a surface process, as a sequence of elementary steps, is one of the primary objectives in Surface Science. Molecular beam epitaxial growth (MBE) is one the first areas where extensive and systematic studies, both experimental and theoretical, have led to such kind of understanding, at least for simple processes such as nucleation and two-dimensional growth on inert, bare and non-reconstructed substrates.@footnote 1@ In this talk I will focus on complications which arise when these conditions are not fulfilled, predominantly on the effect of coadsorbed species on nucleation and growth processes. These coadsorbates, which are generally present, e.g., in the case of chemical vapor deposition (CVD), are shown to affect not only the nucleation behavior, but may lead also to the formation of new, (metastable) film structures. A second topic to be discussed involves nucleation and growth on 'instable' surfaces, where growth competes with exchange processes and surface alloy formation. On such systems and under certain conditions metal deposition was found to cause a severe restructuring of the substrate, leading to pit formation. Mechanistic ideas will be presented and discussed. @FootnoteText@@footnote 1@H. Brune, Surf. Sci. Rept. 31, 121 (1998).

10:20am **SS2+NS+TF-MoM7 Preferential Nucleation of Metal Nanoclusters on S(4x4)/W(111)***, **Q. Wu,** W. Chen, T.E. Madey,* Rutgers, The State University of New Jersey

Interactions of several metals (Cu, Pt and Pd) with the highly ordered S(4x4)/W(111) surface have been studied by means of Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). The substrate is a sulfur-induced nanoscale reconstruction of W(111) with (4x4) periodicity, characterized by broad, planar terraces (~ 30 nm in width). We find that fractional monolayers of vapor-deposited Cu grow as 3D clusters on the S(4x4) surface over a wide coverage range. At low Cu coverages (@<=@ 0.1 ML), Cu nanoclusters are observed to nucleate preferentially at characteristic 3-fold hollow sites on the S(4x4) surface; there is a clear energetic preference for one type of site over others. The formed Cu nanoclusters are uniform in size (~ 0.7 nm) up to 0.25 ML, indicating self-limiting growth. As coverage increases, additional sites are populated and Cu clusters grow in size. On the other hand, Pt and Pd exhibit a different behavior, disordering the (4x4) reconstruction and adsorbing beneath the outer S-layer. STM data are supported by LEED and AES measurements. The data are interpreted in terms of relative surface free energy, relative reactivity, and the metal-W, metal-S, and S-W binding energies, as supported by our previous TPD data.

10:40am **SS2+NS+TF-MoM8 Ultra-thin Al Films Grown Epitaxially on CaF@sub 2@/Si(111)***, **Y.V. Shusterman,** N.L. Yakovlev, L.J. Schowalter,* Rensselaer Polytechnic Institute

Electron scattering at metal boundaries becomes increasingly important as interconnect structures shrink further. To improve our understanding of this phenomenon, studies of electron transport through ultra-thin metal films are needed. In such experiments, it is desirable to have smooth, single crystal metal layers grown on an insulating substrate. For this reason, we are studying epitaxial growth of Al on CaF@sub 2@/Si(111), with metal thickness as low as several nanometers. The structures discussed in this work were grown by molecular beam epitaxy and investigated by reflection high-energy electron diffraction (RHEED), scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Hydrogen-terminated Si(111) was used as a substrate. The CaF@sub 2@/Si interface was formed at 700°C, followed by fluoride overgrowth at temperatures below 200°C, which resulted in improved continuity of the subsequent Al layer. The roughness of the final CaF@sub 2@ surface was below 1nm, as measured by AFM. The Al films grew epitaxially, as revealed by RHEED patterns that only contained streaks. The spacing between the streaks from Al was about 4/3 times larger than that from CaF@sub 2@, in agreement with bulk lattice mismatch. The growth proceeded through formation of 3-dimentional islands that then coalesced as the thickness increased. Using an Al deposition rate above 1nm/s at room temperature, we were able to obtain continuous films as thin as 10nm with roughness less then 2nm. The STM images of these films showed atomic steps, some of them originating at screw dislocations. The density of these dislocations was around 10@super 11@ cm@super -2@. The dependence of Al conductivity on film thickness will also be presented.

Surface Science
Room 210 - Session SS3-MoM

Surface Science Opportunities and New Applications

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

8:20am **SS3-MoM1 Out of the Vacuum - Into the Liquid***, **M. Grunze**[1],* University of Heidelberg, Germany **INVITED**

Motivated by the need to establish a knowledge base for microelectronics and heterogeneous catalysis, Surface Science matured as an interdisciplinary research area at the intersection of solid state physics and chemistry. The available experimental probes and theoretical concepts allow today to study surfaces and interfaces in unpreceded detail under vacuum or controlled gas atmospheres, but are less suitable to investigate surfaces in liquid environments. This challenge has been addressed by many members of the Surface Science community by directing their attention to the solid/liquid interface and to biological and biomaterial interfaces. In my presentation, I will discuss some recent examples of a successful transfer of traditional Surface Science concepts to the solid/liquid interface, and of new research areas at the intersection of physics, chemistry, and biology with impact on life science and medical procedures. The need for better experimental and theoretical tools to describe solid/liquid and biological interfaces will be discussed.

9:00am **SS3-MoM3 Probing Interaction Potentials Between Surfaces in Water***, **J.G. Kushmerick,** B.C. Bunker,* Sandia National Laboratories

Adsorbed water layers are known to strongly mediate interactions between non-ionic surfaces. These so-called hydration forces control processes as diverse as protein folding and the undesired adhesion between hydrophobic surfaces in micromachine components. Until recently, most investigations of hydrophobic interactions have been performed using the surface forces apparatus and atomic force microscopy. The former technique is limited to investigations on extended mica surfaces, while the latter technique is limited to probing only the outer regions of force-distance profiles due to "snap-to-contact" problems. The difficulties associated with making localized measurements of the hydration force have now been overcome using an interfacial force microscope (IFM), which allows force-distance profiles to be obtained at sub-nanometer resolution until the tip and surface are in intimate contact. Experiments have been performed in humid atmospheres and under water. Examples of IFM investigations of hydration interactions are provided for a range of hydrophobic-hydrophilic tip-substrate combinations prepared using functionalized self-assembled monolayers (SAMS). Investigations have also been performed on SAM coatings used to control stiction in micromachines

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[1] **Featured Speaker - Science and Technology in the 21st Century**

and on polymeric coatings such as poly n-isopropyl acrylamide that can be switched between hydrophilic and hydrophobic states. Results on the polymers indicate that adhesive interactions can be modified by at least an order of magnitude by conformation changes associated with the adsorption and desorption of water. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94Al85000.

9:20am **SS3-MoM4 Determination of Molecular Structure at Polymer Interfaces by Sum-Frequency Generation***, **K.A. Briggman**, L.J. Richter, J.C. Stephenson, W.E. Wallace,* National Institute of Standards and Technology

The structure of polymer surfaces and interfaces can determine critical interfacial properties such as adhesion, molecular recognition and bonding in applications as diverse as optoelectronics and biomaterials. Linear vibrational spectroscopies (FTIR, ATIR, and Raman) are some of the most widely accepted and utilized diagnostics of bulk polymer systems but typically do not have sufficient specificity to probe interfaces. Vibrationally resolved sum-frequency generation (SFG), a non-linear optical technique, is uniquely interface specific as it is dipole forbidden in media with inversion symmetry. Additionally it has the ability to determine not only the alignment of molecular groups, but also their absolute orientation. We report vibrational SFG studies of the methylene and phenyl groups at the interfaces of thin, annealed polystyrene films. When applied to thin film systems, the contributions from multiple interfaces must be properly assigned. Multilayer systems are designed to separate the contribution of signals from the free surface and buried interface and to allow independent determinations of molecular orientation at each interface. The phenyl rings have polar order at the free surface and oriented away from the film. The degree of order is significantly weaker at the buried interface. We will present a detailed analysis of the orientational distibution of the rings.

9:40am **SS3-MoM5 Nanocrystal Surface Melting -- A UHV X-ray Diffraction Study on n-Pb***, **K.F. Peters**,* Northwestern University, FRANCE*; Y.-W. Chung,* Northwestern University

Discovery of a nanocrystal surface phase transition is reported. The surface influence on the melting of nanoparticles has been debated since seminal concepts of surface melting and of a size-dependent melting temperature were given by Faraday and Thompson. On macroscopic Pb crystals, surface melting occurs on certain surface orientations yet not others. On highly curved surfaces of nanoparticles, 3 competing melting theories are based on liquid skin formation before melting, during melting, or never. Each theory also predicts a depression of the melting temperature Tm(D) as a function of crystallite diameter D. To measure the surface melting and melting temperature of Pb nanocrystals, we applied x-ray powder diffraction in situ in UHV.@footnote 1,2@ An array of Pb nanoparticle islands of 5-50 nm diameter was fabricated on a silica substrate by evaporation and annealing. The Pb 111/200 powder diffraction peaks were collected versus temperature. Narrowing of the diffraction peak revealed the melting of smaller particles at lower temperatures. Fourier analysis of the peak shape shows the evolution of the size distribution of 'crystallites' with increasing temperature. The size-dependent melting temperature was found to be Tm(D)=1-0.62/D, in close agreement with the Liquid Skin Melting Model. To measure directly the liquid skin growth on the crystallites, we rely on the undercooling of liquid particles without solidification. First the sample is heated to within 3K of the melting temperature of the largest particles in the sample (to melt the smaller particles). Upon slight cooling, we observed a reversible increase in the diffraction intensity and a narrowing of the diffraction peak shape. These changes in the crystallite volume and size are due to small changes in the liquid skin thickness (up to 0.5nm over a 20K temperature excursion for crystallites of 20 and 50nm diameter). @FootnoteText@ @footnote 1@Appl.Phys.Lett., 71 (16), 1997, 2391-2393. @footnote 2@Phys.Rev.B, 57, 21, 1998, 13430-13438.

10:00am **SS3-MoM6 How to Study a High-Vapor Pressure Liquid under Ultrahigh Vacuum: Organic Chemistry at and near the Surface of Sulfuric Acid***, **J.T. Roberts**, R. Michelsen,* University of Minnesota

10:20am **SS3-MoM7 Atomic Structure of Sulfide Natural Crystal Surfaces by Combined Photoelectron Imaging and Diffraction Methods***, E.M. Kneedler,* Surface/Interface Inc.*; X. Chen, S. Banerjee,* University of Wisconsin, Milwaukee*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; **B.P. Tonner**,* University of Central Florida

Natural surfaces of minerals play an important role in the chemistry of the environment. Advances in the sophistication of surface structural techniques makes it possible to tackle an atomic structure determination of such surfaces with some degree of confidence. We have studied a number of sulfur bearing mineral surfaces using high resolution x-ray photoelectron diffraction, and x-ray photoemission microscopy. A model system with a large unit cell, Cu(100)-S, is a starting point for evaluating the accuracy of photoelectron diffraction methods on complex surfaces. Results are also presented for natural crystals of galena (PbS), pyrite (iron sulfide), and some preliminary results of chalcopyrite.

10:40am **SS3-MoM8 DNA Sequence Information Obtained by TOF-SIMS Analysis***, **K.F. Willey**, W.L.B. White, T.J. Whitaker,* Atom Sciences, Inc.

A high-speed DNA screening technology is currently being developed at Atom Sciences. Our approach utilizes gene chip technology, which has paved the way for widespread DNA diagnostics. Current technology utilizes DNA hybridization to complementary oligonucleotides of known sequence immobilized to a surface. Unknown DNA is typically labeled with radioisotopes, stable isotopes, or fluorescent tags in order to detect hybridization sites. This labeling is costly and can be an impediment to the widespread use of gene chips. We are developing a new technology that requires no labeling. In this technique, target DNA hybridizes to an array of known sequences of peptide nucleic acid (PNA) probes attached to a silicon substrate. The naturally occurring phosphate groups in DNA provide an ideal intrinsic label because PNA contains no phosphorous. PNA is an analog of DNA in which the sugar/phosphate backbone of DNA is replaced by a peptide backbone. Target DNA and PNA probes undergo hydrogen bonding of AT and GC base pairs (Watson-Crick rules). Diagnostic information is obtained by identifying DNA hybridization sites within the array using negative SIMS detection of phosphate fragments. The sensitivity of SIMS detection and use of PNA probes gives our technology distinct advantages over existing diagnostic techniques (e.g. fluorescence). The major drawback, however, is the cost of commercial SIMS instrumentation. Therefore, at Atom Sciences, we have developed an inexpensive TOF-SIMS instrument. We will discuss the advantages of using a DNA/PNA hybridization scheme and its application to identifying single base mismatches. We will also discuss the current SIMS instrument used for technology development and how it could be simplified for a clinical diagnostic setting.

Semiconductors
Room 306 - Session SC+EL+SS-MoA
Reactions on Semiconductors

Moderator: R.A. Wolkow, National Research Council of Canada

2:00pm **SC+EL+SS-MoA1 Adsorption of SiH@sub 4@ on Si(001)(2x1) Investigated by Infrared Spectroscopy***, **M. Shinohara**, A. Seyama, Y. Kimura, M. Niwano,* Tohoku University, Japan

Adsorption of silane molecules, SiH@sub 4@ and Si@sub 2@H@sub 6@, onto Si(001) has so far been investigated extensively, because of the potential of using the silane molecules as the source gas for gas source molecular beam epitaxy (GS-MBE) for the growth of Si. Previous studies on Si deposition using silanes have suggested that during the course of Si crystal growth, silanes dissociatively adsorb on Si surface dangling bonds as trihydride (SiH@sub 3@) and dihydride (SiH@sub 2@) species and then decomposes to surface monohydride species, SiH. However, there has been only a little amount of information about the type of hydride species that are generated during the adsorption of silane on Si surfaces. In this study, we used infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR) to investigate the adsorption of SiH4 on the Si(001)(2x1) surface. IRAS-MIR provides us with valuable information about the hydrogen bonding configurations on semiconductor surfaces. Comparing infrared data with the density functional cluster calculation, we show that the silane molecule dissociatively adsorbs on Si(001)(2x1) to populate a dihydride (SiH@sub 2@) at the bridge site between two adjacent dimers and a monohydride species; the latter is formed by terminating the unsaturated dangling bonds of dimers by hydrogen atoms that are released from the silane molecule. We found that at high surface hydrogen coverage, surface silyl (-SiH@sub 3@) group and monohydride (SiH) species are generated. We interpret that at high hydrogen coverage, silane adsorbs onto a single dimer that has two unsaturated dangling bonds on which a hydrogen atom and a sylil group (-SiH@sub 3@) stick. We also show that a dihydride species that was initially generated by silane adsorption, dissociates even at room temperature and the released hydrogen atoms migrate on the surface to produce more monohydride species.

2:20pm **SC+EL+SS-MoA2 Si(001):As Gas-source Molecular Beam Epitaxy: As Incorporation and Film Growth Kinetics***, **H. Kim**,* University of Illinois*; G. Glass,* PTD, Intel Corp.*; J.A.N.T. Soares,* University of Illinois*; P. Desjardins,* Ecole Polytechnique de Montreal*; J.E. Greene,* University of Illinois

Arsenic-doped Si(001) layers with concentrations C@sub As@ up to 5x10@super 18@ cm@super -3@ were grown on Si(001)2x1 at temperatures T@sub s@ = 575 - 900 °C by GS-MBE using Si@sub 2@H@sub 6@ and AsH@sub 3@. At constant flux ratio, C@sub As@ decreases, while the film growth rate R@sub Si:As@ increases, with T@sub s@. TPD measurements show that As segregates strongly to the growth surface and that the observed decrease in C@sub As@ at high T@sub s@ is primarily due to increasingly rapid arsenic desorption from the segregated layer. Decreasing T@sub s@ enhances As incorporation. However, it also results in lower R@sub Si:As@ due to higher steady-state As surface coverages which decrease the total dangling bond coverage and, hence, the Si@sub 2@H@sub 6@ adsorption rate. At constant T@sub s@, C@sub As@ increases, while R@sub Si:As@ decreases, with increasing AsH@sub 3@ flux. All incorporated As resides at substitutional electrically active sites for concentrations up to 3x10@super 18@ cm@super -3@, the highest value yet reported for Si(001):As growth from hydride source gases. D@sub 2@ TPD spectra exhibit @beta@@sub 1@ and @beta@@sub 2@ peaks associated with Si monodeuteride and dideuteride desorption as well as a new peak @beta@@sub 3@ attributed to desorption from Si-As mixed dimers. Steady-state arsenic surface coverages during film growth, and the As segregation enthalphy, were quantitatively determined as a function of C@sub As@ by comparison with As-adsorbed Si(001) reference samples with known As coverages. From AsH@sub 3@ adsorption kinetics and incorporation data, the AsH@sub 3@ reactive sticking probability on Si(001) was determined and As incorporation kinetics were quantitatively modeled. Initial experiments have demonstrated that temperature-modulated growth can be used to increase both R@sub Si:As@ and C@sub As@ while providing layers which are atomically flat.

2:40pm **SC+EL+SS-MoA3 Scanning Tunneling Microscopy of Impurity Dimers on Hydrogen-Terminated Si(100)-2x1 Surface***, **S. Matsuura**,* University of Tokyo, Japan*; M. Fujimori, S. Heike, Y. Suwa, H. Kajiyama, T. Onogi,* Hitachi, Ltd., Japan*; K. Kitazawa,* University of Tokyo, Japan*; T. Hashizume,* Hitachi, Ltd., Japan

We report a new dimer structure on a hydrogen-terminated n-type Si(100)-2x1-H surface found by a scanning tunneling microscopy (STM). The dimer structure is observed almost same as regular surface Si dimers at filled state, at empty state, however, is observed as different structure showing spatial variation of electronic density of states. Similar results were obtained in the case of As-doped surface. The surface density of the structures derived from measurement of the samples with different dopant concentrations was found to be proportional to the dopant density. Electronic structures calculated by first-principles calculations for a phosphorous dimer or an arsenic dimer on the Si(100)-2x1-H surface are in good agreement with the bias dependent STM images of the newly-found structure on the P-doped or As-doped Si(100) surface, respectively. We concluded that the dimer structure represents dopant atoms incorporated on the Si surface and forming a dimer. The calculation also revealed that the surface phosphorous and arsenic atoms are more stable forming dimers than being isolated on the hydrogen-terminated Si surface.

3:00pm **SC+EL+SS-MoA4 Adsorption and Reaction of Fluorinated Fullerenes on Silicon***, **Y. Fujikawa**, J.T. Sadowski,* Tohoku University, Japan*; K.F. Kelly,* Pennsylvania State University*; K.S. Nakayama, T. Sakurai,* Tohoku University, Japan

The adsorption structure of fluorinated fullerene molecules deposited on silicon was studied using scanning tunneling microscopy (STM) and high-resolution electron energy loss spectroscopy (HREELS). The results of HREELS indicated that the fluorine atoms around the molecules were detached from the molecules and chemisorbed to the surface. These fluorine adsorption sites were directly observed around the adsorbed molecules in the STM images. Some of the fluorine-adsorbed sites were found to form thread-like structures, suggesting that the molecules print the fluorine atoms on the terrace due to the rolling movement of the molecules. Annealing produced different degrees of defluorination of the fullerenes and etching of the silicon surface depending on the temperature. By imaging the intermolecular structure of the molecules with the STM, we can directly observe the loss of the fluorine atoms.

3:20pm **SC+EL+SS-MoA5 STM Study of Self-Assembled Quantum-Dot Arrays of Sn on Si(111)-(7x7) Surface***, **M. Yoon**, R.F. Willis,* The Pennsylvania State University

The adsorption and diffusion mechanisms of Sn on the Si(111)-(7x7) at sub-monolayer coverages have been studied by scanning tunneling microscopy (STM). It is found that the preference of Sn adsorbates on the faulted-halves of the 7x7 unit cell is dependent on adsorbate coverage up to @THETA@ ~ 0.3 monolayer (ML). At higher coverages (~0.3 - 0.5 ML), the tin atoms cluster together on both halves of the 7x7 unit cell, forming a two-dimensional array of self-assembled quantum dots. This is in contrast to the behavior recently reported@footnote 1@ for Tl condensation on Si(111)-(7x7). In this latter case, the element occupies faulted half-cells preferentially and the surface remains metallic. In the present case, the Sn clusters are semiconducting, the surface showing an energy bandgap which increases with increasing coverage. The surface returns to metallic behavior as the number of Sn atoms approaches that of one monolayer of Si. @FootnoteText@ @footnote 1@L. Vitali, M. G. Ramsey, and F. P. Netzer, Phys. Rev. Lett. 83, 316 (1999).

3:40pm **SC+EL+SS-MoA6 Evolution of Surface Morphology During Sb Growth on Ge(100)***, **L.H. Chan**, E.I. Altman,* Yale University

Surfactants such as Sb have been found to promote layer-by-layer growth on metal and semiconductor surfaces. It is known that Sb and Ge intermix only at elevated temperature past 630K. Temperature programmed desorption was performed to study the energetics of Sb adsorption on Ge(100). The results demonstrated a typical high temperature peak that saturated at 1020 K before the appearance of a low temperature sublimation peak below 650 K with increasing Sb exposure. An additional high temperature peak at 1070 K was attributed to bulk incorporation of Sb. On a nominal 1 ML Sb covered Ge(100) surface prepared by deposition at 300K and annealing above the multiplayer desorption peak, scanning tunneling microscopy studies showed three surface layers were exposed. The images displayed bias dependent contrast suggesting the layers were not chemically uniform. To address the reasons for the morphology changes and to identify different components on the surface, a systematic study of Sb growth as a function of coverage and temperature was conducted. At room temperature, Sb adsorbs as tetramers and pairs of dimers. Several Sb@sub 4@ adsorption states are identified. Subsequent island growth leads to a poorly ordered surface with short strands of Sb dimer rows. The growth of longer dimer rows was interrupted by the growth of other nearby dimer rows randomly distributed on the Ge surface. Antimony incorporated into the top layer on either annealing or deposition at 600 K. Annealing gave well-structured dimer rows across the surface in all layers. However, intermixing of Sb and Ge at elevated temperature created ad-dimer clusters, vacancy islands, and reattachment of Sb and Ge ad-dimers on the top layer to the step edges. The implications of these results on surfactant-mediated growth will be discussed.

4:00pm **SC+EL+SS-MoA7 Effects of Exposure on GaSe Passivated Si(111)***,* ***J.A. Adams****, A. Bostwick, S. Meng, B.R. Schroeder, M.A. Olmstead, F.S. Ohuchi,* University of Washington

GaSe growth on Si(111) 7x7 between 500°C and 550°C results in the formation of a bilayer, which passivates the substrate dangling bonds and serves as the interface for further film growth. Ga sits directly atop surface Si, and the resultant interface bonding leaves Se lone-pair states on the surface, similar to Si(111):As. This makes the Si(111):GaSe surface resistant to contamination, and additional GaSe does not stick for T@sub substrate@@>=@500°C. We have studied the effects of exp osure to various atmospheric constituents on the electronic states and surface structure of the bilayer-passivated silicon surface using x-ray photoelectron spectroscopy and diffraction (XPS/XPD), low-energy electron diffraction (LEED) and ultraviolet photoelectron spectroscopy (UPS). We find that exposure to N@sub 2@ at atmospheric pressure has no apparent effect on the atomic or electronic structure and no N@sub 2@ is found to stick on the surface. However, we find that exposure to atmosphere for 5 minutes does change the surface states as observed from UPS, although LEED shows that the atomic structure of the GaSe bilayer does not change. The surface states can be almost completely recovered upon annealing at 500°C for 1 minute. Exposure to other atmospheric constituents such as O@sub 2@ and H@sub 2@O were also studied.

4:20pm **SC+EL+SS-MoA8 Temporal Changes of Photoemission Spectra of the Alkali-metal-induced Ge(111) 3x1 Surface***,* ***G. Lee,*** Korea Research Institute of Standards and Science, Korea*; C. Hwang,* Korea Research Institute of Standards and Science*; Y. Park, S. Cho,* Korea Research Institute of Standards and Science, Korea*; H. Lee,* Korea Research Institute of Standards and Science*; E. Cho,* Chonnam National University, Korea

We investigated the temporal changes of the core-level photoemission spectra of the Ge(111)3x1 reconstructed surface induced by alkali metals (Li and Na) in UHV chamber. It is found that while the spectra from the Ge(111)3x1-Na surface is hardly affected, those from the Ge(111)3x1-Li surface change significantly in time. We identify that the changes of the core-level spectra from the Ge(111)3x1-Li surface are due to the contamination by residual oxygen gas in the chamber. The contamination rate of the Ge(111)3x1-Li surface is even higher than that of the clean surface, contradicting the expectation that alkali-metal-induced 3x1 reconstruction passivates the surface against oxidation. We discuss the difference in the contamination rate between the Ge(111)3x1 surfaces induced by different alkali-metal adsorbates.

4:40pm **SC+EL+SS-MoA9 Role of Excited Electronic States in Reactions on Si(100)***,* ***J.S. Hess****, D.J. Doren,* University of Delaware

Low-lying excited electronic states of the Si(100) surface can play a role in activated adsorption reactions. The nature of the lowest surface excited state and its coupling to the surface ground state will be described. Density functional theory calculations on cluster models of Si(100) have been used to predict the minimum energy difference between the optimized ground state and first excited state levels. The minimum energy crossing point between the two states was explicitly calculated, as was the spin-orbit coupling between them. The energy needed to reach the excited state surface is low enough, and the coupling between the states is strong enough, that crossing between the two states will be facile. The two states will be in thermal equilibrium and a significant population of the excited state is expected at typical reaction temperatures. The role of the excited state in selected reactions will also be discussed.

5:00pm **SC+EL+SS-MoA10 Dynamics of Photo-induced Reaction on a Chlorinated Si(111) Surface***,* ***S. Haraichi****, F. Sasaki,* Electrotechnical Laboratory, Japan

In order to study photo-induced reaction of Si/Cl in the low fluence region, which is an influential candidate for low-damage manufacturing at the atomic level, the reaction mechanism was examined in terms of the photo-excitation dynamics using femtosecond second-harmonic generation (SHG). SH signals on a clean 7x7 surface show a rapid dip induced by the pump beam, which is finished within several 100 fs. It is ascribed to charge transfer from the bulk Si to the 7x7 surface and subsequent surface recombination of photo-produced carriers through surface dangling bond states. The rapid dip is not seen on the chlorinated surface, because the surface dangling bond states are disappeared. With the increase of the pump beam power the decay profile of SH signals drastically changes and an upward peak clearly appears on the chlorinated surface. The upward peak is due to the precursor of surface reaction on the Si/Cl system. Though we observed both of photo-excitation SH dynamics on an n-type and a p-type Si surface, the difference was not found. The band bending near the chlorinated surface does not contribute to the reaction dynamics, because it is most likely that the photo-produced carriers immediately flatten the bands. We also observed the reaction dynamics dependence on the pump photon energy. The threshold pump power of the reaction induced by a 1.55 eV pump peam and a 3.1 eV pump beam were 45 mW and 4 mW, respectively. This difference is not only due to an absorption coefficient but also the excitation levels and the relaxation paths, because the upward peak position of SH dynamics was different in two pump photon energy.

Surface Science
Room 208 - Session SS1-MoA
Model Catalysts at High Pressures

Moderator: A.G. Sault, Sandia National Laboratories

2:00pm **SS1-MoA1 A New Mechanism for Hydrocarbon Dehydrogenation on Pt under Conditions of High Hydrogen Coverage***, J.C. Hemminger,* University of California, Irvine*;* ***D.A. Perry,*** University of Illinois

In 1978 Demuth and Ibach published the HREELS vibrational spectrum of cyclohexane (C@sub 6@H@sub 12@) adsorbed on clean Pt(111) at low temperature showing strong softening of some C-H modes. Subsequently, data from several laboratories resulted in a consistent picture for the initial step in the dehydrogenation of cyclohexane on clean Pt. The mechanism of the dehydrogenation involves the weakening of one of the axial C-H bonds of the cyclohexane by interaction with a Pt 3-fold hollow site (leading to the soft C-H modes). This is followed by C-H bond breaking to form Pt-H and Pt-C bonds. The initial dehydrogenation product is cyclohexyl (C@sub 6@H@sub 11@). Work from our laboratory has shown that in the presence of high coverages of surface hydrogen the dehydrogenation actually occurs at a lower surface temperature, indicative of a 20% reduction in the activation energy for the initial step. In combination with our HREELS data, that shows no C-H mode softening, this reduction of the activation energy strongly indicates a different mechanism for the dehydrogenation in the presence of high surface coverages of hydrogen. The high surface coverages of hydrogen will effectively fill the 3-fold hollow sites on Pt(111). This leads to a more weakly adsorbed cyclohexane and the lack of softening of the C-H modes. Under these conditions we propose that the dehydrogenation occurs via a @sigma@ bond metathesis mechanism. In this mechanism, which is well established in metal-hydride organometallic chemistry, a hydrogen that is bonded to the Pt interacts strongly with a hydrogen of the cyclohexane. The metal-hydride hydrogen combines with the hydrogen from the cyclohexane to directly form H@sub 2@ at the same time that a C-Pt bond is formed. This concerted mechanism is consistent with our observations that the C-H modes are not softened when the 3-fold hollow sites are blocked with hydrogen and yet a lower activation barrier path to the initiation of the dehydrogenation exists.

2:20pm **SS1-MoA2 The Role of Surface Hydrocarbon Species during Palladium-Catalyzed Reactions at High Pressures***,* ***D.J. Stacchiola****, W.T. Tysoe,* University of Wisconsin, Milwaukee

It now appears clear that many, if not all, transition-metal-catalyzed hydrocarbon conversion reactions proceed in the presence of a relatively strongly bound carbonaceous layer adsorbed on the surface of the catalyst. In the case of Pd, ethylidyne species are present during ethylene hydrogenation, and vinylidenes in the case of reactions involving acetylene. In order to investigate adsorption on these carbonaceous-layer-covered surfaces, we have studied the adsorption of small molecules on both an ethylidyne-covered and a vinylidene-covered Pd(111) surface using molecular beam strategies and infrared spectroscopy under high pressure conditions. Results on the influence of carbonaceous layers on the hydrogenation kinetics of small hydrocarbons under high pressures are also discussed.

2:40pm **SS1-MoA3 Effect of the Environment on the Surfaces of Metals and Metal Oxides***, **M. Scheffler,*** Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

Surface Science UHV studies, in particular when concerned with metals or metal oxides, in some sense often investigate an artificial state. This means, the surface stoichiometry, and as a consequence the electronic properties, of the studied systems are significantly different to those that would exist in a realistic environment, which typically contains oxygen and water at higher pressure and temperature. This talk summarizes concepts for describing how the pressure and temperature of the environment or atmosphere affect surfaces.@footnote 1-3@ --- I will also describe recent developments in methodology: By combining density functional theory calculations with a lattice-gas Hamiltonian approach and the kinetic Monte Carlo method, surface phenomena can be described over time scales of the order of seconds and length scales of the order of micron.@footnote 4,5@ Examples of such calculations consider long-ranged adsorbate-adsorbate interactions,@footnote 5@ island formation and crystal growth, as well as surface structures with disorder, and thermal desorption.@footnote 4@ --- Using Ru as the main example (but also mentioning Al, Cr, Fe, Rh, Ag) I will show that the interaction with an oxygen atmosphere gives rise to a dramatic restructuring of the surface, yielding to mesoscopic domains of different stoichiometry and very different chemical activity.@footnote 1, 6-8@ The results will be discussed in view of their possible relevance for oxidation catalysis. --- @FootnoteText@@footnote 1@X.-G. Wang et al., Phys. Rev. Lett. 81, 1038 (1998). @footnote 2@ X.-G. Wang, A. Chaka, and M. Scheffler, Phys. Rev. Lett. 84, 3650 (2000). @footnote 3@ X.-G. Wang and M. Scheffler, to be submitted to Phys. Rev. B. @footnote 4@C. Stampfl et al., Phys. Rev. Lett. 83, 2993 (1999). @footnote 5@K.A. Fichthorn and M. Scheffler, Phys. Rev. Lett., May (2000). @footnote 6@A. Böttcher, H. Conrad and H. Niehus, J. Chem. Phys. 112, 4779 (2000). @footnote 7@ A. Böttcher et al., submitted to Surf. Sci. Lett. @footnote 8@H. Over et al., Science 287, 1474 (2000).

3:20pm **SS1-MoA5 Low Temperature CO Oxidation on the Pt(111) Surface Studied Over an Extended Pressure Range***, **D.J. Burnett**, A.M. Gabelnick, A.T. Capitano, A.L. Marsh,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; J.L. Gland,* University of Michigan

In-situ Fluorescence Yield Soft X-ray methods and Temperature Programmed Reaction Spectroscopy (TPRS) experiments were used to characterize the oxidation of CO in the temperature range where molecular oxygen dissociates. Taken together, these experiments enable characterization of this reaction over an extended pressure range (UHV to 0.01 Torr). Coadsorbed molecular oxygen and carbon monoxide TPRS experiments show that molecular oxygen must be adsorbed prior to carbon monoxide in order for low temperature (145 K) carbon dioxide to be produced. When molecular oxygen is preadsorbed with CO, the leading edge of molecular oxygen desorption is lowered nearly 20 degrees with a shoulder emerging at 127 K. When CO is preadsorbed, the molecular oxygen desorption peak remains unchanged (single peak with maximum at 142 K). Temperature Programmed Fluorescence Yield Near Edge Spectroscopy (TP-FYNES) experiments, capable of monitoring reactions under reactive atmospheres, were performed in pressures up to 0.01 Torr. For preadsorbed molecular oxygen with a CO overlayer, the same amount of low temperature carbon dioxide is formed when heated in vacuum and in oxygen pressures up to 0.002 Torr. For preadsorbed partial CO monolayers, the low temperature CO oxidation channel can be reached using pressures of oxygen (0.0005 to 0.01 Torr), as opposed to UHV experiments. Based on these results, oxygen dissociation appears to be limited in the vicinity of CO. Since coadsorbed CO enhances molecular oxygen desorption, these results suggest that competition between desorption of molecular oxygen and dissociation limits the reaction with coadsorbed CO. Detailed isothermal kinetic studies were performed with preadsorbed CO to establish a more detailed understanding of the oxidation mechanism.

3:40pm **SS1-MoA6 Rapid Reactions on Nanofabricated Catalyst Pt Particles***, **L. Österlund**, S. Johansson, B. Kasemo,* Chalmers University of Technology, Sweden

The CO oxidation steady-state kinetics has been measured at atmospheric pressure on nanofabricated catalysts. The Pt/ceria and Pt/SiO@sub 2@ catalyst samples used in the present study were prepared by electron-beam lithography (EBL) technique as previously described.@footnote 1@ This technique offers unprecedented opportunities of preparing catalyst particles of well-defined size distribution. Simultaneously it opens the possibility of independently changing particle size, inter-particle distance and the interface between different components, respectively. Here we report results on fairly large, polycrystalline particles (700 nm diameter), as well as smaller crystalline particles formed by disintegration of Pt particles at well-controlled exposures to a H@sub 2@/O@sub 2@ gas mixture.@footnote 2@ The reaction kinetics of the CO oxidation, including the kinetic phase transition and the bistability region has been explored in detail theoretically.@footnote 3@ However, experimental results at high pressures are still by and large lacking. The results presented here fills this gap and provides new information of the kinetic parameters governing the reaction. Rapid reactions on nanometer particles can be very different from those on an infinite surface. Results of the reaction kinetics on the small Pt particles are discussed in this context . @FootnoteText@ @footnote 1@ S. Johansson et al. J. Vac. Sci. Technol. A 18, No 4 (2000). @footnote2@ K. Wong, S. Johansson, and B. Kasemo, Faraday Discuss. 105, 237 (1996). @footnote 3@ V. P. Zhdanov and B. Kasemo, Surf. Sci. Rep. 20, 111 (1994).

4:00pm **SS1-MoA7 Co-adsorption and Reaction of Ethylene and NO over Rh Loaded Ceria Surfaces***, D.R. Mullins, **S.H. Overbury**,* Oak Ridge National Laboratory

In ceria containing emission control catalysts, such as three-way convertors in automobiles, the ceria plays an important role in oxygen exchange in both reduction and oxidation reactions. It is important to understand this role in catalytic reaction pathways. We have used soft x-ray photoelectron spectroscopy and TPD to study the co-adsorption and reaction of ethylene and NO on model catalysts surfaces composed of Rh deposited onto ceria films of controlled oxidation state. Studies focused on the effect of the oxidation state of the ceria upon the reaction pathways. The reactions occur predominantly on the Rh particles but are affected by oxygen spillover, interfacial reactions and modulation of the Rh reactivity by the ceria. Following adsorption at 100 K and subsequent programmed temperature increase, the ethylene decomposes in stages on the Rh particles leading to hydrogen evolution and leaving a reactive C species capable of reducing the ceria to produce CO. Correspondingly, NO reacts with both Rh and ceria. NO oxidizes the ceria resulting in N@sub 2@ evolution. NO dissociation occurs on Rh to an extent dependent upon the oxidation state of the ceria support. There is little interaction between co-adsorbed NO and ethylene when the ceria support is fully oxidized, except for site competition on Rh at low temperature. As temperature is increased water and N@sub 2@ are evolved followed by higher temperature CO evolution. However, for highly reduced ceria, water desorption is eliminated in favor of H@sub 2@, due to oxygen spillover onto ceria. Also, there is strong interaction between the N and C species on Rh which stabilizes them with respect to evolution of CO and N@sub 2@. Except for the absence of isocyanate and the presence of hydrogen and its branching between H@sub 2@ and water, the results are similar to reactions between CO and NO. Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, USDOE.

4:20pm **SS1-MoA8 Reducibility of Model Catalytic Converter Oxygen Storage Materials: Thin Ce@sub x@Zr@sub 2-x@O@sub 2@(111) Films Grown on Y-Stabilized Zirconia Single Crystals***, **C.H.F. Peden**, T. He, G.S. Herman,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology*; Y. Gao, S. Thevuthasan,* Pacific Northwest National Laboratory

Dramatic improvements have been made in automobile exhaust converter catalysts by the incorporation of oxygen storage (OS) materials, usually consisting of ceria (CeO@sub 2@) or modified ceria, that can effectively damp deviation in the exhaust air/fuel (A/F) ratio bringing the gas phase closer to the stoichiometric point. We have been growing and characterizing thin films of CeO@sub 2@ and ceria-zirconia (Ce@sub x@Zr@sub 2-x@O@sub 2@) for use as model materials for fundamental studies of their oxygen uptake, storage, and release properties. In this presentation, the growth and 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 low-energy ion scattering spectroscopy) of model CeO@sub 2@ and Ce@sub x@Zr@sub 2-x@O@sub 2@ 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. We will also report results of XPS and temperature-programmed desorption experiments that have probed the rates of oxygen incorporation and removal from these materials. In particular, we have found that doping of the CeO@sub 2@ by Zr markedly enhances the kinetics of these processes.@footnote 1@ @FootnoteText@ @footnote 1@Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

4:40pm **SS1-MoA9 Mocart: A Tool for Simulation of Heterogeneous Reactions Systems by a Monte-Carlo Method***, R. Kissel-Osterrieder, **F. Behrendt**, J. Warnatz,* Universität Heidelberg, Germany

A general purpose program called mocart for dynamical Monte-Carlo simulations of catalytic surface reactions has been developed. The stochastic model is based on the Master equation. Inputs for the program are the catalytic surface and its structure, the adsorbates and their initial distribution, the elementary reaction steps and their rate coefficients, and the adsorbate-adsorbate interactions, which can be defined for a variety of systems. The Monte-Carlo program is embedded in a computational fluid dynamics code for simulation of stagnation flow fields directed towards a reactive surface. Various aspects of performance improvements are discussed for three applications of this code. These cover the effects of defect sides on the evolution of reaction waves, the formation of spatio-temporal pattern, and models systems for supported catalyst. For all cases, the numerical results are compared with experimental observations.

5:00pm **SS1-MoA10 In Situ Soft X-ray Studies of CO Oxidation on Pt(411): Studies of Defect Reactivity***, **H.D. Lewis**, D.J. Burnett, A.M. Gabelnick, J.L. Gland,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology

The oxidation of preadsorbed CO on a Pt(411) single crystal surface has been studied over a temperature range of 100 to 600 K and in oxygen pressures up to 0.002 Torr using temperature-programmed fluorescence yield near-edge spectroscopy (TP-FYNES) above the carbon K edge. CO desorption from the Pt(411) surface shows that two-site desorption from step and terrace sites occurs. CO desorbs from terrace sites at 365 K and at 460 K from step sites, showing that CO is more strongly bound at the step sites. At low oxygen pressures (10@super-7@ Torr) oxidation occurs in two steps, beginning at terrace sites and then proceeding to step sites. At higher oxygen pressures (10@super-4@ Torr), one step oxidation at both the terrace and step sites is observed. Measuring surface carbon concentration it was determined that 60% of the CO adsorbed on the Pt(411) surface was on step sites, while the remaining 40% occupied the terrace sites. Isothermal kinetic studies were performed to establish a more detailed understanding of the oxidation mechanism. Kinetic parameters obtained in high oxygen pressures compare favorably to those on the Pt(111) surface.

Surface Science

Room 209 - Session SS2+EL-MoA

Electronic Structure and Excitations

Moderator: R.A. Bartynski, Rutgers University

2:00pm **SS2+EL-MoA1 Recent Photoemission Studies of Quasi-1D Solids***, **K.E. Smith**, J. Xue, L.C. Duda,* Boston University*; A. Fedorov, P.D. Johnson,* Brookhaven National Laboratory*; W. McCarroll, M. Greenblatt,* Rutgers University **INVITED**

Much controversy surrounds the interpretation of the results of angle resolved photoemission spectroscopy (ARP) studies of the electronic structure of quasi one-dimensional (1D) solids. In principle, ARP should provide valuable information about quasi-1D solids, including the structure of the Fermi surface and possible non-Fermi liquid behavior of electrons close to the Fermi level (E@sub F@). In practice, straightforward interpretation of the spectra is often difficult. It has been reported that photoemission from states near E@sub F@ in quasi-1D conductors differs significantly from that measured from two and three dimensional solids. There are a number of possible explanations for these observations, including problems with surface defects and stoichiometry, charge density wave fluctuations leading to a pseudogap, or a Luttinger liquid state. We report here the results of a temperature dependent ARP study of the electronic structure close to E@sub F@ in the quasi-1D conductors Li@sub 0.9@Mo@sub 6@O@sub 17@ and K@sub 0.3@MoO@sub 3@.@footnote 1@ These materials are ideal for ARP studies since large high quality crystals can be grown, and surfaces suitable for ARP measurements can be prepared by cleaving in vacuum. Using very high momentum and energy resolution ARP, we clearly measured for both materials: i) quasi-1D bands dispersing across the Fermi surface; ii) substantial emission intensity at E@sub F@ in the metallic phase; and iii) a gap opening at E@sub F@ as the samples are cooled through the metal-semiconductor transition. Our results differ from many earlier ARP studies of quasi-1D solids. The differences are likely due to an order of magnitude improvement in angular resolution (and corresponding improvement in momentum resolution) for the spectrometer used here. The reported non-Fermi liquid behavior in photoemission from these solids will be discussed. @FootnoteText@ Supported in part by the DOE under DE-FG02-98ER45680 (KES) and DE-AC02-98CH10886 (PDJ).

2:40pm **SS2+EL-MoA3 Fermi Contours and Adsorbate Phonon Anomalies for Li/Mo(110) and Li/W(110)***, **E. Rotenberg**,* Lawrence Berkeley National Laboratory*; S.D. Kevan,* University of Oregon

Angle-resolved photoemission was used to measure the Fermi contours of surface-localized states on the Mo(110) and W(110) surfaces with varying amounts of adsorbed lithium up to 1 ML. In analogy with recent results for H on Mo and W(110), we find that the contours are well nested and therefore can drive a surface phonon anomaly. The nesting vector parallel to the @Sigma@ azimuth on Mo(110) at monolayer coverage is in good agreement with recent phonon measurements.@footnote 1@ We also report the variation of this nesting vector as a function of coverage, and show that a more complete understanding of the electron-phonon coupling on these surfaces might be obtained from coverage-dependent measurements of surface phonon dispersion relations. Finally, our results suggest even better nesting along the @Gamma@ --> S direction and that a more pronounced anomaly might be observed there. @FootnoteText@ @footnote 1@J. Kroger, D. Bruchmann, S. Lehwald, and H. Ibach, Surface Science 449(1-3),227 (2000).

3:00pm **SS2+EL-MoA4 Thickness Dependence of the Unoccupied Electronic States in the Pd/Ru(0001) System***, **W.-K. Siu**, T. Mensing, R.A. Bartynski,* Rutgers University

The unoccupied electronic structure of the Pd/Ru(0001) system has been examined using inverse photoemission spectroscopy for Pd thicknesses in the 1 - 15 monolayers range. Previous studies indicate that in the sub-monolayer coverage range, the desorption temperature of CO on Pd/Ru(0001) is less than that of CO/Pd(111) or CO/Ru(0001). Similarly, we have previously shown that the desorption temperature for CO from the Cu/fccCo/Cu(100) metallic quantum well (MQW) system is a non-monotonic function of film thickness and is correlated with MQW states crossing the Fermi level. This suggests that quantum size effects can influence the strength of the chemisorption bond. As Pd interacts more strongly with CO, our objective is to investigate the occurrence of MQW states in the Pd/Ru(0001) system and determine their influence in CO chemisorption. Metallic quantum well (MQW) states are observed at the @Gamma@ point of the Pd thin film. The energies of these states change as a function of the film thickness. A simple phase accumulation model provides a semiquantitative understanding of this behavior. There is also an unoccupied surface state at @Gamma@, which shifts to higher energy with increasing film thickness, approaching that of the single crystal Pd(111) surface state. We have also determined the energy dispersion with parallel momentum of the unoccupied Pd states along the @Gamma@K and @Gamma@M directions. Finally, the influence of MQW states on the adsorption of CO on the Pd/Ru(0001) system will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Supported by NSF-DMR #98-01681 and ACS-PRF #33750-AC6,5.

3:20pm **SS2+EL-MoA5 High Resolution Photoelectron Spectroscopy of Pu at the Advanced Light Source***, **D.A. Arena**, J.G. Tobin,* Lawrence Livermore National Laboratory*; D. Shuh, E. Rotenberg,* Lawrence Berkeley National Laboratory*; J. Terry, R.K. Schulze, J. Lashley, T. Zocco, D. Farr,* Los Alamos National Laboratory

High resolution photoelectron spectroscopy of Pu has been performed at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source in Berkeley. Based upon an initial analysis of the data, two key results are immediately obvious. (1) The 5d-5f Resonant Photoemission of the Pu 5f levels exhibits a dependence upon the Pu phase and structure. For example, the results from alpha and delta Pu differ significantly. This strongly suggests that electronic behavior is linked to atomic ordering and structure in Pu. (2) Contamination with oxygen and carbon may be more insidious and subtle than initially believed. Photoemission measurements at a photon energy of 800eV exhibit oxygen and carbon core level peaks, while the same sample shows no contamination utilizing a photon energy of 1253eV, a typical laboratory source energy used in ECSA machines (i.e., Mg k-alpha). In other words, what was thought to be "clean" may not have been. Furthermore, contamination issues like these have a crucial impact upon interpretation of Pu core level spectra, e.g. localized and delocalized screening by 5f electrons. Additionally, 5f-6p Resonant Photoemission, core level spectra (particularly the Pu 4f's) and X-Ray absorption data, all from the Pu will be presented and discussed. Future plans, including ideas about studying magnetic effects in Pu, will also be described. UCRL-JC-133518 Abs.

3:40pm **SS2+EL-MoA6 Plasmon Resonance Spectroscopy of Plutonium Metal Allotropes***, **R.K. Schulze**, J.D. Farr,* Los Alamos National Laboratory

We have measured the plasmon resonance response of the cleaned and well characterized surfaces of the six plutonium thermal allotropes (@alpha@, @beta@, @gamma@, @delta@, @delta@', @epsilon@) using backscatter electron energy loss spectroscopy (EELS). The energy of the plasmon resonance is highly dependent upon the electronic structure of the solid surface, and in particular, the density of electrons available for conduction. Using this method we probe directly, for the first time, the number of free elec trons, and the changes in the electronic structure of the plutonium. EELS spectra were acquired on a high purity sample of plutonium with primary electron beam energies of 150, 200, 500, 700, and 1000 eV, and with the sample at seven different temperatur es: -125 (@alpha@), 45 (@alpha@), 156 (@beta@), 250 (@gamma@), 410 (@delta@), 465 (@delta@'), and 525°C (@epsilon@). Changes in the plasmon resonance spectra over the 150 to 500 eV primary beam energy range indicate that a surface reconstruction e xists for each of the Pu allotropes. The 700 and 1000 eV EELS measurements are alike, indicating that bulk characteristics are being probed at these energies. The bulk plasmon resonance energies for the allotropic series (@alpha@, @beta@, @gamma@, @delta@, @delta@', @epsilon@) are 12.23, 11.18, 11.16, 10.81, 10.94, and 10.92 eV. From these measurements, we extract the volume density of free electrons in each allotrope. In electrons per nm@super 3@ these are, for the series, 108.5, 90.7, 90.3, 84.8, 86.8, and 86.5. These results correlate directly with measurements of resistivity and magnetic susceptibility for the series of allotropes, indicating that the changes in free electron density are identically responsible for the changes in these physical properties. The implications of these results in terms of the electronic properties of Pu and in the changes of electronic structure between the allotropes will be discussed.

4:00pm **SS2+EL-MoA7 Lifetimes of Conduction Band States at Semiconductor Surfaces***, **Th. Fauster**, M. Kutschera, C. Kentsch, M. Wiets, I.L. Shumay, M. Weinelt,* University Erlangen, Germany

In time-resolved two-photon photoemission electrons are emitted after absorption of two photons. By a suitable delay between the two photons the lifetimes of conduction band states can be directly measured in pump-probe experiments. Using time-resolved two-photon photoemission we have studied several semiconductor surfaces. On the Si(100)-(2x1) surface several bulk and surface transitions with unoccupied intermediate states between the conduction band minimum and the vacuum energy are observed. Below the conduction band minimum we find a lifetime in the ps range, which we attribute to the unoccupied surface state. This unoccupied as well as the occupied surface state which originate from the silicon dangling bonds are clearly resolved within the same experiment. On epitaxial, metallic CoSi@sub 2@(111) films on a Si(111)-substrate three unoccupied states could be identified. Their lifetimes lie in the 10 fs range. Neither the lifetimes nor the energetic positions of those unoccupied states depend on the film thickness. On the SiC(0001)-(@sr@3x@sr@3)R30° surface the occupied and unoccupied Mott-Hubbard surface bands are observed. An asymmetric splitting relative to the Fermi level is found in agreement with recent theoretical calculations.

4:20pm **SS2+EL-MoA8 Oscillating Band-bending at the Initial Stage of Sb Growth on Si(100) held at 60K***, **J.M. Seo**,* Chonbuk National University, Korea

Using the synchrotron photoemission spectroscopy, the band-bending, the work-function and the valence band edge were simultaneously monitored at the initial stages of Sb growth on Si(100) held at 60 K. By the intensity attenuation of Si 2p with increasing Sb coverage, it can be deduced that Sb forms a relatively uniform overlayer on Si(100) at 60 K. The band-bending, determined by the bulk Si 2p position, oscillates within 0.15 eV up to about 4 ML of Sb, while the corresponding work-function, monitored by the secondary-cutoff position of biased substrate, negligibly changes. The metallicity, monitored by the valence band edge, indicates that the surface becomes semiconductor-like up to about 1.5 ML but recovers its metallic character with additional Sb coverage. These results implicate that the oscillating band-bending is due to the local charge exchange between the dimer row and Sb at the interface, while the corresponding metallicity of Sb film is determined by the amount of confined and available charges within the film.

Surface Science
Room 210 - Session SS3-MoA
Surface Diffusion and Wetting

Moderator: E.D. Williams, University of Maryland

2:00pm **SS3-MoA1 Theory of Surface Electromigration on Heterogeneous Metal Surfaces***, **P.J. Rous**,* University of Birmingham, U.K., UK

We report a calculation of the magnitude and direction of the wind force for the self-electromigration of adatoms on heterogeneous metal surfaces. Using layer-KKR and jellium methods we have computed the wind valence of adatoms interacting with adatom islands and voids on the low Miller index surfaces of several simple and noble metals. In the vicinity of an island, we find that the magnitude and direction of the electromigration driving force is significantly different from the force felt by an isolated adatom on a large terrace. Therefore, the usual assumption that driving force in surface electromigration is uniform and isotropic is shown to be inaccurate. Using the results of these calculations as input to kinetic Monte-Carlo simulations, we explore how this inhomogeneity of the wind force is manifest in the driven surface diffusion of adatom islands on a current-carrying metallic substrate.

2:20pm **SS3-MoA2 Direct Measurement of Long Jumps of Pd on Cu(001) using Atom-Tracking STM***, **B.S. Swartzentruber**,* Sandia National Laboratories*; M.L. Grant, J.B. Hannon,* Carnegie Mellon University

When Pd atoms are deposited onto a Cu(001) crystal surface, they readily place exchange with the surface Cu atoms, forming a 2-d surface alloy phase. At low coverage, Pd atoms are distributed randomly in the surface layer. At coverages approaching 0.5 ML, an ordered (2x2) alloy phase forms. The kinetic processes by which the incorporated Pd atoms form ordered structures are currently poorly understood. Using atom-tracking STM, a technique in which the probe tip is locked onto the diffusing species using lateral, XY, feedback, we have directly measured the diffusion of the Pd atoms as a function of temperature. The position of individual Pd atoms is recorded as a function of time with millisecond time resolution, thus recording the diffusion path of the incorporated atom. From these data, the relative binding energies of the sites visited by the atom, as well as the local diffusion barriers, are determined. We find that a large percentage (~25%) of the diffusion events involve displacements that are greater than a single lattice spacing - so-called long jumps. The distribution of jump lengths is well described by a process in which a Pd atom is thermally activated to a metastable binding-energy state, perhaps to a site on the surface, where it can perform several unit-length hops before it comes to rest in another stable binding site. Measuring the details of this atomistic process allows us to better understand the formation, growth, and mass transport kinetics of binary surface alloy structures. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US-DOE under contract DE-AC04- 94AL85000.

2:40pm **SS3-MoA3 Bronze Formation through the Motion of Tin Islands on Cu(111)***, **A.K. Schmid**, N.C. Bartelt, R.Q. Hwang,* Sandia National Laboratories

When Sn atoms are deposited on top of a Cu (111) surface at room temperature, they exchange into the surface to form a surface bronze alloy. One might have expected that this process would be rather simple, the understanding of which would be largely complete when one understood how a single Sn atom exchanged with a single Cu atom. We find, however, that the alloying occurs by an entirely unanticipated cooperative process that is considerably more intriguing than this. Using a combination of atomic resolution scanning tunneling microscopy (STM) and low-energy electron microscopy (LEEM) we find that shortly after Sn deposition large, 100,000 atom 2-D Sn islands coalesce on the Cu surface. These islands proceed to run across the surface. As they move, Sn atoms within the islands randomly exchange with Cu atoms in the surface. The exchanged Cu atoms are ejected from the Sn islands in the form of ordered 2-D bronze crystals. Sn islands consistently move away from their trail towards unalloyed regions of the Cu surface. We are able to trace the motion of the Sn islands to a simple atomic fact: Sn atoms on top of the Cu surface are strongly repelled by Sn atoms already incorporated into the Cu. The islands thus lower the free energy of the surface by moving. We find that island velocity is independent of size, consistent with a model in which the mobility of the Sn islands is determined by diffusion through the interior of the islands.

3:00pm **SS3-MoA4 Low Energy Electron Microscope Investigations of Pb Film Growth on Cu Surfaces***, G.L. Kellogg, R. Plass,* Sandia National Laboratories **INVITED**

To develop a more fundamental understanding of the microscopic processes that control the dynamics of liquid-metal wetting and spreading, we are using low energy electron microscopy (LEEM) to investigate the properties of Pb overlayers on Cu surfaces. The experiments probe a wide range of surface processes -- from the dynamic properties of submonolayer films to the growth, ripening and melting of three-dimensional islands. Measurements of changes in morphology during surface alloying and de-alloying provide new insights into the nature of submonolayer Pb structures on Cu(100). By combining different imaging modes of the LEEM, we have discovered an interesting correlation between the shape of three-dimensional Pb islands and the domain structure of the Pb/Cu(100) overlayer upon which they grow. Direct observations of Ostwald ripening combined with modeling studies indicate that mass transfer between three-dimensional islands is inhibited at domain boundaries of the submonolayer structure. The implication o f these and other results as they relate to liquid-metal flow processes will be discussed. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. DOE under Contract DE-AC04-94AL85000.

3:40pm **SS3-MoA6 Comparison of Behavior of Wetting-related Adsorption Transitions in the Ga-Pb, Ga-Tl, Ga-Pb-Tl Systems***, H. Shim, P. Wynblatt,* Carnegie Mellon University*; D. Chatain,* CRMC2-CNRS, France

In this presentation, we summarize investigations of prewetting behavior in three Ga-rich liquid alloy systems, Ga-Pb, Ga-Tl and Ga-Pb-Tl. The adsorption of Pb and/or Tl at the surfaces of these alloys was determined by Auger electron spectroscopy, as a function of temperature and composition. Most of the surface composition measurements reported were performed below the freezing points of the alloys (~300 K) where the alloys exist in a supercooled liquid state. However, measurements cannot be conducted below about 240 K, where the alloys undergo non-equilibrium freezing (presumably by homogeneous nucleation). Extrapolation to lower temperatures of the results obtained in the meta-stable liquid state (between 300 and 240 K) indicates the existence of possible prewetting critical points at about 240 K for Ga-Pb alloys, and at about 150 K for Ga-Tl alloys. The motivation for studying Ga-Pb-Tl ternary alloys was that small additions of Tl might raise the prewetting critical point of Ga-Pb to temperatures above 240 K, and lead to more definitive observations of prewetting behavior. However, although ternary Tl additions do lead to increased Pb adsorption, as expected, the temperature of a possible prewetting critical point is lowered even further to about 215 K.

4:00pm **SS3-MoA7 Shape Relaxation of Crystals via Layer-by-Layer Pealing Observed in Real Time***, K. Thürmer, J.E. Reutt-Robey, E.D. Williams,* University of Maryland

How does a small faceted crystal adjust its shape to a changing temperature and is it possible to reach its equilibrium shape? A positive answer to the latter question would allow an elegant experimental determination of absolute values of surface and step free energies.@footnote 1@ Small defect-free crystals near equilibrium experience an energy barrier for both growth and removal of atomic layers on a facet. Under growth conditions the 2D nucleation barrier gives rise to shape oscillations.@footnote 2@ Recently Mullins et al.@footnote 3@ concluded that for crystals larger than a few nm the magnitude of this barrier prevents surface free energy driven reshaping. We studied µm sized Lead crystals with an variable temperature STM under UHV-conditions. By tracking several crystals during a temperature increase from 110°C up to 205°C we confirmed Mullins suggestion that these crystallites are immobilized in their initial shapes. To investigate how a crystal establishes its shape we quenched the sample to temperatures between 65 and 110°C. STM observations of the (111) top facet starting shortly after the quench reveal a scenario of facet growth, where all layers smaller than a critical size peal off one-by-one. Uwaha@footnote 4@ treated the kinetics of such a collapse of step loops applying a constant critical size. Our experiments indicate a modification of the critical radius by a slow redistribution of atoms over the curved region of the crystal. @FootnoteText@ Work supported by NSF-MRSEC @footnote 1@ H.P. Bonzel et al, to be published @footnote 2@ J. Tersoff et al, Phys Rev. Lett. 70, 1143 (1993) @footnote 3@ W.W. Mullins et al, J. Am. Ceram. Soc., 83, 214 (2000) @footnote 4@ M. Uwaha, J. Phys. Soc. Jap., 57, 1681 (1988).

4:20pm **SS3-MoA8 LEEM Study of Mass Transport on Si(111)***, H. Hibino, C.-W. Hu,* Arizona State University*; T. Ogino,* NTT Basic Research Laboratories, Japan*; I.S.T. Tsong,* Arizona State University

How does the surface morphology change during annealing, growth, and/or sublimation? In order to ask the question, we need understanding of the process of the mass transport. In this paper, we investigate two aspects of mass transport on Si(111) using LEEM. One aspect is the decay of 2-dimensional islands or holes near the phase transition between 1x1 and 7x7. The evolution of the island or hole provides the information about the rate-limiting process. The radii of the islands and holes show power-law dependences on time. The measured exponents are close to 1/3 rather than 1/2. This means that the decay is governed by the diffusion of atoms on the terraces rather than the attachment and detachment of atoms at the steps. We also measure the decay rate as a function of the temperature, and clarify that the decay rate changes steeply at the phase transition between 1x1 and 7x7. The decay rate is faster on 1x1 than on 7x7. The other aspect is the shape changes of the islands and holes during the 1x1-to-7x7 phase transition. The atom density in 1x1 is higher than that in 7x7. This difference in the atom density causes the steps to advance during the 1x1-to-7x7 phase transition. Comparing the changes of the islands and holes, the island tends to capture more atoms than the hole. More atoms are incorporated into the step from the lower terrace than the upper terrace. The 7x7 reconstruction nucleates at the upper step edges. Therefore, this result as well as the faster decay rates of islands and holes on 1x1 than on 7x7 suggest that the mass transport is faster on 1x1 than on 7x7.

4:40pm **SS3-MoA9 First-Principles Study of Vacancy Ionization Effects on Surface Diffusion***, H.Y.H. Chan, E.G. Seebauer,* University of Illinois, Urbana-Champaign

While the effects of charged point defects on diffusion in bulk semiconductors have been studied extensively for many years, such phenomena have received almost no attention in connection with diffusion on surfaces. Recent studies in our laboratory using second harmonic microscopy (SHM) on Si have strongly suggested that charged vacancies can significantly affect observed activation energies and prefactors in a manner analogous to that observed for bulk diffusion. Furthermore, these studies have revealed significant non-thermal effects of photon illumination that also appear to be mediated by charged vacancies. Unfortunately, a more quantitative and complete description of these various phenomena requires a knowledge of the energy levels of the various surface vacancy charge states. Until now these energy levels have remained unknown on Si. We report herein the results of density-functional-theory based quantum calculations that fill this gap. Total-energy calculations using a plane-wave/pseudopotential approach within the local-density approximation were used to determine the charge-state dependent formation energies of vacancies as a function of Fermi level. The computed electronic structure, lattice reconstruction, and their effects on surface diffusion are discussed.

5:00pm **SS3-MoA10 Surface Supercooling and Stability of Si(111)-"1x1" High Temperature Phase***, C.-W. Hu,* Arizona State University*; H. Hibino, T. Ogino,* NTT Basic Research Laboratories, Japan*; I.S.T. Tsong,* Arizona State University

Si(111) high temperature phase transition is one of the most studied surface processes. It is well known that high temperature "1x1" phase converts into the most stable (7x7) surface reconstruction at about 830°C by the first order phase transition. However, the high temperature "1x1" phase can be locked down to 10~20°C below the phase transition temperature. This supercooling behavior is in situ observed by low energy electron microscopy within µm-sized two-dimensional depressions on Si(111) surface. The phenomenon can be readily explained as the lack of the nucleus of (7x7) reconstruction in depressions because the step edges of upper terrace take the roles of nucleation centers for stable (7x7) reconstruction. The supercooling temperatures are observed strongly depending on the sizes of depressions and the cooling rates of Si substrate. A normal depression with (7x7) reconstruction on it is formed by fast cooling through phase transition temperature. In this way, the filling-up rates can be measured respectively for supercooling depressions and normal depressions. The preliminary experimental results exhibit the downward movement of Si adatoms from (7x7) upper terrace and the step-edge attachment within depressions are responsible for the stability of Si(111)-"1x1" supercooling phase.

Semiconductors
Room 306 - Session SC+EL+SS-TuM
Compound Semiconductors

Moderator: J.W. Rogers, Pacific Northwest National Laboratory

8:20am **SC+EL+SS-TuM1 Reconstructions and Steady-state Surface Structures on InAs(001)-(2x4): Implications for Atomistic Modeling of Growth***, **W. Barvosa-Carter**, F. Grosse,* HRL Laboratories and University of California, Los Angeles*; M. Gyure,* HRL Laboratories*; J.H.G. Owen, C. Ratsch,* HRL Laboratories and University of California, Los Angeles*; R.S. Ross, J.J. Zinck,* HRL Laboratories

Heterostructures involving InAs, GaSb, and AlSb are increasingly finding applications in high-frequency, infrared, and 'spin-tronic' devices. Interface structure in these devices can be critical in determining device performance. The robustness of any model that seeks to relate process parameters and in-situ sensor signals to the surface chemistry or roughness of the growing film ultimately depends on our understanding of the relevant surface reconstructions and epitaxial growth mechanisms. Using MBE, RHEED, and atomic-resolution STM, we have studied the reconstructions and 'steady-state' surface structures present on MBE-grown InAs homoepitaxial surfaces in the (2x4) growth regime. On InAs we find two reconstructions that are relevant for growth: the familiar @beta@2(2x4) (as on GaAs) and the less familiar @alpha@2(2x4). We find excellent agreement between detailed atomic-resolution STM and first-principles simulated images of these structures. Upon quenching, we find that "steady-state" InAs surfaces exhibit small islands and adatom-like structures residing on a disordered mixture of the @beta@2 and @alpha@2 reconstructions, and that the proportions of these structures vary as a function of As pressure and temperature. Hence, the growth surface structure for InAs is remarkably different than for GaAs, where only the @beta@2 reconstruction is present with relatively few defects under device growth conditions. These results are in excellent qualitative agreement with an ab initio-based Monte Carlo model that is being developed in parallel with the experimental effort to describe reconstructions and growth on this surface.

8:40am **SC+EL+SS-TuM2 Oscillations of Local Density of States at the Epitaxially Grown InAs(111)A Surfaces Characterized by Low-temperature Scanning Tunneling Microscopy***, **K. Kanisawa**, M.J. Butcher, H. Yamaguchi, Y. Hirayama,* NTT Basic Research Laboratories, Japan

The characterization of semiconductor surface electrons is very important for understanding microscopic electron behavior. Though the local density of states (LDOS) has been studied at metal surfaces by using low-temperature scanning tunneling microscopy (LT-STM), the only studies that have been reported for semiconductors are on cleaved (110) surfaces. A LT-STM study of an epitaxial semiconductor surface makes it possible to compare the electron behavior directly with nanometer-scale morphology. We have performed a LT-STM study of the epitaxially grown InAs(111)A surface on the GaAs(111)A substrate in layer-by-layer growth mode at 5 K. Topographic and dI/dV images were obtained simultaneously by using a lock-in technique. In the dI/dV images, LDOS oscillation patterns were clearly imaged at surface defect sites, which were identified in the corresponding STM images. At an isolated defect, clear LDOS Friedel oscillations made of concentric circles were observed. From the dependence of the oscillation period, the effective mass was calculated to be 0.043m@sub 0@, which is consistent with that of InAs with a relatively high electron concentration. In the case of steps with a height difference of integral monolayers, the oscillation patterns showed dark bands along the steps. In contrast the Frank partial dislocations, with height differences of fractional monolayers, showed bright bands. This implies that there are large differences between the electron scattering phases at the steps and at the dislocations. During the InAs growth, triangular regions are formed on the surface by three {111} stacking fault planes. Such boundaries showed symmetric and regular patterns inside. Our detailed analysis suggests that these patterns are related to zero-dimensional electron systems confined within the InAs nanostructures.

9:00am **SC+EL+SS-TuM3 Something Old, Something New, Something Borrowed, Something BLUE - Fifty Years of III-V Compound Semiconductors!***, **R.D. Dupuis**[1],* University of Texas, Austin **INVITED**

III-V compound semiconductors, first identified in 1950, have become critically important for the commercial development of advanced semiconductor devices and systems. In the past fifty-some years, many workers from all over the world have contributed to this outstanding success. The epitaxial growth of III-V films began in 1960 with the early work of Holonyak who used iodine transport in a closed tube to produce epitaxial layers of GaAs/GaAs, GaAs/Ge, and various GaAsP alloys. Open-tube VPE and LPE for III-Vs were developed soon after this work. In 1967, Manasevit, et al., demonstrated the metalorganic chemical vapor deposition (MOCVD) epitaxial growth process and in 1970 Cho, et al. reported the first molecular beam epitaxy (MBE) growth of GaAs. Thus, twenty years after the first identification of III-Vs as semiconductors, all of the epitaxial growth processes we use today had been developed. It has taken 30 more years of technological and scientific advances to arrive at the understanding of these materials that we take for granted today. In fact, much of the new advanced communications systems that will be employed in the next 10 years depend fundamentally upon III-V epitaxial growth. In this talk, I will briefly review some aspects of the history of the development of these material systems and growth processes and I will discuss some of the recent results as well as speculate on the future development of III-V compound semiconductor materials.

9:40am **SC+EL+SS-TuM5 Strain-Induced Anisotropy of Gallium Phosphide Islands on Gallium Arsenide***, **C.H. Li**,* University of California, Los Angeles*; L. Li,* University of Wisconsin, Milwaukee*; Q. Fu, M.J. Begarney, R.F. Hicks,* University of California, Los Angeles

We have undertaken a study to produce ordered nanostructures on compound semiconductor surfaces by the heteroepitaxial growth of highly strained island structures. Phosphorous-rich (2x4) islands are produced by decomposing phosphine on gallium arsenide (001)-(4x2) surfaces in ultrahigh vacuum. These islands exhibit anisotropy of approximately 10 to 1 with the (2x4) domains dramatically elongated along the [110] direction. The island width increases with the phosphorous coverage from 24 @Ao@ at 0.1 ML to 48 @Ao@) at 0.75 ML. This is attributed to strain induced by the lattice mismatch of phosphorous dimers on gallium arsenide. The implication of this finding to the epitaxial growth of GaP/GaAs heterostructure will be discussed at the meeting.

10:00am **SC+EL+SS-TuM6 Relative Reactivity of Arsenic and Gallium Dimers and Backbonds during the Adsorption of Molecular Oxygen on GaAs(100)(6x6)***, **P. Kruse**, J.G. McLean, A.C. Kummel,* University of California, San Diego

The semiconductor industry has a strong interest in understanding and employing the reactions of oxygen with III-V materials for fabrication of GaAs CMOS devices. We have monitored the initial stages of the chemisorption of molecular oxygen on the GaAs(100)(6x6) reconstructed surface by means of room temperature scanning tunneling microscopy. This surface is terminated by both gallium dimers and arsenic dimers, allowing for a direct comparison of their reactivity. Neither the As nor Ga dimer bonds react with thermal molecular oxygen. Likewise, the Ga-As back bonds of the Ga dimers do not exhibit any reactivity. Instead, the chemisorption proceeds with 100% chemical selectivity via the reaction of molecular oxygen with the As-Ga back bonds of the As dimers. The interaction between the highly electronegative oxygen atoms and the surface is initiated through the high electron density at the arsenic atoms. One oxygen atom displaces the attacked arsenic atom while the other oxygen atom bonds to two neighboring gallium atoms, resulting in the thermodynamically most stable reaction products: metallic arsenic clusters and gallium oxide.

10:20am **SC+EL+SS-TuM7 Role of Ligand Termination in Atomic-Layer-Controlled Growth***, **R.M. Osgood**, N. Camillone III, Y. Luo, M. Han,* Columbia University **INVITED**

We describe employment of a series of in situ UHV diagnostics to study the surface chemistry of ligand capping in limiting reactions for atomic-layer-defined growth of semiconductor thin films. In the study, molecular precursors were on surfaces held at temperatures from 180-300K in a UHV chamber. The terminating groups, formed by the dosing, were identified and their chemistry investigated using thermal desorption spectroscopy, NEXAFS, Auger, spectroscopy, and LEED. Using CdS growth on ZnSe(100) as the model system, we have found that CH@sub 3@ and H terminal groups

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[1] **Featured Speaker - Science and Technology in the 21st Century**

deposited by reactions with Cd(CH@sub 3@)@sub 2@ and H@sub 2@ S, respectively, effectively limit growth precisely on all except the first monolayer. A study of intermixing in the first layer shows clearly the role of surface temperature in controlling the reaction chemistry and coverage of terminating species. The implications with regard to atomic-layer-controlled growth of other systems will also be discussed.

11:00am **SC+EL+SS-TuM9 Two-step MOCVD Growth of Piezoelectric ZnO Thin Film on SiO@sub 2@/Si Substrates***, **S. Muthukumar**, N.W. Emanetoglu, G. Patounakis, C.R. Gorla, S. Liang, Y. Lu,* Rutgers University

ZnO is a wide bandgap semiconductor with a direct bandgap of 3.3eV. Piezoelectric ZnO has high electro-mechanical coupling coefficient. Thin film piezoelectric ZnO deposited on semiconductor substrates is used for surface and bulk acoustic wave (SAW & BAW) devices, which offer advantages such as low power consumption, circuit miniaturization and cost reduction by integration with main stream MMIC technology. Furthermore, temperature compensation may be achieved in the ZnO/SiO2/Si system as ZnO and Si have positive temperature coefficient of delay (TCD), while SiO2 has negative TCD. Temperature compensated SAW devices are attractive for both communication and sensor technologies. In the present work, ZnO thin films were grown on SiO2/Si substrates by MOCVD. The structural properties of the films were investigated using XRD, SEM, and scanning probe microscopy. The films grown at 300°C were dense and had a smooth surface morphology, but poor crystallinity. In contrast, the films grown at 500°C were predominantly c-oriented, but had a rough surface. A two-step growth process was developed to obtain films with both good crystallinity and smooth surface. A high temperature (450-500°C) buffer layer was initially deposited, to provide a highly crystalline template for the subsequent low temperature (300-330°C) growth. Annealing was done on the thin films in N2 and O2 ambient for different durations to improve film resistivity, essential for fabricating low-loss SAW devices. The SAW velocity, coupling coefficient and TCD of the ZnO/SiO2/Si system were investigated through modeling and computer simulation based on Adler's transfer matrix method and Green's function analysis. The test devices with the proper ZnO and SiO2 thickness exhibited multiple temperature compensated frequency points in the 1.42 GHz to 2.15 GHz range. These results show that temperature compensated ZnO/SiO2/Si system is promising for fabricating low-loss SAW devices.

11:20am **SC+EL+SS-TuM10 Spontaneous Island Formation Caused by Reconstruction Changes During III-Sb Homoepitaxy@footnote 1@***, **A.S. Bracker**, B.Z. Nosho, B.R. Bennett, J.C. Culbertson, B.V. Shanabrook, L.J. Whitman,* Naval Research Laboratory

Most III-V semiconductor surfaces exhibit reconstructions with compositions that differ from the bulk material. These nonunity III:V stoichiometries constitute an inherent source of interfacial roughness during molecular beam epitaxy when the reconstruction changes during growth. This issue is especially important for the AlSb and GaSb(001) surfaces, because several reconstructions exist over the range of substrate temperatures and beam fluxes typically used for growth. For AlSb, the relevant reconstructions include @alpha@(4x3), @beta@(4x3), @gamma@(4x3), and c(4x4), in order of increasing Sb:Al coverage.@footnote 2@ We have used scanning tunneling microscopy (STM) and reflection high-energy electron diffraction (RHEED) to characterize how the initial stages of homoepitaxy depend on the surface reconstruction and growth conditions. When the growth conditions cause a transition between reconstructions, islands spontaneously form on the surface. In addition to roughening an otherwise flat surface, these islands change the island size distribution during subsequent growth. Unfortunately, the RHEED patterns for the three (4x3) surfaces all have a similar streaky (1x3) symmetry during growth, making it difficult to optimize growth conditions based on this diagnostic alone. However, because of its sensitivity to surface roughness, RHEED intensity oscillations may be used to monitor the reconstruction-mediated roughening. We will discuss the realistic growth situations where this type of roughening should be important. @FootnoteText@ @footnote 1@This work was supported by ONR and DARPA. @footnote 2@Barvosa-Carter et al., Phys. Rev. Lett. 84, 4649 (2000).

11:40am **SC+EL+SS-TuM11 Photon-activated Electron-Transfer-Reaction Surface Modification of GaAs(001)***, **N. Camillone III**, K.A. Khan,* Columbia University*; J.A. Yarmoff,* University of California, Riverside and Lawrence Berkeley National Laboratory*; R.M. Osgood, Jr.,* Columbia University

UHV methods for adjusting the reconstruction and composition of the top layer of atoms on a semiconductor surface are expected to have important implications for precise control of growth surfaces and surface reactions. In this talk we will describe a transformation of the surface reconstruction resulting from a photoinduced electron transfer reaction occurring thereupon. We have carried out preliminary studies which demonstrate that variation in photon exposure and thermal treatment allows the surface reconstruction to be controllably adjusted from the Ga-rich c(8x2) to the (4x6), (3x1) and As-rich c(2x8) terminations. The modification of the reconstruction is the result of a modification of the surface stoichiometry due to the extraction of surface Ga atoms as a result of reaction with bromine. The bromine is produced at the surface by photoinitiated dissociative electron attachment to methyl bromide molecules physisorbed in a single monolayer at ~ 90 K. Subsequent to the photoinduced surface reaction, the gallium is removed by annealing to desorb a gallium bromide product. A comparison of the results obtained with low energy electron diffraction, temperature programmed desorption and energy-resolved photofragment angular distribution measurements shows that the most As-rich surface obtained by our technique is identical in structure to that of a control surface prepared using the standard iodine thermal reaction method. In principle, the use of this photon-activated reaction, and others like it, could allow for precise patterning of the surface structure based on control of photon or electron exposure, molecular coverage, thermal treatment and lateral patterning of the incident photon or electron beam.

Surface Science
Room 208 - Session SS1-TuM
Reactions on Oxides and Environmental Chemistry

Moderator: C.H.F. Peden, Pacific Northwest National Laboratory

8:20am **SS1-TuM1 Ethylene Polymerization on a CrOx/SiO2 Model Catalyst: XPS, SIMS, RBS and AFM***, **P.C. Thuene**, J. Loos,* Eindhoven University of Technology, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

Achieving realistic catalytic activity on a model catalyst consisting of Cr on 1 cm2 of planar SiO2 at a loading of 1 Cr per nm2 has proven to be the major challenge in designing a surface science model for the Phillips ethylene polymerization catalyst. Poisons like water or acetylene can deactivate the catalyst within a fraction of a second even if they are present in minute (1ppm) quantities. By using special filters we can now run polymerization reactions at 160Â°C for at least 30 minutes without deactivation of the catalyst. The polymer yield after each polymerization run is measured most conveniently by analyzing scalpel scratches with atomic force microscopy (AFM). The catalyst shows a constant activity with a pseudo turnover frequency of 2.5 C2H4 / Cr s. This corresponds to 250 g PE / gcat h atm if rescaled to the surface area of an industrial catalyst (286 m2/g, Crossfield) which represents a realistic catalytic activity. Owing to the planar geometry, the state of Cr can be determined in detail by using XPS and SIMS, while the polymer morphology can be analyzed with AFM.

8:40am **SS1-TuM2 Structurally Ordered Magnesium Vanadate Model Catalysts for Oxidative Dehydrogenation***, **A.G. Sault**, J.E. Mudd, J.A. Ruffner, J.E. Miller,* Sandia National Laboratories

A fundamental understanding of active sites in mixed metal oxide oxidative dehydrogenation (ODH) catalysts continues to be elusive. In an effort to simplify the complexities inherent in these materials we are growing single phase, oriented mixed metal oxide thin films. Using RF sputter deposition, we have grown 10-2000 Å films of Mg@sub 3@(VO@sub 4@)@sub 2@, a known ODH catalyst. Bulk and surface analysis of films grown on silicon wafers show the desired stoichiometry, but the films are amorphous. Deposition on a 500 Å gold layer grown on oxidized silicon results in films strongly oriented toward the (021) plane of Mg@sub 3@(VO@sub 4@)@sub 2@. This orientation is due to the tendency of gold to grow with (111) planes exposed, which provides an ideal epitaxial substrate for Mg@sub 3@(VO@sub 4@)@sub 2@ (021). This plane consists of close packed oxygen layers, with Mg and V ions in octahedral and tetrahedral sites, respectively. By varying oxygen pressure we can deposit films with stoichiometries ranging from fully oxidized Mg@sub 3@(VO@sub 4@)@sub 2@ to partially reduced Mg@sub 3@V@sub 2@O@sub 6@. We will detail the effects of heat treatments in reactive environments (e.g., oxygen/propane mixtures) on the structure and composition of these films, and report on the catalytic activity of these films for ODH. In general, heating the films above 623 K in vacuum or 100 Torr propane results in at least partial reduction of V(V) to V(III) and segregation of V to the surface. Prolonged reduction at higher temperatures results in complete reduction to Mg@sub 3@V@sub 2@O@sub 6@. Treatment in oxygen reverses these changes. This reversible redox chemistry is consistent with the known mechanism for ODH, which involves participation of lattice oxygen. Catalytic measurements of propane ODH show very low conversions due to the low surface areas of the films. Measurements with more facile ODH reactions (such a 1-butene to butadiene) are underway and will be reported.

9:00am **SS1-TuM3 Reactive Scattering Studies of Organophosphorous Compounds on Semiconducting Metal Oxides***, J.L. Duncan, S. Ma, R.H. Jackson, **B.G. Frederick**,* University of Maine

Semiconducting metal oxides (SMOs) are promising materials for the development of conductivity-based chemical sensors with a broad range of applications. The reactions of organophosphorous compounds are of interest for detection of pesticides and nerve agents. Improvement of the selectivity of SMO sensors requires an understanding of the steps in the decomposition or reaction mechanism which lead to changes in conductivity. We present results of reactive, molecular beam scattering studies for dimethyl methyl phosphonate (DMMP), and related compounds from tungsten oxide based sensors. The experiments utilize molecular beam doser sources with known flux distributions and a differentially-pumped, calibrated mass spectrometer system allowing the coverage, sticking coefficients, and reactive scattering probabilities to be quantified. Reactive scattering of methanol, formic acid, trimethyl phosphine oxide, and trimethyl phosphonate, contribute to understanding the decomposition mechanism of DMMP and the associated conductivity changes observed in the SMO films.

9:20am **SS1-TuM4 Chemistry of SO@sub 2@ and NO@sub 2@ on ZnO(0001)-Zn and ZnO Powders: Changes in Reactivity with Surface Structure and Composition***, **J.A. Rodriguez**, T. Jirsak, J. Dvorak, J. Hrbek,* Brookhaven National Laboratory

Synchrotron-based photoemission and x-ray absorption spectroscopy have been used to study the interaction of SO@sub 2@ and NO@sub 2@ with ZnO(0001)-Zn and polycrystalline surfaces of zinc oxide (films and powders). Important differences are observed when comparing the behavior of the adsorbates on these oxide surfaces. These differences are in a part a result of changes in structural properties (flat vs rough surfaces), but in some cases they clearly originate in variations in surface composition (Zn-adsorbate vs O-adsorbate interactions). For example, the Zn-terminated (0001) face of ZnO interacts weakly with SO@sub 2@ (desorption temperature of adsorbate < 200 K). In contrast, the SO@sub 2@ molecules interact readily with O sites of Ar@super +@ sputtered ZnO(0001)-Zn or polycrystalline ZnO forming very stable SO@sub 3@ species. Due to its radical nature, adsorbed NO@sub 2@ is more chemically active than SO@sub 2@. After dosing nitrogen dioxide to ZnO(0001) at 100 K, chemisorbed NO@sub 2@ and NO@sub 3@ coexists on the surface. Partial transformation of NO@sub 2@ into NO@sub 3@ is observed from 150 to 300 K. The data for the NO@sub 2@/ZnO(0001)-Zn system clearly prove that large quantities of NO@sub 3@ can be formed on metal sites of an oxide surface as a consequence of partial decomposition or disproportionation of NO@sub 2@.

9:40am **SS1-TuM5 Adsorption of S and Cl on TiO@sub 2@(110) Studied by Ultra-violet Photoelectron Spectroscopy***, E.L.D. Hebenstreit, W. Hebenstreit, U. Diebold,* Tulane University*; H. Geisler,* Xavier University*; D.A. Hite, P.T. Sprunger,* Louisiana State University*; S.N. Thornburg, **C.A. Ventrice, Jr.**,* University of New Orleans

One of the most severe poisonings of metal and metal oxide catalytic systems is induced by sulfur contamination. In order to obtain a better knowledge of the mechanism for contamination of catalysts at a microscopic level, an ultra-violet photoelectron spectroscopy (UPS) study of the adsorption of elemental S and Cl on reduced TiO@sub 2@(110) surfaces has been performed. A previous study of the adsorption of S on TiO@sub 2@(110) has shown that a variety of overlayer structures can be obtained, depending on the temperature of adsorption.@footnote 1@ Below ~120 °C, S adsorbs preferentially on the exposed Ti rows and forms a weakly ordered overlayer. Above ~120 °C, there is a change in the S adsorption site from on top of the Ti rows to a replacement of the surface O. UPS measurements show that the surface defect state of the reduced TiO@sub 2@ substrate is quenched upon adsorption of S at RT. In addition, there is a shift of 0.4 eV in the valence emission to lower binding energy that results from an "un-bending" of the valence band. Adsorption of S at ~350 °C results in an enhancement of the surface defect state and the appearance of new emission features within the band gap of the TiO@sub 2@. Both the defect state and the emission features within the band gap resonate at the Ti 3p to 3d absorption threshold. A shift in the Ti 3p core emission of ~0.5 eV to lower binding energy and a reduction in the O 2s emission are also observed. These results indicate that there is an increase in the population of Ti 3d states from a loss of surface O. Cl adsorption at RT behaves similarly to S with a quenching of the surface defect state and a 0.4 eV shift of the valence band. Although adsorption of Cl at 200 °C results in an enhancement of the surface defect state, no new emission features are observed within the band gap of the TiO@sub 2@. @FootnoteText@ @footnote 1@ E. L. D. Hebenstreit, W. Hebenstreit, and U. Diebold, Surf. Sci. (in press).

10:00am **SS1-TuM6 Thermal Production of Phosgene from Carbon Tetrachloride Reactions on Natural Single Crystal @alpha@-Fe@sub 2@O@sub 3@ Surfaces in Ultrahigh Vacuum***, **K. Adib**, N. Camillone III, J.P. Fitts, D. Mocuta, K.T. Rim, G.W. Flynn, R.M. Osgood, Jr.,* Columbia University*; S.A. Joyce,* Pacific Northwest National Laboratory

Oxides of iron have important applications as catalysts and reactive sites for various classes of chemical reactions. They have a significant environmental role in the speciation of toxic metal cations and the dehalogenation of halocarbons. This environmental role is important due to the abundance of iron oxides in the Earth's crust and due to their higher reactivity compared to other metal oxides. We use ultrahigh vacuum for a detailed study of the chemistry of a well-characterized surface of @alpha@-Fe@sub 2@O@sub 3@ (hematite). Natural single crystal samples of hematite were cut and polished in the (0001) orientation. They were processed in-situ to produce a surface selvedge of Fe@sub 3@O@sub 4@ 2x2 reconstruction, as verified by LEED, and dosed at ~100K with CCl@sub 4@. The surface reactions were studied by temperature-programmed desorption (TPD). The multiplicity of desorption waves observed indicates a complex chemistry involving molecular adsorption and dissociative adsorption on at least two distinct kinds of surface site. The TPD results indicate the formation of COCl@sub 2@ (phosgene) as well as C@sub 2@Cl@sub 4@ and high temperature desorption of iron chlorides. We observe significant differences in the TPD spectrum following the first dosing of the surface as compared to those measured following subsequent dosings indicating a marked change in the surface upon initial exposure. This change is commensurate with the titration of surface defects during the initial reaction stages. Preliminary measurements of the UV photochemistry of the adsorbed CCl@sub 4@ on this surface will be presented.

10:20am **SS1-TuM7 Multiplet Splitting and Crystal Field Strengths at Iron Oxide Surfaces***, **T. Droubay**, S.A. Chambers,* Pacific Northwest National Laboratory*; B.P. Tonner,* University of Central Florida

The metal core-level spectra of 3d-transition metal oxides exhibit complex lineshapes due to multiplet splitting in the final state. The crystal field splitting largely determines the degree of multiplet structure. We have measured surface and bulk-sensitive Fe 2p core-level spectra at high energy resolution for several MBE-grown iron oxide epitaxial films. Line shape differences are observed between surface and bulk sensitive photoemission spectra, indirectly revealing differences in crystal field strength. In order to determine the surface crystal field strength, we have utilized XAS L-edge spectra of bulk iron oxides, and have calculated these spectra from first principles using an atomic multiplet theory. Agreement of ultra-high resolution experimental absorption spectra and theoretical models is excellent. We then used the theoretical multiplet model to simulate the bulk-sensitive XPS core-level spectra by broadening to account for the increased lifetime and adjusting peak heights to optimize agreement between theory and experiment. This step produced an accurate value for the bulk crystal field strength. The metal ion site symmetry was then reduced in the calculation and agreement re-optimized between theory and surface sensitive XPS spectra to obtain the equivalent surface crystal field strength. Determination of the crystal field strength at the surface may provide an insight into oxide surface reactivity.

10:40am **SS1-TuM8 Scanning Electron Microscopy Studies of the Hydration of Alkali Halides***, **S.A. Joyce**, J.P. Cowin,* Pacific Northwest National Laboratory

Morphological and phase changes of several salts which are important constituents of sea-salt aerosols were examined in an environmental scanning electron microcospe as function of both water vapor pressure (from ~2 to 18 Torr) and temperature. For highly soluble materials, dissolution can occur by incorporation of water from the gas phase. The dissolution of NaCl and NaBr samples upon exposure to water vapor have been imaged and the observed temperature dependence of the deliquescence pressures agree well with previous studies. The deliquescence is initially observed as the surface of a crystal becomes featureless, followed by a rounding and spreading of the solution droplet on the sample holder. NaBr converts to the dihydrate (NaBr*2H@sub 2@O) at water pressures roughly half the deliquescence pressure. The formation of the hydrate can be readily observed in the SEM. Unlike the case of deliquescence, no significant changes in the microtopography are initially observed, rather hydration results in a change in the contrast. Dark regions on the surface nucleate and grow as the hydration proceeds. The rate of hydration/dehydration is a strong function of the pressure (i.e. the saturation ratio). Prolonged hydration results in an increase in the roughness of the surface presumably due to microcrystallite formation as a stress-relief mechanism. Cycling hydration/dehydration results in higher roughness. Delamination and spalling have been observed upon rapid dehydration. Both effects increase the net surface area. Such cycling is very common in the atmosphere versus changes in altitude, time, and the day/night cycle, and should have a strong impact on water-soluble aerosol morphology. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:00am **SS1-TuM9 Reactivity of Water toward NaCl(100)**, ***A.J. Leavitt**, R.D. Huffstetler, Jr., J.W. Russell, J.I. Brauer, J.K. Cutchins, C.D. Lane, M.B. Reddy, F.A. Khan,* State University of West Georgia

The role of water-mediated reactions that occur on particulate NaCl surfaces is relevant to atmospheric chemistry. A temperature-programmed desorption (TPD) study of water adsorbed onto NaCl(100) was performed. Water was adsorbed onto the surface held at a temperature of 130 K at a variety of water fluences, then thermally desorbed into a quadrupole mass spectrometer in an ultrahigh vacuum chamber. Water molecularly adsorbs onto the surface and desorbs in a first-order process at ~143 K for fluences corresponding to 10% of a monolayer. As the water fluence is increased, the temperatures of maximum desorption shifts higher suggesting stabilization of the water layer through hydrogen bonding. Further increases in water fluences lead to a constant area under the desorbing peak suggesting the buildup of a condensed layer of the water on the NaCl surface. This desorption feature does not appear to saturate at very high fluences of water. These results are consistent with previous work by Falsch and Henzler (UPS study) and Peters and Ewing (IR study). This work was supported by Research Corporation.

11:20am **SS1-TuM10 Surface Segregation of Bromine in Bromide Doped NaCl: Implications for the Seasonal Variations in Arctic Ozone**, ***S. Ghosal**, J.C. Hemminger,* University of California, Irvine

Episodes of ozone depletion attributed to chemistry of gas phase bromine compounds in marine regions of the Arctic boundary layer have been reported at polar sunrise. Models for the source of brominated compounds in the marine Arctic troposphere have focussed on surface chemistry of sea salt ice and aerosols even though the molar ratio of Cl@super-@ to Br@super-@ in sea salt is expected to be ~660 to 1. X-ray photoelectron spectroscopy (XPS) studies described here show, for the first time, substantial segregation of Br@super-@ to the surface of NaCl samples with low level Br@super-@ dopant. Water exposure plays an important role as it provides enhanced ionic mobility in such systems allowing the surface segregation as the system approaches thermodynamic equilibrium. Our XPS results are confirmed by scanning electron microscopy (SEM) imaging of the salt sample surface after water vapor exposure, which shows NaBr crystallites that form at the surface. Our experiments provide the first experimental evidence of surface segregation in mixed alkali halide solids.@footnote 1@ The segregation phenomenon displayed here is likely to play an important role in a wide range of atmospheric phenomena that involve surface reactions of sea salt particles and aerosols. @FootnoteText@ @footnote 1@ This work was supported by the NSF Grant ATM-9707285.

11:40am **SS1-TuM11 Isothermal Desorption Kinetics of H@sub 2@O from @super 1@H@sub 2@@super 16@O, @super 1@H@sub 2@@super 18@O and @super 2@H@sub 2@@super 16@O Ice Multilayers**, ***J.A. Smith**, F.E. Livingston, S.M. George,* University of Colorado at Boulder

The mechanism of H@sub 2@O desorption from ice can be explored by examining the H@sub 2@O desorption kinetics from ice composed of the various H@sub 2@O isotopomers. The isothermal desorption kinetics of H@sub 2@O from @super 1@H@sub 2@@super 16@O, @super 1@H@sub 2@@super 18@O and @super 2@H@sub 2@@super 16@O ice multilayers were measured using optical interferometry. These experiments were performed at temperatures between 175-195 K using ice multilayers grown epitaxially on a Ru(001) surface. The desorption rates of @super 1@H@sub 2@@super 16@O and @super 1@H@sub 2@@super 18@O were very similar. The desorption kinetics for @super 1@H@sub 2@@super 16@O were E@sub d@ = 13.9 +/- 0.2 kcal/mol and @nu@@sub d@ = 10@super 32.6 +/- 0.3@ molecules/cm@super 2@ s. In contrast to the expectation that the H@sub 2@O desorption rate should scale with the square root of molecular mass, the desorption rate of @super 2@H@sub 2@@super 16@O was approximately a factor of two slower over the measured temperature range. The desorption kinetics for @super 2@H@sub 2@@super 16@O were E@sub d@ = 14.8 +/- 0.4 and @nu@@sub d@ = 10@super 33.4 +/- 0.5@ molecules/cm@super 2@ s. The desorption kinetics for the three H@sub 2@O isotopomers are explained using transition state theory. Th e rotational degrees of freedom yield the main differences. The differences in the activation energies are related to the zero-point energies of frustrated rotations on the ice surface. The differences in pre-exponentials are associated with the moments of inertia of the desorbing molecules.

Surface Science
Room 209 - Session SS2+NS+BI+EL-TuM
Self-Assembled Monolayers

Moderator: D.H. Fairbrother, Johns Hopkins University

8:20am **SS2+NS+BI+EL-TuM1 Creating Highly Selective Organic Surfaces using Self-assembly: A New Family of Organothiols**, ***R. Arnold**,* Ruhr-Universität Bochum, Germany*; A. Terfort,* Universität Hamburg, Germany*; C. Wöll,* Ruhr-Universität Bochum, Germany

The creation of organic surfaces with specific properties via the adsorption of correspondingly functionalized organothiols has recently attracted considerable interest, e.g. in the context of bio-sensors and biomimetics. In case of alkanethiols some functional groups, however, interact so strongly with each other that the ordering within the SAMs is affected, e.g. in the case of -COOH functional groups.@footnote 1@ The situation can be improved by using more rigid backbones, e.g. oligophenyl units.@footnote 2@ With regard to biochemical applications in many cases the distance between adjacent organothiol units (4.97 Å) is too small to immobilize larger molecules, e.g. small proteins. In the past these problems could be overcome in some cases by diluting the functionalized organothiol in a shorter, nonfunctionalized thiol. Here, we present a different approach where a more bulky thiol is used, which increases the nearest neighbor distance. We will present the results of a study using several homologues of triptycenethiols. SAMs formed from these compounds were characterized by using XPS, IRRAS, NEXAFS, LEED and TDS. The results reveal the formation of well ordered monolayers, which are anchored to the gold surface in a more distant lateral structure than alkane- or p-terphenylthiols. @FootnoteText@ @footnote 1@ Dannenberger, O.; Weiss, K.; Himmel, H.-J.; Jäger, B.; Buck, M.; Wöll, C. Thin Solid Films 1997, 307, 9885-9893 @footnote 2@ Himmel, H.-J.; Terfort, A.; Wöll, C. J. Am. Chem. Soc. 1998, 120, 12069-12074.

8:40am **SS2+NS+BI+EL-TuM2 Characterization of the Alkanthiol/Metal Interface by High Resolution Core Level Spectroscopy**, ***K. Heister**, H. Rong, M. Buck,* University Heidelberg, Germany*; L. Johansson,* University Karlstad, Sweden*; M. Zharnikov, M. Grunze,* University Heidelberg, Germany

During the last decade X-ray Photoelectron Spectroscopy with a laboratory X-ray source became a conventional technique to characterize thiol derived SAMs. However, due to the mostly poor energy resolution, a strong attenuation of the photoelectron signal, and a low photoionization cross-section of the relevant core levels at high photon energies a precise binding energy analysis of an important building block of a SAM, the SAM/metal interface was hardly possible, even though high resolution photoelectron spectroscopy could give important information about the chemical state of the atoms in this region. Taking advantage of the high performance and tunebility of the third generation synchrotron sources we have firstly applied the synchrotron-based High Resolution Core Level Spectroscopy to study the SAM/metal interface. The variable photon energy of the synchrotron light and a high energy resolution of the spectrometer (0.1-0.3 eV) enabled us to resolve the bulk and surface components of the substrate emission peak (Au 4f / Ag 3d) and monitor the evolution of these components upon the alkanethiol and biphenylthiol adsorption. Simultaneously, the interaction of the thiol-derived molecules with the substrate was followed by monitoring the S2p doublet attributed to the sulfur head group of these molecules. Only one sulfur species was found in the densely packed SAMs, which implies an equivalent bonding geometry for all adsorbed molecules. In SAMs comprising of specially designed, mixed aliphatic-aromatic molecules a periodical, 'odd-even' shift of the S2p binding energy with the varying length of the aliphatic part was observed. This shift can be attributed to the distortion of the substrate-S bonding angle resulting from the unfavorable package conditions occurring at definite lengths of the aliphatic part. This work has been supported by the German Bundesministerium für Bildung, Wissenschaft und Technologie through grant No. 05 SL8VHA 2 and by DAAD.

9:00am **SS2+NS+BI+EL-TuM3 The Influence of the Endgroup and the Chain Length on the Growth of CH@sub 3@- and CF@sub 3@-terminated Alkanetiols on Au(111)***, **J. Pflaum,*** Princeton University*; G. Bracco,* University of Genova, Italy*; G. Scoles,* Princeton University*; R. Lee,* University of Houston*; A. Kahn,* Princeton University

The influence of the functional endgroup and the CH@sub 2@ chain length on the growth of alkanethiols on Au(111) was studied by scanning tunneling microscopy (STM) and x-ray surface diffraction in grazing-incidence geometry (GIXD). Thiols are model systems for self-assembled monolayers (SAMs) and exhibit a complex phase diagram as function of coverage. The structure and the electronic properties of the SAMs are determined by the sulfur headgroup, the CH@sub 2@ backbone and the functional endgroup. Leaving the sulfur headgroup unchanged, we studied how the film structure depends on the endgroup by comparing CH@sub 3@- and CF@sub 3@-terminated thiols. All films were prepared from solution on an atomically ordered Au(111) surface. The lateral order of the as-grown CH@sub 3@-terminated films corresponds to the c(4x2) phase, i.e. the highest density standing-up phase. From STM studies we conclude that the arrangement of CH@sub 3@ endgroups corresponds to a pinwheel-like structure rather than to a zig-zag-like structure. In contrast, CF@sub 3@(CH@sub 2@)@sub 9@SH showed no lateral ordering as seen by STM and GIXD. However, the difference between electron densities at the CF@sub 3@/vacuum and the SH/Au interfaces induces an oscillation of the GIXD reflectivity. Fitting the periodicity of the modulation using the Parratt formalism leads to an estimate of the film thickness and its roughnesses at both interfaces. In spite of the lack of lateral order the film appears to be made by standing-up molecules. Differences between the thickness measured by ellipsometry and x-rays will be discussed. We will also explore the lying-down phase of alkanethiols and fluorinated thiols as organic templates for organic heterostructures. Initial results on the growth of PTCDA on such templates will be presented. This work was supported by the MRSEC program of the National Science Foundation (DMR-9809483). J.P. thanks the Deutsche Forschungsgemeinschaft for support (Grant No. PF 385/1-1).

9:20am **SS2+NS+BI+EL-TuM4 Self-Assembled Monolayers of Terphenyl Derivatized Thiols; Adsorption, Insertion Process and Electrical Conduction***, **T. Ishida,*** JRCAT-NAIR and PRESTO-JST, Japan*; W. Mizutani,* JRCAT-NAIR, Japan*; N. Choi,* JRCAT-ATP, Japan*; H. Tokumoto,* JRCAT-NAIR, Japan

The investigation of SAMs made from conjugated molecules is highly activated from a viewpoint of molecular electronics as well as stable SAM formation. In the present study, we have investigated an insertion process of conjugated molecules, terphenylthiol (TP0), terphenyl methanethiol (TP1), terphenyl propanethiol (TP3), into nonanethiol self-assembled monolayers (SAMs) on Au(111) by STM. STM observation revealed that the insertion process is dependent on the molecular length of conjugated molecules. At the initial stage of insertion, replaced area of TP1 is larger than those of TP0 and TP3. However, when the immersing time is more than 12h, the replaced area of TP3 is larger than those of TP0 and TP1. The insertion process is likely to be determined by the solubility of the conjugated molecules and thermal dynamics. The single molecular resistance were increased with the number of the methylene groups, and obtained about 20G-ohm (TP0), 40 G-ohm (TP1) and 66 G-ohm (TP3). The vertical conduction of the conjugated molecular domains of TP1 and TP3 depended on their lateral sizes, while strong dependence was not observed in the case of TP0, suggesting that methylene group is necessary between the sulfur and aromatic rings to increase the vertical conduction of molecular domain.

9:40am **SS2+NS+BI+EL-TuM5 Structure and Chemistry of Alkanethiol Self-Assembled Monolayers***, **G.E. Poirier**, T.M. Herne, C.C. Miller, M.J. Tarlov,* National Institute of Standards and Technology **INVITED**

Derivatized alkanethiols form dense, physically blocking films on Au surfaces thereby providing an effective and parsimonious method to control the chemical, physical, and electron-transfer properties of electrode surfaces. To predict the function of these monolayers in device applications, scientist require an understanding the molecular-scale structure and chemistry. Our structure studies were conducted using gas-phase transport of decanethiol onto clean Au(111). Characterization was accomplished using ultrahigh vacuum scanning tunneling microscopy. At low surface coverage, decanethiol exists as a 2-dimensional gas. With increasing coverage the molecules sequentially condense into islands of three discrete commensurate crystalline lattices, each characterized by alignment of the molecular axes with the surface plane (striped phases). Above saturation coverage of the densest striped phase, the monolayer undergoes an edge-mediated melting transition forming a supercooled 2-dimensional liquid. Domains of the c(3x2*3) phase, characterized by alignment of the molecular axes close to the surface normal, nucleate and grow from this surface liquid. The reaction of these monolayers with ozone was characterized using scanning tunneling microscopy and x-ray photoelectron microscopy; our results show that exposure to ozone results in oxidation of the thiol terminus. The reaction initiates at the c(3x2*3) domain boundary network and propagates into the domains. Above a threshold surface oxygen content, the monolayer converts to a two-dimensional fluid that can subsequently recrystallize to a commensurate monolayer of partially oxidized thiol. Further exposure to ozone results in conversion of the monolayer to a fluid phase and a 10% to 30% expansion of the Au lattice at the Au-thiol interface with concomitant formation of Au islands. Our results demonstrate that crystallographic defects in monolayer films can play an important role in their chemical reactions.

10:20am **SS2+NS+BI+EL-TuM7 Characterization of SAMs with Contrast Variation SPR Technique***, **K. Tamada,*** NIMC and RIKEN Frontier Program, Japan*; H. Akiyama, J. Nagasawa,* NIMC, Japan

We report characteristics of azobenzene-containing self-assembled monolayers (SAMs) which is designed and synthesized for surface photo-isomerization reaction. The surface reaction was monitored by Surface Plasmon Resonance Spectroscopy (SPR), in which the contrast variation technique with various organic solvents was used to improve the accuracy for determination of the optical thickness change by surface reaction. The SAM formation was monitored by kinetic mode experiment with SPR in 0.1mM hexane solution, and after rinsing, refractivity change by UV-VIS photo irradiation was studied in various solvents. In this study, hexyl azobenzene thiol (12-(4-((hexylphenyl)azo)phenoxy)dodecane-1-thiol) SAM was used as an unreactive surface and unsymmetrical azobenzene-disulfides SAMs with the same azobenzene functions were used as reactive ones. Following the previous reports, monomeric dispersion of dye function with disordered chains seems to be necessary to realize highly reactive surface. For our unsymmetrical azobenzene-disulfides SAMs, the free volume for photo-isomerization reaction are guaranteed by 50% dilution of dye functions on surface at monomolecular level. As a result, it was confirmed that unsymmetrical azobenzene-disulfides SAMs were highly reactive, especially, in good solvents (alkanes: C5, C6, C7, C8) and the length of alkyl side chains was quite efficient for surface reactivity.

10:40am **SS2+NS+BI+EL-TuM8 Characterization of a Polymerized Self-Assembled Monolayer Using NEXAFS***, A.L. Marsh, D.J. Burnett,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; C.E. Evans, **J.L. Gland,*** University of Michigan

Near-edge X-ray Absorption Fine Structure, or NEXAFS, at the C-K-edge was used to characterize the orientation of the polymeric backbone in a self-assembled monolayer of 15,9-polydiacetylene. Monolayers were fabricated from the assembly of molecules of dinonacosa-10, 12-diyn-disulfide from a chloroform solution onto a 2000 Angstrom gold film on a mica substrate. Polymerization occurs across one of the C-C triple bonds in the chain, which results in a polymeric network located within the monolayer. Since resonance intensities in NEXAFS spectra are dependent on electric dipole selection rules, it is possible to determine the orientation of the polymeric backbone by comparing spectra at normal incidence (E vector parallel to the surface plane) with spectra at glancing incidence (E vector perpendicular to the surface plane). From the two spectra it was determined that the polymeric backbone is oriented parallel to the surface, while the alkyl chains are oriented perpendicular to the surface. Since NEXAFS probes unfilled molecular orbitals, it is capable of distinguishing between various bonds, i.e. a C-C double bond versus a C-C triple bond, making it possible to determine structural changes as a function of temperature. Upon increasing the temperature, the C-C double bond pi* resonance increases, while the C-C triple bond pi* resonance decreases. These changes would be consistent with a degradation of the polymer backbone. Above a threshold temperature, the changes are irreversible, leading to eventual thermal degradation of the monolayer.

11:00am **SS2+NS+BI+EL-TuM9 An Estimation of Effective Mean Free Path of Photo- and Auger Electrons in Partial Yield Measurements using Self-assembled Monolayers**, ***M. Zharnikov***, *S. Frey*, *K. Heister*, *M. Grunze*, Universität Heidelberg, Germany

In the partial electron yield (PEY) acquisition mode commonly used in X-ray absorption spectroscopy both elastically and inelastically scattered electrons contribute to the signal with the latter contribution presumably dominating. In this case a majority of inelastic scattering events will not result in the signal attenuation as it happens in the X-ray photoelectron spectroscopy (XPS). The scattered electrons will still have a kinetic energy in the acquisition range of the spectrometer. The related values of mean free path (MFP) should be, therefore, noticeably larger than the well-known inelastic mean free paths for electrons of definite kinetic energy. We have performed XPS and near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements for series of self-assembled monolayers of alkanethiols on gold substrate. The length of the alkyl chain and, subsequently, the film thickness was varied. In agreement with the expectations, the obtained effective MFPs for the Au 4f photoelectrons and C@sub KLL@ Auger electrons in the PEY acquisition mode exceed the respective values for the elastically scattered electrons of the same kinetic energies (the Au 4f and C@sub KLL@ electrons made up the elastic component of the acquired PEY signals). Furthermore, the PEY-MFP for the C@sub KLL@ Auger electrons increased with decreasing retarding voltage of the PEY detector, which correlates with the increasing contribution of the inelastically scattered electrons in the acquired signal. The obtained results are of importance for the analysis of NEXAFS spectra in both self-assembled monolayers and polymers. This work has been supported by the German Bundesministerium fuer Bildung, Wissenschaft und Technologie through grant No. 05 SF8VHA 1 and by the Fonds der Chemischen Industrie.

11:20am **SS2+NS+BI+EL-TuM10 Growth Process and Thermal Stability of Semifluorinated Alkanethiol Self-Assembled Monolayers on Au(111)**, ***M. Hara***, Frontier Research System, RIKEN, Japan; *A. Suzuki*, Tokyo Institute of Technology, Japan; *K. Tamada*, National Institute of Materials and Chemistry, Japan; *H. Fukushima*, Seiko Epson Co., Japan; *T.R. Lee*, University of Houston

Growth process and thermal stability of semifluorinated alkanethiol (CF@sub 3@(CF@sub 2@)@sub m@(CH@sub 2@)@sub n@SH) self-assembled monolayers (SAMs) on Au(111) have been investigated by thermal desorption spectroscopy (TDS) and scanning tunneling microscopy (STM). The growth kinetics showed nearly the Langmuir adsorption isotherm and the etch pits were formed in the upright phase, while the striped phases were not observed in the initial growth stage for shorter (CH@sub 2@)@sub n@ semifluorinated SAMs. In TDS, no significant peaks can be obtained for dimer molecules and decomposed species, suggesting no associative desorption nor dimerization and thermal stability of the semifluorinated molecules during heating up to 650 K. Since longer (CH@sub 2@)@sub n@ semifluorinated SAMs remained the same chemisorbed state in the monolayer after annealing at around 480 K, it has been confirmed that also the alkyl chain part plays an important role for the thermal stability and the ordering in the semifluorinated alkanethiol SAMs. Following those results, we propose more detailed surface phase transition model of semifluorinated alkanethiol SAMs in the growth and annealing processes.

11:40am **SS2+NS+BI+EL-TuM11 Multi-technique Study of Self-Assembled AuCN Monolayers on Au(111) Formed by Electrochemical Deposition**, ***T. Yamada***, Waseda University, Japan; *R. Sekine*, Shizuoka University, Japan; *T. Sawaguchi*, AIST/MITI, Japan

Two kinds of monolayers of AuCN electrodeposited on Au(111), indexed (1.15x@sr@3R-30°) and (1.41x2@sr@3R-30°), have been investigated by XPS, UPS and HREELS as well as LEED, AES and STM to determine the geometrical, electronic and vibrational properties. Electrodeposition was performed in an aqueous 1 mM KAu(CN)@sub 2@ solution by applying an electrode potential about 0 - +0.1 V vs SCE on the Au(111) crystal. Sharp LEED patterns were obtained for these two kinds of adlayers. AES indicated that both of these adlayers were composed Au, C and N without impurity. Well ordered adlattices composing domain structures (domain size ca. 10 nm) were observed by STM. XPS yielded Au 4f signals from AuCN indicating small fractional positive charges on the Au atom incorporated in AuCN. The UPS of AuCN/Au(111) was composed of the Au orbitals and weak signals from CN orbitals, assigned by relativistic DV-Xa molecular orbital calculation. The binding energies of CN orbitals are in the order of 4@sigma@ > 5@sigma@ > 1@pi@, which indicates that the C-Au bond is essentially covalent. HREELS yielded vibrational spectra similar to that obtained for AuCN crystalline powder.@footnote 1@ The C-N stretching frequencies were found to be 2140-2160 cm@super -1@, which are consistent with the covalent nature of the C-Au bond. In the frequency region below 300 cm@super -1@, loss peaks related to the Au-N bonds were seen. The (1.15x@sr@3R-30°) adlayer is concluded to be composed of -AuCN- linear chains (polymer chains) that are identical to those embedded in the AuCN crystal. For the (1.41x2@sr@3R-30°) adlayer, HREELS indicated distortion or breaking of Au-N bonds. Some structural models are proposed for this. These results reveal a special inorganic polymeric feature of the self-assembled AuCN adlayers lying parallel along the surface. @FootnoteText@ @footnote 1@G. A. Bowmaker, B. J. Kennedy and J. C. Reid, Inorg. Chem. 37, 3968 (1998).

Surface Science
Room 210 - Session SS3+MC-TuM
Technique Innovations: Experiment, Theory and Simulation

Moderator: S.B. Sinnott, The University of Kentucky

8:20am **SS3+MC-TuM1 Twenty-First Century Modeling: Multiscale Coupling and its Impact on Surface and Interface Science**, ***E.A. Carter***, University of California, Los Angeles **INVITED**

Multiscale modeling is all the rage among computational material scientists in this new century. This refers to a type of simulation which considers phenomena whose length and/or time scales span several - possibly many - orders of magnitude. Examples of such phenomena include, e.g., time scale disparities in surface diffusion and thin film growth, length scale disparities in corrosion-induced cracking of solid materials, etc. In the first example, surface diffusion is "fast" while the flux of material is "slow". In the second example, corrosion involves chemical reactions on the atomic scale while cracking takes place on the meso-to-macroscale. Future materials modeling will account for the complexities across scales. An overview will be given of new techniques being developed that: (i) provide a first principles quantum mechanical description of thousands of atoms (via a linear scaling kinetic energy density functional - KEDF - theory); (ii) couple atomic level interactions, described by KEDF molecular dynamics simulations, to quasi-continuum simulationsof behavior on the micron scale; and (iii) connect first principles quantum mechanics calculations to cohesive zone continuum mechanics simulations of crack propagation in solids. The impact of such coupled simulations on understanding how surface and interface phenomena affect materials behavior on scales beyond the atomic will be emphasized.

9:00am **SS3+MC-TuM3 The KMLYP Density Functional Approximation: A New Method for Accurate Prediction of Activation Barriers and Enthalpies of Reaction**, *J.K. Kang*, ***C.B. Musgrave***, Stanford University

We develop the KMLYP hybrid DFT method which is shown to predict activation energies and enthalpies of reaction with smaller errors than B3LYP, G2, QCISD(T), CCSD(T), and CBS-APNO. The accuracy of the method is demonstrated on over 100 reactions. The KMLY P exchange functional is a hybrid functional that combines Hartree-Fock exact exchange with Slater exchange. The correlation functional is a hybrid functional combining Lee-Yang-Parr (LYP) correlation and Vosko-Wilk-Nusair (VWN) correlation. For reactions with reliable experimental data, the RMS deviation of the activation energies are 0.64 kcal/mol, 1.59 kcal/mol, 3.20 kcal/mol, and 3.10 kcal/mol for the KMLYP, CBS-APNO, G2, and B3LYP methods, respectively. The RMS deviations from experiment of the entha lpy of reaction are 1.57 kcal/mol, 2.24 kcal/mol, and 2.87 kcal/mol for the KMLYP, G2 and B3LYP methods, respectively. The KMLYP maximum absolute deviation of the activation barriers is 1.2 kcal/mol while the KMLYP maximum absolute deviation of the enthalpy of reactions is 3.8 kcal/mol. Furthermore, KMLYP is significantly more efficient than the G2, QCISD(T), CCSD(T), and CBS-APNO methods and is practical for the simulation of surface reactions using relatively large clusters.

9:20am **SS3+MC-TuM4 Probing Chemical Interactions at the Single Bond Level**, ***M.K. Weldon***, Bell Laboratories, Lucent Technologies; *J.D. Batteas*, City University of New York, College of Staten Island; *K. Raghavachari*, Bell Laboratories, Lucent Technologies

The measurement of chemical bond strengths is a fundamental goal of much of chemistry; indeed the making and breaking of bonds between atoms is the essence of chemical science. Despite this, the direct measurement of bond strengths has remained an elusive goal due primarily to the inherent difficulty in localizing the requisite excitation along a single bond coordinate. Here we demonstrate a methodology for measuring the strength of individual chemical bonds at solid surfaces. We have used atomic force microscopy (AFM) to probe the pH-dependent changes in the surface chemistry of silica in the single bond limit. We observe quantized adhesion forces that, when referenced to the results of ab initio quantum chemical cluster calculations, can be unambiguously assigned to single neutral hydrogen bonds (OH..OH), single ionic hydrogen bonds (OH@super -@..OH) and single covalent bonds (Si-O-Si) between the tip and surface. We have subsequently extended this work to measure the interaction (bond) energetics in a number of aqueous and organic solvent systems. Remarkably, we find that we able to observe individual H@sub 2@O..H@sub 2@O hydrogen bonds under the appropriate conditions, as well as the attendant isotopic shift and bond weakening upon raising the temperature, again demonstrating the potential of this approach for exploring the nature of chemical bonds in solution. In summary, this breakthrough in chemical analysis is predicted to be generalizable to all solution reactions for which the constituent reagents can be chemically functionalized onto a solid surface. To this end, we are currently investigating the interaction energetics in a variety of reactive organic systems.

9:40am **SS3+MC-TuM5 Surface Vibrational Spectroscopy Beyond the Harmonic Approximation, Experiments and Calculations***, **P. Uvdal**, M.P. Andersson, R. Asmundsson,* Lund University, Sweden*; A.D. MacKerell, Jr.,* University of Maryland

Vibrational analysis of surface adsorbates involves in general the assignment of fundamental normal modes. Based on such assignment conclusions about chemical identity and geometry can be drawn. It is however well known from fundamental textbooks on molecular vibrations that if one goes beyond the harmonic approximation of the intramolecular bond potential overtone and combination modes are allowed. Binary modes, i.e. excitation of one vibration with two quanta or excitation of two vibrations with one quanta, will be the most intense even though higher excitations are allowed. The presence or absence of binary modes will contain information about bond anharmonicity and coupling between different modes. The latter may reveal surface induced changes of activation barriers of importance for the understanding of e.g. heterogeneous catalysis. The former reveal dynamical properties of the system as the extent of coupling governs the dissipation and randomization, within the molecule, of the energy initially localized in a single bond excitation. Using methoxy and ethoxy adsorbed on Cu(100) and W(110) surfaces as model systems we will demonstrate binary intramolecular modes in the presence and absence of Fermi resonance coupling. We will also show a combination mode consisting of the C-O stretch and the hindered motion of methoxy with respect to the surface.

10:00am **SS3+MC-TuM6 Time Resolved Fourier Transform Infrared Spectroscopy***, **M. Kovar**, P.R. Norton,* University of Western Ontario, Canada

We have developed a data acquisition system based on digital signal processing for a broadband time-resolved Fourier Transform Infrared Spectrometer. In FTIRS, broadband infrared radiation is modulated by means of a Michelson interferometer. The position of the moving mirror is tracked by the fringe pattern of a reference He/Ne laser, whose beam follows the same optical path as the infrared radiation. Pulses used for time resolution as fast as 500 ns are modulated on a reference He/Ne laser signal. We have chosen a slower mirror speed which permits observation of an external perturbation of a system under investigation which often limits the mirror speed. Different external perturbations can be used, such as thermal, mechanical, photochemical or those caused by external potential. We discuss characteristics of time resolved FTIRS and its performance. The system will permit grazing incidence IR reflection-absorption measurements of surface and thin film processes with sub-microsecond time resolution.

10:20am **SS3+MC-TuM7 Momentum Space Line Narrowing by Angle Resolved Auger-photoelectron Coincidence Spectroscopy***, A. Danese, **R.A. Bartynski**,* Rutgers University*; R. Gotter,* Lab. Nazionale TASC-INFM, Trieste, Italy*; S. Iacobucci,* CNR-IMAI Montelibretti, Italy*; G. Stefani,* U. di Roma III, Italy

We have measured the Ag N@sub 23@VV Auger electron diffraction pattern from the Ag(100) surface in coincidence with Ag 4p photoelectrons under high energy and angular resolution conditions. Measurements were performed using the ALOISA beamline at the ELETTRA synchrotron in Trieste. It is well known that the Auger and photoemission spectra associated with the shallow 4p (3p) core levels of the late 4d (3d) transition metals are unusually broad in energy owing to the rapid decay of the core hole. Furthermore, it has been shown for the Cu 3p and Ag 4p levels that this energy broadening can be eliminated in Auger-photoelectron coincidence (APEC) energy distribution curves. However, this lifetime broadening is expected to generate a concomitant momentum broadening and the resultant Auger diffraction pattern has only a very weak intensity modulation of ~15%. By performing an APEC measurement with high energy and angular resolution, this momentum broadening should be eliminated. In our APEC angular distribution curves, intensity modulations are enhanced to ~50%, consistent with a significant reduction of the momentum uncertainty of the outgoing Auger electrons. These results provide direct evidence that the photoexcitation/Auger decay of these levels is a coherent process. The implications of these results in the context of Auger electron diffraction will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Supported by NSF grant NSF-DMR9801681 and NATO grant CRG97-0175.

10:40am **SS3+MC-TuM8 A Microarray Technique for Measuring Adsorption/Desorption Kinetics***, **M.C. Wheeler**, R.E. Cavicchi, G.E. Poirier, S. Semancik,* National Institute of Standards and Technology

We have developed a novel method for characterizing the kinetics and thermodynamics of adsorption and desorption that uses a 340-element array of micromachined Si hotplates as the sample platform. The method takes advantage of the microhotplates' rapid heating characteristics (10@super 6@ °C/s), intermediate between traditional temperature programmed desorption methods and pulsed laser desorption. The method is isobaric, particularly useful for studying many systems where the desorption rate is significant at room temperature, and readily automated to efficiently produce large data sets for adsorption systems. Under constant gas exposure, all of the array elements are simultaneously subjected to square temperature pulses as short as 5 ms. An example sequence is a high-T cleaning pulse (as high as 800 °C), a low-T adsorption pulse, an intermediate-T desorption pulse, and a final high-T cleaning pulse. Variation of the pulse amplitude and duration allows determination of the adsorption and desorption rate constants and energies. Signal-to-noise is enhanced by using a large array of microhotplate devices and averaging of repeated pulse sequences. The pressure range is extended to over 10@super -5@ Torr using a differentially pumped mass spectrometer system (even higher effective pressures can be achieved with a directed doser). We illustrate the technique by mapping adsorption isotherms and extracting parameters for methanol on CVD-deposited SnO@sub 2@ polycrystalline films, such as are used in gas sensing; however, wide ranges of materials and adsorbates can be investigated with this technique. In addition to emphasizing the convenience, flexibility, simplicity, and efficiency of this automated technique, we will also discuss challenges that we have had to address - the most significant relating to temperature calibration and uniformity.

11:00am **SS3+MC-TuM9 Scanning Probe Energy Loss Spectroscopy: Spectroscopic Analysis of Reflected Electrons in Field Emission STM***, **B.J. Eves**,* University of Birmingham, UK*; F. Festy, K. Svensson,* University of Birmingham, UK, U.K.*; R.E. Palmer,* University of Birmingham, UK

Spectroscopic (i.e. chemical) analysis is a key frontier in scanning probe microscopy. We have employed a scanning tunnelling microscope (STM) operating in field emission mode to act as a nanometre scale electron source while the resulting backscattered electrons have been detected with a hemispherical energy analyser. Angular measurements show that the flux of reflected electrons peaks parallel to the surface, consistent with simulations which include the long range field generated by the tip bias voltage. The measured energy loss spectra contain information on the surface and bulk plasmons, and other surface excitations. The Si (111)-7x7 surface was found to show losses at 5, 7.5, 11, 15, and 18 eV. These inelastic losses correspond to an interband transition (5 eV), two surface states (7.5 and 15 eV), and the surface and bulk plasmons (11 and 18 eV, respectively). Spectra have also been measured for a number of different exit angles. With improvements it is believed that the scanning probe energy loss spectrometer (SPELS) can be built to perform electron energy loss spectroscopy with spatial resolution on the scale of 5-50 nm.

11:20am **SS3+MC-TuM10 Application of a Direct Method in Surface X-ray Crystallography***, **P.F. Lyman**, R. Harder, D.K. Saldin,* University of Wisconsin, Milwaukee*; C.-Y. Kim, K.W. Evans-Lutterodt,* Lucent Technologies

The electron density of the near-surface region of a crystal could be recovered from x-ray scattering data if the phases of the scattered radiation were known. In the case of surface scattering, the diffracted intensities arise from the square of a linear combination of bulk and surface amplitudes. Since the phases and amplitudes of the bulk component can be calculated accurately, it is possible to use the bulk scattering as a reference wave, and to thereby estimate the phases of the surface component, in analogy with holography. We have developed an algorithm to estimate the most likely set of surface phases, and to thereby recover the electron density of the near-surface region. We present preliminary applications of this method to (2x1)-reconstructed Ge(001) surfaces. It has been shown that the (001) face of Ge or Si can be passivated by 1 ML of a group V element. Although there is general acceptance of the existence of symmetric group V dimers for most adsorbate/substrate combinations, a controversial result of asymmetric Sb dimers for the Sb/Ge(001) system was concluded from an x-ray scattering study: Each Sb dimer was found to have shifted along the axis of the Sb-Sb bond.@footnote 1@ However, a number of first-principles calculations have found no evidence for the shift. We will use our direct reconstruction algorithm on experimental x-ray scattering data to address the possibility of shifted dimers in a model-independent way. @FootnoteText@ @footnote 1@ M. Lohmeier, H.A. van der Vegt, R.G. van Silfhout, E. Vlieg, J.M.C. Thornton, J.E. Macdonald and P.M.L.O. Scholte, Surf. Sci. V. 275, p.190 (1992).

11:40am **SS3+MC-TuM11 Line of Sight Techniques: Providing an Inventory of all Species Arriving at and Departing from a Surface***, R.G. Jones,* University of Nottingham, UK, U.K.*; A.S.Y. Chan, M.P. Skegg,* University of Nottingham, UK

Line of sight techniques comprise those methods in which species emanating from a surface (atoms, molecules and radicals) undergo just a single pass through the ionisation volume of a mass spectrometer before being pumped. This is achieved by enclosing the mass spectrometer within a cryoshield fitted with appropriate apertures, such that line of sight is established only between a patch on the sample surface (ca 7 mm diameter) and the ionisation volume. All LOS techniques are inherently angle resolved, free from extraneous signals and have approximately equal detection probabilities for all species. Line of sight temperature programmed desorption (LOSTPD)@footnote1@ is a particularly reliable way of obtaining TPD data. By applying an over pressure of gas to the sample and monitoring the reflected flux, we get line of sight sticking probability (LOSSP) measurements@footnote 2@ giving S to an accuracy of 0.02; while monitoring of the reaction products at constant temperature gives line of sight product desorption (LOSPD) data. These techniques provide new, powerful and reliable ways of studying all aspects of surface kinetics, by allowing an inventory of all species arriving at and departing from a surface, for any combination of partial pressures, surface temperature, surface composition and surface structure. In this paper we illustrate these methods using the reactions of 1-bromo-2-chloroethane (BCE) and ioodotrifluoromethane with Cu(111). For BCE we show that it undergoes non-activated dissociative adsorption with a transition state 13 kJ/mol below zero (0 = molecule at infinity). For CF@sub3@I we observe emission of CF@sub3@ radicals and coupling reactions forming, among others, C@sub2@F@sub4@. @FootnoteText@ @footnote 1@ R.G. Jones and S. Turton, Surface Sci. 377-379 (1997) 719. @footnote 2@ R.G. Jones and C. J. Fisher, Surface Sci. 424 (1999) 127.

Processing at the Nanoscale/NANO 6
Room 302 - Session NS+NANO6+SS+MC-TuA

Self-assembly and Self-organization

Moderator: R. Wiesendanger, University of Hamburg, Germany

2:00pm **NS+NANO6+SS+MC-TuA1 Dip-Pen Nanolithography: A New Tool for Generating and Studying Soft Nanostructures***, **C.A. Mirkin**, S.A. Brennan, L.M. Demers, S. Hong, P.V. Schwartz, D.A. Weinberger,* Northwestern University **INVITED**

A new type of ultrahigh resolution soft-lithography, Dip-Pen Nanolithography (DPN) that is interfaceable with biomolecules and biofunctionalized building blocks will be presented. This soft lithography allows one to routinely pattern structures, in serial or parallel fashion, with sub 50 nm spatial and line-width resolution with near-perfect alignment. Implications in materials synthesis, electronics, and biodiagnostics will be discussed.

2:40pm **NS+NANO6+SS+MC-TuA3 A Step Toward Making and Wiring-up Molecular-Scale Devices with a Self-Directed Growth Process***, G.P. Lopinski, D.D.M. Wayner, D.J. Moffatt,* National Research Council of Canada*; **R.A. Wolkow**,* National Research Council of Canada, Canada

Our understanding of and control over molecular adsorption on silicon has advanced very significantly in the last several years. It is now possible to provide a microscopic picture of structure and bonding in covalently attached molecule-silicon surface systems. This detailed understanding of adsorbate-surface structures was entirely lacking when the first wave of enthusiasm for molecular devices crested roughly 20 years ago. While many ideas for molecule-scale devices have been put forward in the past, the tools - both synthetic and analytical - to pursue those ideas did not exist. Now, the control necessary to begin exploring ways to incorporate organic function into existing technologies or, eventually, to make new molecule-scale devices is within reach.@footnote 1@ Experimental and modeling methods have emerged that effectively extend the resolution of STM to see the details of adsorbed molecule structure and bonding. In the next several years it is now realistic to expect structures and concepts dreamed about for decades to begin to be realized. This talk will focus on a self-directed growth process for creating molecular nanostructures on silicon.@footnote 2@ @FootnoteText@ @footnote 1@ Controlled Molecular Adsorption on Si: Laying a Foundation for Molecular Devices, R.A. Wolkow, Annual Review of Physical Chemistry, volume 50, 413-41, 1999. @footnote 2@ Self-Directed Growth of Molecular Nano-Structures on Silicon, G.P Lopinski, D.D.M. Wayner and R.A. Wolkow, Nature in press.

3:00pm **NS+NANO6+SS+MC-TuA4 Control of Spatial Distribution of Self-Assembled Diacetylene Compounds by Co-deposition with Fatty Acid Molecules***, **Y. Kuwahara**, G.-M. Zhang, J.-W. Wu, M. Akai-Kasaya, A. Saito, M. Aono,* Osaka University, Japan

Control of self-assembled surface structure of functional organic molecules has been attracting intensive interest from a viewpoint of future applications such as novel material structures for nanometer-scale molecular devices. We have investigated self-assembled surface structures of two different chain organic molecules co-adsorbed on HOPG by use of scanning tunneling microscopy. The subject molecule was 10,12-tricosadiynoic acid, which is one of the diacetylene compounds possessing the possibility of being polymerized into macromolecular wire and/or sheet, and several kinds of fatty acids were used as buffer molecules. We used Langmuir Blodgett method for the fabrication of the molecular monolayers. In order to achieve the parallel molecular arrangement, the surface pressure for the deposition was deliberately controlled much lower than the saturate pressure and the substrate was horizontally oriented. A variety of molecular patterns inside the two-component monolayers were revealed, which could be briefly grouped into 'phase separation pattern', where microscopically pure 10,12-tricosadiynoic acid and fatty acid were observable respectively, and 'alternative pattern', in which the lamellae of the two sorts of molecules emerged alternatively. In order to evaluate the mechanism for the two dimensional surface ordering, we have also done the ab-initio molecular orbital calculation and the proposed structural model of the surface self-assembly is in good agreement with the theoretical simulations. Consequently, the possibility of controlling the spatial distribution of the diacetylene compounds on the solid surface has been demonstrated.

3:20pm **NS+NANO6+SS+MC-TuA5 The Interaction of Metal Atoms with Self-assembled Organic Monolayers***, **A.V. Walker**, B.C. Haynie, N. Winograd,* The Pennsylvania State University

Organic monolayers show great promise as materials for a wide range of technological applications. An understanding of the nature of the metal atom - organic monolayer interaction is vital in the development of molecular electronic devices. Recently it was demonstrated that deposited Al atoms can penetrate through an n-alkyl monolayer to the monolayer / Au (111) interface. This phenomenon is believed to occur via thermally activated transient defects in the monolayer. In this paper, we explore the thermodynamics of this system using time-of-flight secondary-ion-mass-spectrometry (TOF SIMS) and demonstrate that at low temperatures the rate Al atom penetration into the monolayer is reduced. We have also studied the interaction between other promising molecular wire candidates and metal atoms.

3:40pm **NS+NANO6+SS+MC-TuA6 Chiral Surface Reconstruction by Largish Molecules***, **M. Schunack**, L. Petersen, A. Kühnle, E. Laegsgaard, I. Steensgard, F. Besenbacher,* University of Aarhus, Denmark

Temperature-controlled scanning tunneling microscopy studies provide insight into the bonding, ordering and mobility of large organic molecules at metal surfaces. This is illustrated by investigations of disc-like molecules on a Cu(110) surface with a variable temperature STM, which can be operated down to 25 K.@footnote 1@ Hexa-tert-butyl decacyclene (HtBDC) self-assembles upon deposition onto Cu(110) above 250 K and forms a double-row structure in two directions surrounded by fast-diffusing single molecules. Nano-manipulation experiments with the STM at low temperatures revealed an underlying chiral reconstruction of the Cu surface. This consists of holes of approximately 14 Cu atoms pulled out of the surface. Surprisingly, the observed reconstruction is chiral. By gently annealing of the molecule structure at higher coverages, large enantiomerical pure domains with two different orientations build up. By means of simple effective medium theory calculations, we estimate the lower bound of the adsorption energy to be E@sub ad@ = 0.45 eV, and can give a plausible explanation for the observed structure. @FootnoteText@ @footnote 1@ L. Petersen, M. Schunack et al., submitted to Review of Scientific Instruments.

4:00pm **NS+NANO6+SS+MC-TuA7 From Functionalisation of Single Molecules to Self-organisation of Nano-structured Thin Films***, **Q. Guo**,* University of Birmingham, U.K. **INVITED**

The combination of functionalisation of individual molecules with self-organisation of the molecules into functional structures is a promising route for the fabrication of nanoscale electronic and optoelectronic devices. In this talk I will present experimental findings of nanostructured thin films prepared using this method. The dependence of the structure of molecular monolayers on the functionality of individual molecules will be demonstrated using chemisorbed acetate and benzoate species on TiO@sub 2@ surfaces as an example. Both acetate and benzoate attach to the substrate through strong bonding between the carboxyl end of the molecules and the metal cations at the surface of TiO@sub 2@. In the case of benzoate, the phenyl ring offers an extra functionality for intermolecular linkage, leading to the formation of dimerised rows of benzoate. Self assembled monolayers (SAMs) of functionalised alkanethiols adsorbed on Au(111) surfaces will also be discussed. Functionalisation of the tail group of thiol molecules gives rise to SAMs with different surface energies, allowing the fine tuning of the reactivity of the surfaces towards binding of deposited atoms and molecules. The formation of nano-particles of gold on carboxyl terminated SAMs has been investigated using scanning tunnelling microscopy (STM) and electron energy loss spectroscopy(EELS) and results will be presented to demonstrate the important role of functionality of individual molecules on nano-structure formation.

4:40pm **NS+NANO6+SS+MC-TuA9 Ion Beam Assisted Self-Organization of Periodic Nanowire-Arrays on CaF2 Substrates***, **M. Batzill**[1], F. Bardou, K.J. Snowdon,* University of Newcastle, UK

The fabrication of well ordered nanowire arrays over large areas is a challenge with many potential applications. Here we report a novel glancing incidence ion beam assisted self-organisation approach to form periodic wire-arrays over large areas on a CaF2(111) substrate. Preferential erosion of fluorine by the ion beam creates a surface enriched in calcium. The calcium self-organises in elongated island structures of preferential width and separation. If the sample is irradiated along a fixed azimuth we observe formation of nanowires with ~10 nm periodicity and wire lengths

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[1] **NSTD Student Award Finalist**

of at least several micrometers oriented along the azimuthal direction of ion beam incidence. Electrical conductivity measurements reveal a three order of magnitude lower conductivity normal to the wires than along the wires.

5:00pm **NS+NANO6+SS+MC-TuA10 Quantum Engineering of a Pb Nanostructure: Controlling the Thickness with Monolayer Precision***, **C.-S. Jiang**, H.-B. Yu, X.-D. Wang, C.-K. Shih,* University of Texas at Austin

We report a novel quantum engineering of Pb mesas on Si(111), designing the quantum number (N) of the electron resonator of Pb by modifying its thickness with monolayer precision. Pb deposition on Si(111) forms mesas on the surface, and the mesas serve as electron resonators because of the strong quantization along the surface normal direction. To modify the mesas into desired thickness, mass-transfer was first triggered by an STM-tip under controlled conditions. The triggering lead to the formation of single layer with annular shape at the edge of the mesa by transferring the Pb mass from the wetting layer. Once triggered, the mass transfer from the wetting layer to the top of the mesa continue until the new layer involving millions of atoms is completed. Once this layer is completed, no more mass transfer is observed unless a new triggering is performed. Each triggering leads to addition of one complete monolayer on top of the plateau. Using this process, the Pb mesa thickness can be engineered in a quantized fashion. Detailed mechanisms involved in the engineering will be discussed.

Surface Science
Room 208 - Session SS1-TuA
Mechanisms and Control of Surface Reactions

Moderator: A.V. Teplyakov, University of Delaware

2:00pm **SS1-TuA1 Bestowing Chirality: The Ultimate Control of a Surface Reaction***, **R. Raval**,* University of Liverpool, UK **INVITED**

Enantioselective surface reactions represent the ultimate expression of selectivity in catalysis, involving stereodirecting processes where only one optical component of a product is formed. A case in point is the hydrogenation of b-ketoesters, which occurs readily on metal surfaces, but with no stereoselectivity so that both optical products are produced. However, catalytic studies show that this reaction pathway can be rigidly controlled if the metal is first modified by pre-adsorption of particular chiral molecules. But how is stereocontrol is achieved by the presence of these chiral modifiers?. Here, we report surface spectroscopic results from chirally modified metal surfaces created under controlled environments. We show that the adsorbed modifiers display rich and complex phase diagrams in which the chemical nature and 2-dimensional organisation of the chiral molecules is a dynamic function of surface coverage and temperature. Of particular interest is that at certain points of the phase diagram, extended supramolecular assemblies of the chiral molecules impose growth directions that destroy existing symmetry elements of the underlying metal and, thus, directly bestow chirality to the achiral metal surface! These supramolecular assemblies also create chiral channels and chiral spaces at the metal surface that we believe are responsible for imparting enantioselectivity by forcing the reactant molecules to dock in one particular orientation, which subsequently directs the hydrogen attack. Our work shows that it is possible to sustain a single chiral domain across an extended surface. The implications of creating structured chiral metal surfaces go beyond catalysis, with potential applications in molecular electronics, non-linear optics and molecular recognition, and we conside general principles which govern the expression of true extended chirality in 2-dimensional space.

2:40pm **SS1-TuA3 Artificial Control of Catalytic Functions for Reaction Selectivity by Thickness-extensional Mode Resonance Oscillation of Acoustic Wave***, **Y. Inoue**, Y. Yukawa, N. Saito, H. Nishiyama,* Nagaoka University of Technology, Japan

Thickness-extensional mode resonance oscillation (TERO) of bulk acoustic waves generated by a piezoelectric effect was applied to a 100 nm Ag or Pd film catalyst deposited on a positively polarized ferroelectric single crystal of z-cut LiNbO3 (z-LN), and the TERO effects on reaction selectivity of the catalyst surfaces were studied. For ethanol decomposition on Ag and Pd, TERO with a resonance frequency of 3.5MHz caused remarkable increases in ethylene production without changing acetaldehyde production. The increased activity decreased to an original low level with turning TERO off. Increases in selectivity for ethylene production with TERO were from 56 to 86% for Ag and 31 to 97% for Pd. The activation energy of ethylene production was lowered significantly by the TERO. For comparison, x-cut LiNbO3 (x-LN) having thickness-shear mode resonance oscillation (TSRO) was employed as a ferroelectric substrate, for which no significant activity enhancements for both ethylene and acetaldehyde production were observed with the resonance oscillation. Laser Doppler measurements showed that TERO caused large dynamic lattice displacement vertical to the surface. The surface potential and photoelectron emission behavior varied with the TERO. TERO has been shown to have influences on the work function of the catalyst surfaces, which permits to change the catalytic functions with selectivity.

3:00pm **SS1-TuA4 Surface Science Models of Sulfided NiW, CoW, NiMo and CoMo Hydrodesulfurization Catalysts***, L. Coulier, **G. Kishan**,* Eindhoven University of Technology, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

Industrial catalysts used in the hydrotreating of crude oil can successfully be modeled using silicon single crystals as the planar support for the catalytically relevant sulfides. Wet chemical deposition techniques on the basis of spin coating enable the preparation of these catalysts via industrially relevant chemistry. The catalytic behavior of these models in the desulfurization of thiophene to butenes has been measured in a batch reactor. Clear relations between the order in which the elements convert to sulfides and the catalytic activity have been observed: The key step in the preparation is to retard the sulfidation of Ni and Co with respect to that of Mo and W. To this end, stabilizing chelating agents may be added in the preparation stage.

3:20pm **SS1-TuA5 Chemistry of Thiophene, H@sub 2@S, and SO@sub 2@ on Carbide-Modified Mo(110) and Mo@sub 2@C Powders***, **J. Dvorak**, T. Jirsak, J.C. Hanson, J.A. Rodriguez,* Brookhaven National Laboratory

The most widely used catalysts in hydrodesulfurization (HDS) reactions consist of a mixture of cobalt and molybdenum sulfide on an alumina support. More stringent environmental legislations stress the need to develop a new generation of HDS catalysts that lead to the ultimate goal of clean burning fuels. Recently, it has been shown that molybdenum-carbide catalysts have the potential to replace sulfided Mo catalysts in industrial HDS reactors. We have investigated the chemistry of a series of S-containing molecules on carbide-modified Mo(110) [i.e. MoC@sub x@] and Mo@sub 2@C powders using synchrotron-based photoemission, x-ray absorption near-edge spectroscopy and time-resolved x-ray diffraction. Thiophene adsorbs molecularly on MoC@sub x@ at 100 K. By 200 K, upon desorption of the thiophene multilayer, chemisorbed thiophene and its decomposition products (S and C@sub x@H@sub y@ fragments) coexist on the MoC@sub x@ surface. At 250 K, no C-S bonds are left. H@sub 2@S and SO@sub 2@ are also very reactive on MoC@sub x@, with the cleavage of H-S and S-O bonds taking place at temperatures well below 300 K. For these systems, the chemistry observed on carbide-modified Mo(110) is quite similar to that seen on Mo@sub 2@C powders.

3:40pm **SS1-TuA6 Selective Surface Reactions of Single Crystal Metal Carbides: Alkene Production from Short Chain Alcohols on Titanium Carbide and Vanadium Carbide***, **R.L. Guenard**, L.C. Fernández-Torres, S.S. Perry,* University of Houston*; P. Fantz, S.V. Didziulis,* The Aerospace Corporation

The reaction of short chain alcohols on the (100) surface of single crystal vanadium carbide (VC) and titanium carbide (TiC) have been studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and x-ray photoelectron spectroscopy (XPS). The short chain alcohols form an alkoxide upon adsorption at 153K on both VC(100) and TiC(100). The alkoxide intermediate selectively reacts with the carbides to produce an alkene and water. Specific isotopic labeling revealed @gamma@ C-H bond scission as a key step in alkene formation. A comparison of the TPD intensities of reaction products on both surfaces indicates that VC(100) has a higher reactivity towards alcohols, with an approximately four-fold higher reaction yield as compared to TiC(100). This difference in reactivity is accounted for by a difference in the electronic structure of these carbide surfaces. This study implicates potential pathways of lubricant degradation in tribological applications and highlights the possible need for passivating additives for carbides used in such applications.

4:00pm **SS1-TuA7 Alkylidenes on Molybdenum Carbide; Stable Carbenes on the Surface of a Catalytically Active Material***, E.M. Zahidi, H. Oudghiri-Hassani, **P.H. McBreen**,* Laval University, Canada

Molybdenum carbide competes well with platinum and ruthenium as a catalyst for various hydrocarbon transformation reactions. This reactive material can activate both CC and CH bonds. Yet, the present study shows that it is possible to form a layer of thermally stable carbenes on the carbide surface. Dissociative chemisorption of ketones leads to the formation of surface alkylidene groups which are stable to above 900 K. Extensive RAIRS, photoemission and XPS results will be used to describe the mechanism for the formation of these groups, and to outline their stability and their high temperature surface chemistry. This novel method for coupling relatively complex organic species to reactive surfaces may find application in the preparation of tailored catalysts, such as chiral modified systems. The observation of surface alkylidenes is also of direct interest for heterogeneous metathesis chemistry.

4:20pm **SS1-TuA8 Radical Rearrangement as a Probe of Partial Oxidation Mechanisms: Reaction of (Bromomethyl)cyclopropane on Oxygen-Covered Mo(110)**, ***J.A. Levinson***, *M.A. Sheehy, L.J. Deiner, I. Kretzschmar, C.M. Friend,* Harvard University

Rearrangement reactions were used to study the transient intermediates formed during partial oxidation on oxygen-covered (0.75 ML) Mo(110) surfaces using (bromomethyl)cyclopropane. Using temperature programmed reaction spectroscopy, a competition between desorption and reaction was observed, with 1,3-butadiene, butene, ethylene, water, and dihydrogen as reaction products; these were evolved between 450 and 600 K. No cyclic or three-carbon species were observed in the mass spectroscopic data. Two linear analogues, 4-bromo-1-butene and 3-buten-1-ol, were also studied and produced similar product spectra. Coadsorption experiments with deuterated species revealed that the hydrogen incorporated into butene and ethylene arises at the time of reaction from the reaction intermediate. Mass spectra indicated that there may be both alkyl and alkoxide species at the surface for the Br-containing compounds, as the hydrocarbon products are evolved at two temperatures. X-ray photoelectron spectroscopy experiments are in progress to determine the surface bonding and the temperature of C-Br bond scission. Fourier transform infrared spectroscopy was used to determine conformational and structural changes in the surface intermediates as a function of temperature. For (bromomethyl)cyclopropane, a double bond appears near 400 K. These data imply that a ring-opened intermediate forms following C-Br bond scission, which is then followed by H-elimination or incorporation. The use of isotopically labeled oxygen on Mo(110) revealed that the alkoxide species for the Br-compounds bind through surface oxygen, whereas the alcohol binds through its original hydroxyl group. Lowering reactant coverage reduces butene and butadiene formation and favors ethylene production. Variation of oxygen coverage from saturation to clean Mo(110) surfaces causes selective product formation to convert to non-selective decomposition.

4:40pm **SS1-TuA9 Reaction Kinetics on Supported Model Catalysts: A Molecular Beam / In-Situ IRAS Study of the CO Oxidation on Pd/Al@sub 2@O@sub 3@**, ***J. Libuda***, *I. Meusel, J. Hoffmann, J. Hartmann, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

We have employed molecular beam techniques combined with time-resolved in-situ IR reflection absorption spectroscopy to study the CO oxidation kinetics on oxide-supported model catalysts. As model systems we have used Pd particles of different size and morphology grown under UHV conditions on a well-ordered alumina film on NiAl(110). Previously, these systems have been characterized in detail with respect to their geometric and electronic structure. Sticking coefficient measurements demonstrate that - contrary to what is observed for densely packed Pd single crystal surfaces - at room temperature and above the Pd crystallites rapidly incorporate a large amount of oxygen. This subsurface and bulk oxygen is not accessible to CO oxidation at low temperature. Once the bulk reservoir is saturated, stable oxidation rates are obtained. Taking advantage of the single-scattering conditions in a molecular beam experiment, we quantitatively address effects which are specific for supported metal catalysts, such as support mediated adsorption. Also, activation energies for the LH reaction step as a function of adsorbate coverage are derived. Various coverage regimes are considered, in particular the limiting cases of high CO or O coverage. The transient behavior and the steady-state CO@sub 2@ production rate are probed over a wide range of reactant fluxes and CO/oxygen flux ratios. In particular, we discuss the origin of the different transient behavior of the oxidation rate on supported Pd particles. Time-resolved IR absorption spectroscopy is employed during the reaction to monitor changes in the occupation of different adsorption sites in transient beam experiments and under steady-state conditions.

5:00pm **SS1-TuA10 Dissociative Chemisorption of Chloromethanes on Ir(110), Ir(111) and Oxygen Modified Ir(111)**, ***R.J. Meyer***, *C.T. Reeves, D.J. Safarik, D.T. Allen, C.B. Mullins,* University of Texas at Austin

Chlorinated hydrocarbons are a primary component of the waste streams from the manufacture of many commodity chemicals. Noble metal catalysts, including iridium on alumina, have been shown to be active for both oxidative and reductive catalytic treatment methods. However, the causes of deactivation and mechanisms by which these reactions proceed are not precisely known. Dissociative chemisorption of CH@sub 3@Cl, CH@sub 2@Cl@sub 2@, CHCl@sub 3@, and CCl@sub 4@ on Ir(110) and Ir(111) has been examined at surface temperatures from 77-1200 K using molecular beam methods. From our ongoing studies two particularly exciting results have emerged. (1) We have identified the reactive site for methyl chloride on Ir(110). An examination of CH@sub 3@Cl on hydrogen precovered Ir(110) indicates that the reaction pathway for dissociative chemisorption can be shut off by filling the high temperature desorption state. This result implies that methyl chloride chemisorbs in the hollow site of the rows of the (110) surface. (2) The production of phosgene was observed when a CCl@sub 4@ beam was impinged on an oxygen modified Ir (111) surface. We propose that phosgene forms via a Langmuir-Hinshelwood mechanism from the reaction of absorbed oxygen with CCl@sub 2@ surface species formed during the decomposition of carbon tetrachloride. Competing reactions involving the oxidation of completely dissociated carbon tetrachloride become significant as the surface temperature increases. COCl@sub 2@ formation was maximized at an oxygen surface coverage of approximately 0.3 ML. At higher oxygen coverages, the production of phosgene decreases due to a diminished reactive adsorption of carbon tetrachloride but the efficiency of COCl@sub 2@ formation per dissociatively chemisorbed CCl@sub 4@ increases dramatically.

Surface Science
Room 209 - Session SS2-TuA

Stimulated Processes and Excitations

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

2:00pm **SS2-TuA1 Ultra-Fast Dynamics Measurements of One- and Two-Dimensional Surface State Electrons on Stepped Cu(775)**, *X.J. Shen, H. Kwak,* ***D. Mocuta***, *S. Smadici, R.M. Osgood, Jr.,* Columbia University

Dynamical questions regarding surface state electrons on metallic surfaces can best be answered in the time domain using ultra-fast nonlinear probes. Of particular interest is the effect of controlled nano-size features on the femtosecond scale dynamics of surface states. In this connection, we have employed the momentum- and time-resolved two photon photoemission technique to study the dispersion and lifetimes of these states on a prototypical nano-structured surface, stepped Cu(775). Here we report on a newly observed one-dimensional surface state (0.27 eV below Fermi level) and an image-like unoccupied state on stepped Cu(775). Both states are dispersive along the step direction but are localized in the direction perpendicular to the steps. The origin of the states is attributed to the step-edge potential confinement and to an Anderson localization mechanism. The lifetime of n=1 electrons on the regular step array of Cu(775) has been measured as a function of their translational momentum, k@sub //@. At the terrace normal, this lifetime is equal to that for flat Cu(111), i.e., t = 16±2 fs. The lifetime decreases symmetrically with k@sub //@ about k@sub //@ = 0 for electrons moving parallel to the step orientation. This is in good agreement with a theoretical calculation of k@sub //@ dependent n=1 lifetime done on Cu(111) by Echenique, et al.@footnote 1@ In contrast, the lifetime is asymmetric in k@sub //@ for the direction perpendicular to the step edges. The asymmetric behavior is attributed to direction-dependent coupling between image and bulk states, leading to a decrease in lifetime of the electrons climbing the steps and an increase for descending electrons. The overlap between the unoccupied localized state and the n=1 image state at k@sub //@ = 0.2 Å@sup -1@ results in an increase in the measured lifetime at this value of the momentum. @FootnoteText@ @footnote 1@J. Osma, I. Sarria, E. V. Chulkov, J. M. Pitarke, and P. M. Echenique, Phys. Rev. B59, 10591 (1999).

2:20pm **SS2-TuA2 Electron-Stimulated Oxidation of Al(111)**, ***V. Zhukov***, *I. Popova, J.T. Yates, Jr.,* University of Pittsburgh

The electron stimulated dissociative adsorption of O@sub 2@ on Al(111) has been studied at surface temperatures from 90 to 300 K. A rastering electron beam technique has been used to deliver electrons with energies from ~1 to 200 eV to the aluminum surface during O@sub 2@ exposure.

Experimental evidence for the presence of an O@sub 2@ precursor was found for the oxidized Al(111) surface at low temperature. Precursor adsorption energy of 70-80 meV was estimated from the temperature variation of the oxide growth rate, stimulated by 100 eV electrons. The effect was found to be proportional to the primary beam current. A threshold electron energy of 7 ± 0.5 eV for the electron stimulated oxidation was observed when utilizing electrons with variable energies. This threshold value is in agreement with the 6.8 eV electron attachment cross-section resonance for the gaseous O@sub 2@ species. In contrast to the significant increase of oxidation rate on the oxide-precovered aluminum surface, no effect of electrons was found on the initial stages of oxide growth on the clean Al(111) surface over the temperature range studied. This suggests that the O@sub 2@ precursor is stabilized on oxide clusters.

2:40pm **SS2-TuA3 Ion-Influenced Nucleation and Surface Diffusion: A Computational Study*, Z. Wang*,** *E.R. Blomiley, E.G. Seebauer,* University of Illinois, Urbana-Champaign

Ion-beam assisted deposition (IBAD) has been used to improve material properties for a wide variety of semiconductors, metals and oxides. In many applications, beneficial effects derive from ion-induced surface diffusion, while deleterious effects derive from ion-induced damage to the substrate. Process optimization involves finding a kinetic balance between these opposing effects, which in turn demands useful rate expressions. We have recently demonstrated experimentally both the enhancement and inhibition of surface diffusion by low-energy ions in the case of Ge/Si(111). We have simulated this system via molecular dynamics, and have developed a fairly nuanced picture of the interplay between sputtering, knockin, and vacancy formation on the surface and within the bulk. Our simulations show marked thresholds for both ion energy and substrate temperature, with a previously unknown conservation law relating these two parameters: E + bT = constant. The physical significance of the proportionality constant b we derive is discussed. The ideas deriving from these simulations are then applied to continuum simulations of ion-influenced nucleation during IBAD, with the goal of explaining why ions sometimes increase nucleation densities and other times decrease them.

3:00pm **SS2-TuA4 Surface Modification of CaF@sub 2@ for Improved Heteroepitaxy*, A. Bostwick*,** *B.R. Schroeder, S. Meng,* University of Washington*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; M.A. Olmstead,* University of Washington

Fluorite (CaF@sub 2@) is a candidate epitaxial insulator for three dimensional circuits. However, heteroepitaxial growth of semiconductors and metals on CaF@sub 2@(111) surfaces is inhibited by CaF@sub 2@s low surface energy. We have investigated use of electron irradiation and surfactant incorporation to alter the surface energy balance and promote laminar growth of silicon and related materials on CaF@sub 2@(111). We report here photoelectron diffraction studies of the interaction of electrons and arsenic with CaF@sub 2@(111) surfaces. Irradiation of CaF@sub 2@ with 40 eV electrons creates fluorine vacancies in the film, raising the fluorite surface energy. The resultant defects are extremely reactive. Exposure of this surface to arsenic passivates the surface to oxygen and water contamination. We find As@sub 4@ does not stick to pristine CaF@sub 2@(111) between room temperature and 600C, but sticks only in the presence of surface defects. Room temperature exposure results in As on the fluorite surface. At elevated temperature, however, arsenic diffuses into CaF@sub 2@. It occupies two ordered sites, neither of which is a bulk fluorine site. As-stabilized, irradiated CaF@sub 2@ is more stable than either pristine or irradiated CaF@sub 2@ with regard to photon-stimulated desorption of fluorine. Deposition of Si on unirradiated CaF@sub 2@ results in an amorphous film at room temperature, but sticking is inhibited at high temperature. Si deposition on As-terminated CaF@sub 2@, on the other hand, leads to laminar growth of Si at 550C. The As acts as a surfactant, floating to the top of the Si film.

3:20pm **SS2-TuA5 Consequences of Electron Irradiation of Hydrated Crystals: Self Organized Nanometer Cone Formation*, S.C. Langford*,** *M. Dawes, J.T. Dickinson,* Washington State University

Radiation effects on hydrated single crystals are poorly understood. We find that dense arrays of conical structures, with aspect ratios on the order of 200, are produced by exposing single crystal brushite (CaHPO@sub4@.2H@sub2@O) to energetic electrons (2 keV). By exposing thin brushite platelets bonded to the surface of a metal heater to energetic electrons, the surface temperature can be controlled independently of electron dose. This work shows that cone formation requires surface temperatures of 400-600 @degree@C. The cones are directed along the direction of the incident electrons, and often display a cap-like structure that may play a role in cone production. Cone formation is accompanied by the development of a distinctive orange luminescence during electron irradiation, presumable due to electronic defects. The waters of hydration in this material may play a role in cone development by enhancing ion mobility in the heated material. Characterization of surfaces covered with conical structures has been performed by TEM, EPS, and IR spectroscopy.

3:40pm **SS2-TuA6 Femtosecond Measurements of Surface-State-Electron Dynamics on Nanostructured Ni Surfaces*, S. Smadici*,** *X.J. Shen, D. Mocuta, R.M. Osgood, Jr.,* Columbia University

Ultra-fast nonlinear optical probes have recently been shown to enable time-resolved measurements of electron dynamics on metal surfaces. While most measurements have been on flat surfaces, we have recently begun an investigation of the ultra-fast dynamics for electrons confined in surface metallic nano-structures. Here we will describe our femtosecond, momentum- and time-resolved two-photon photoemission measurements of electron lifetimes and dispersion curves on systems with controlled nano-size features obtained by Ag deposition on stepped Ni(977) and Ni(111). Ag deposition reduces the Ni work function and permits the observation of surface and image states at the accessible pulse energies. We will present measurements of the dispersion for the occupied surface state and the unoccupied n=1 image state located ~3Å above the metal surface. We report on band-folding of the Ag induced surface state on Ni(977), with a controllable bandwidth, caused by the periodic step potential. As the Ag coverage is increased the width of the allowed band increases as predicted by a Krönig-Penney model which is appropriate to the periodic potential on this Ag-decorated surface. The n=1 state lifetime measurements on the Ag/Ni(977) system showed a downward trend with increasing parallel momentum. This result is similar to that observed by us on Cu surfaces@footnote 1@ and is consistent with theoretical results indicating the increased importance of elastic and inelastic scattering at higher k@sub //@. The n=0 surface state lifetime showed an unexpected similar behavior when moving away from the terrace normal direction with a variation of ~10 fs over a change of k@sub //@ of 0.2Å@super-1@. This result is explained in terms of a resonant excitation of the n=2 image state, with the detector sampling a mixture of two different photoemission channels. @FootnoteText@ @footnote 1@.X. J. Shen, H. Kwak, A. M. Radojevic, S. Smadici, D. Mocuta, and R.M. Osgood, Jr., submitted to Phys. Rev. Lett.

4:00pm **SS2-TuA7 Theory of Single Molecule Vibrational Spectroscopy and Microscopy*, N. Lorente*,** *M. Persson,* Chalmers/Gothenburg University, Sweden

A recent breakthrough in Surface Science has been the experiments demonstrating vibrational spectroscopy and microscopy of single molecules by inelastic electron tunneling using a scanning tunneling microscope.@footnote 1@ Based on density functional theory and a many-body generalization of Tersoff-Hamann theory, we have developed a theory and calculational method for this new spectroscopy.@footnote 2@ We apply our theory to acetylene on copper and explain why only the carbon-hydrogen stretch modes are observed in terms of elastic and inelastic contributions to the tunneling conductance. The calculated values for the changes in tunneling conductance induced by these stretch modes and their spatial images are in good agreement with experiments. We find that the symmetry of the adsorbate-induced states makes the inelastic signal for the anti-symmetric stretch mode to dominate over the signal for the symmetric one. This result is in agreement with experiment and shows that the symmetries of the lowest unoccupied molecular states has an important influence on the spatial dependence of the vibrationally inelastic tunneling.@footnote 3@ @FootnoteText@ @footnote 1@ B. C. Stipe, M.A. Rezaei, and W. Ho, Science 280, 1732 (1998). @footnote 2@ N. Lorente and M. Persson, (submitted to Phys. Rev. Lett.). @footnote 3@ N. Lorente, M.Persson, L.J. Lauhon, and W. Ho, (to be submitted).

4:20pm **SS2-TuA8 Transient Currents as a Tribological Probe*, J.V. Wasem*,** *S.C. Langford, J.T. Dickinson,* Washington State University

When conductors contact and slide on insulator surfaces charge transfer between the surfaces allows one to measure instantaneous transient currents (TC). We have instrumented a vacuum tribological apparatus with high sensitivity normal, lateral, and TC pick-up using metal and semiconductor stylii. Performing single pass wear track formation tests on polymer and ceramic substrates, we observe striking correlations between the mechanical and electrical signals. In particular, the TC exhibit fluctuations with a rich temporal/frequency spectrum, for example during stick-slip events. Through correlations with SEM images of the substrate we are able to relate spatial microscopic damage and corresponding TC behavior. The TC reveals details of the micromechanics during wear on microsecond time scales. Studies on Fomblin Zdol lubricated hard drive surfaces reveals charge transfer events that correspond to free electrons going to the lubricant. Yates et al. have previously shown that electron attachment to such polyperfluoroethers can cause decomposition of the polymer. Thus, our studies can provide quantitative values and rates for the charge deposited which can then be used to predict lubricant lifetimes from measured attachment cross-sections.

Surface Science
Room 210 - Session SS3-TuA
Water/Surface Interactions

Moderator: E.M. Stuve, University of Washington

2:00pm **SS3-TuA1 Alumina-Water Interactions from First Principles***, **K.C. Hass**, W.F. Schneider, C.M. Wolverton,* Ford Motor Company **INVITED**

The chemical formula for aluminas is often written explicitly as Al@sub 2@O@sub 3@@sup .@nH@sub 2@O to emphasize the key role that water plays in this important class of materials. To date, there is little microscopic understanding of this role, despite its clear relevance to fields ranging from catalysis, corrosion, and adhesion to geology, microelectronics, and atmospheric chemistry. This talk will summarize recent progress on two aspects of this problem: (1) the hydroxylation of @alpha@-Al@sub 2@O@sub 3@ (0001)@footnote 1@, and (2) the bulk structure and phase stability of @gamma@- and other transitional aluminas that are produced by the dehydration of boehmite (@gamma@-AlOOH). Both studies are based on accurate planewave pseudopotential, density functional theory methods. Comparisons to related recent work and future prospects and challenges will also be discussed. @FootnoteText@ @footnote 1@ K. C. Hass, W. F. Schneider, A. Curioni, and W. Andreoni, Science 282 (1998) 265, and to appear in J. Phys. Chem. (2000).

2:40pm **SS3-TuA3 The Effect of Boron on Water Dissociation and Surface Diffusion of Atomic Hydrogen on Single Crystal Ni@sub3@(Al, Ti) (110)***, **J. Wang**, Y.-W. Chung,* Northwestern University

Polycrystalline Ni@sub3@Al alloys are severely embrittled in a moist environment at room temperature. Ductility measurements showed that addition of boron suppresses this moisture-induced embrittlement. Previous results indicated that water dissociates on clean Ni@sub3@(Al, Ti) (100) and (110), resulting in hydrogen evolution at ~350 and 400 K respectively. To explore the effect of boron on water dissociation, we first dosed the surface of clean Ni@sub3@(Al, Ti) (110) with controlled amounts of boron, using a specially designed low-energy negative boron ion source, followed by low-temperature exposure to D@sub2@O. The interaction between water vapor and boron-modified Ni@sub3@(Al, Ti) (110) was investigated using temperature-programmed desorption, X-ray photoemission and Auger electron spectroscopy. Auger and X-ray photoemission studies on boron-modified Ni@sub3@(Al, Ti) (110) show that boron reacts with water to form hydroxyls at 130~190 K. Hydrogen desorption occurs at ~950 K from boron-modified Ni@sub3@(Al, Ti) (110), indicating strong B-H bonding. After water dosing at ~130 K, the surface diffusion coefficients of atomic hydrogen on clean and boron-modified Ni@sub3@(Al, Ti) (110) surfaces were measured at 270 K with electron stimulated desorption. The surface diffusion of atomic hydrogen on 0.05 monolayer boron-modified surface is about 10 times slower than that on clean boron-free surface. Therefore, the strong B-H bonding suppresses both hydrogen desorption and the surface diffusion of atomic hydrogen to the crack tip at room temperature. These results may explain the suppression of moisture-induced embrittlement of Ni@sub3@Al and related alloys by boron.

3:00pm **SS3-TuA4 Physicochemical Properties of Water and Ammonia Ice Thin Films***, **D.J. Safarik**, R.J. Meyer, C.T. Reeves, C.B. Mullins,* University of Texas at Austin

We have studied the physical and chemical properties of water and ammonia ice films utilizing surface science techniques. Ultrathin films of amorphous solid water (ASW) and crystalline ammonia ice were grown via supersonic molecular beam on an Ir(111) substrate and characterized with temperature programmed desorption (TPD) and low energy electron diffraction (LEED). Overlayers of ASW dramatically alter the desorption of ammonia, resulting in a TPD spectrum that is distinctly different than free ammonia desorption yet unlike the desorption of carbon tetrachloride through water overlayers (the "molecular volcano") as reported by Smith et al.@footnote 1@ Whereas uncovered ammonia multilayers desorb with zero order kinetics at approximately 100 K, covered films desorb in a sequence of one to three distinct and rapid bursts. The number of ammonia releases, the temperature at which they occur, and their intensity varies with the thickness of both the ASW and ammonia ice films. These phenomena cannot be completely explained by a diffusional model. The overlying water film desorbs with zero order kinetics at approximately 160 K, apparently unaffected by the ammonia discharge. However, TPD, isothermal desorption, and LEED experiments indicate that the ammonia underlayer accelerates the kinetics of ASW crystallization and reduces the volatility of the remaining solid water. @FootnoteText@ @footnote 1@ R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay. The Molecular Volcano: Abrupt CCl4 Desorption Driven by the Crystallization of Amorphous Solid Water. Phys. Rev. Lett. 79, 909-912 (1997).

3:20pm **SS3-TuA5 Water Ion Cluster Formation in High Electric Fields at and Near a Pt Emitter Tip***, **C.J. Rothfuss**, V.K. Medvedev, E.M. Stuve,* University of Washington

Water ion cluster formation in high electric fields has been characterized on a field cleaned Pt emitter tip over temperatures ranging from 110K to 300K. The ion clusters were mass resolved using either an ExB filter or time of flight mass spectroscopy, or imaged directly using Field Ion Microscopy (FIM). Experimental results explain the qualitative trends observed in previous studies of this nature. For H@super +@(H@sub 2@O)@sub n@ cluster formation, the onset potential was found to be dependent upon the value of n and is lower for large masses. This dependency follows from a consideration of the thermodynamics of dissociative ion formation and proton solvation by nearby water molecules. However, the formation of large clusters is entropically unfavorable at high temperatures for low concentrations of water molecules on the surface and dynamically unfavorable at low temperatures. As a result high local concentrations and surface mobility are needed for creation of large n clusters. This local concentration has been experimentally imaged on the surface using FIM, under conditions favoring large n cluster formation, but is absent in the direct field ionization of water (H@sub 2@O@super +@) in space near the surface. With increasing field, each successive (n-->n-1) cluster becomes energetically accessible and becomes the dominant species due to its kinetic advantage. Above the condensation point for water on Pt (~165K), the limiting factor for determining the maximum n in field adsorbed cluster formation is the surface residence time of the water. As temperature increases, the residence time decreases and the propensity for forming large n clusters diminishes. Activation energies for ion cluster desorption were found to be 0.85 eV, 0.76 eV and 0.55 eV for n=3, 4 and 5, respectively. Below the condensation point, surface diffusion limits the supply function for large cluster formation, so lower temperatures result in decreased ion signal for large n clusters.

3:40pm **SS3-TuA6 Interactions of Methanol with Water and Hydrogen in Electrolytic Adlayers on Pt(111)***, **D.S.W. Lim**, E.M. Stuve,* University of Washington

To model the interactions of methanol with water and hydrogen at electrolye/electrode interface, thermal desorption experiments of the co-adsorbed system were performed on Pt(111). In electrochemical environments, adsorption of methanol on Pt(111) is inhibited by chemisorbed hydrogen, and water competes with methanol for available Pt sites. In ultra-high vacuum, methanol desorbed from Pt(111) in a multilayer state B@sub m@ at 142 and a monolayer state A@sub m1@ at 180 K. However, when the surface was pre-adsorbed with hydrogen, the desorption temperature of the methanol monolayer state, A@sub m1@, was lowered by as much as 20 K. The reduction in desorption temperatures was attribited to weakened interactions between methanol and the surface due to chemisorbed hydrogen. When methanol was co-adsorbed with water, mutual displacement between the methanol monolayer and water bilayer occurred on the surface. Water molecules in direct contact with Pt(111) surface form bilayer structure that desorbs at 173 - 178 K. A realistic simulation of the electrolytic adlayers was to co-adsorb all three species: methanol, water and hydrogen on Pt(111). In a water-lean adlayer system, the methanol monolayer state was destabilized by chemisorbed hydrogen. However, with the introduction of a sufficient amount of water, methanol was re-stabilized and, the effects of hydrogen-induced destabilization were completely erased when excess water was added to the adlayer. Methanol behaved as if it was only interacting with water. The results of these experiments illustrate that there is a delicate balance of hydrogen-induced destabilization and water-promoted stabilization in the electrolytic adlayers on Pt(111), and behavior of methanol interactions with co-adsorbed hydrogen and water followed that observed in electrochemical environments.

4:00pm **SS3-TuA7 From Gases to Dust: Ice Chemistry in the Interstellar Environment***, **H.J. Fraser**,* University of Nottingham, UK, NL*; M.R.S. McCoustra,* University of Nottingham, UK*; D.A. Williams,* University College London, UK

It has become clear in the last decade that gas-phase reaction schemes cannot soley account for the variety and richness of chemistry in the Interstellar Medium (ISM). In such environments, gas-dust interactions play a key role. In dense molecular regions, H@sub 2@O is the most abundant ice: it is vital to understand the freeze out, reactivity and desorption processes of atomic and molecular species on such ice surfaces to fully evaluate the chemical evolution of the ISM. A novel surface science experiment has been constructed that simulates the harsh conditions in the ISM. Traditional surface science techniques such as TPD and RAIRS have been combined with a Quartz Crystal Microbalance sample stage, capable of operating below 10 K. The experiment is equipped to study several aspects of the gas-dust interaction that are central to astrophysics, measuring sticking probabilities and rates of desorption empirically and accurately, as well as identifying the nature of the surface bound states. We will present the first results from this experiment, characterising a number of thin molecular ice films prepared under a variety of conditions to reflect a range of substrate morphologies. We will report measurements of the interaction of simple molecular species with these H@sub 2@O ices, concentrating on the behaviour of such systems between 10 and 150 K. The implications of these results to the chemistry and astrophysics of the ISM will be mentioned.

4:20pm **SS3-TuA8 Diffusion of Organic Molecules in Ice Measured Using Laser Resonant Desorption Depth-Profiling***, **F.E. Livingston**, S.M. George,* University of Colorado

Knowledge of the diffusion of organic molecules in ice is important for understanding the history of the Earth's atmosphere preserved in ice cores. Molecular diffusion in ice is affected by chemical and physical properties such as hydrophilicity, size and geometry. To explore these properties, we have measured the diffusion rates of different organic molecules such as carboxylic acids and alcohols. Diffusion was measured using an infrared laser resonant desorption (LRD) technique to depth-profile into the ice. LRD was accomplished using a Q-switched Er:YAG laser that emits light at @lambda@=2.94 µm. The laser radiation is resonantly absorbed by the O-H stretching vibration of H@sub2@O molecules and thermalized to facilitate desorption in the surface region. We have employed LRD depth-profiling to study the diffusion kinetics of formic (HCOOH) and acetic (CH@sub3@COOH) acid. LRD analysis revealed that acetic acid diffuses ~3 times faster than formic acid. The diffusion coefficients for formic acid vary from D~2 x10@super-13@ cm@super2@/s at T=175 K to D~2x10@super-10@ cm@super2@/s at T=195 K. Arrhenius analysis yielded a diffusion activation energy of E@subA@~24 kcal/mol and a diffusion preexponential D@subo@~4x10@super16@ cm@super2@/s. For acetic acid, the measured diffusion coefficients range from D~7x10@super-13@ cm@super2@/s at T=170 K to D~7x10@super-10@ cm@super2@/s at T=195 K. Arrhenius analysis yielded diffusion kinetic parameters of E@subA@~18 kcal/mol and D@subo@~1x10@super11@ cm@super2@/s. The faster diffusion for acetic acid argues that the lower hydrophilicity and larger size of acetic acid does not reduce its diffusion relative to formic acid.

4:40pm **SS3-TuA9 Can Clustering Lower the Barrier to Dissociation of Water on Nickel Surfaces?***, L. Mao, **K. Griffiths**, P.R. Norton,* University of Western Ontario, Canada

The interaction of water with Ni(110) surface has been extensively explored in this group due to its fundamental and practical importance in the fields of heterogeneous catalysis, electrochemistry as well as corrosion. At temperatures ï€¤ 400K, water molecules react rapidly with Ni(110) producing adsorbed O and H2(g). Reaction probabilities can reach as high as 0.24 and our studies indicate that the reaction mechanism involves single water molecules. Dissociation of water can also occur at low temperatures (ï€£220K) provided that we begin with an adsorbed chemisorbed layer. The activation energy for the dissociation reaction is believed to be lowered by some means which involves a cluster of at least two water molecules. The exact mechanism is still speculative at this stage. Between these two temperatures, the Ni surface appears to be inert towards the dissociation of water. Under normal UHV dosing conditions, the surface is sufficiently hot to prevent an appreciable dynamic coverage of dimers. At the same time, the activation energy barrier for the unimolecular , high temperature mechanism cannot be overcome. The aim of this study is to investigate the reaction between water and Ni(110) in this >inert= temperature regime. In this study, we have produced locally relatively high pressures at the surface using a capillary doser to demonstrate that there is a non-linear dependence of reaction rate on dosing pressure. The absolute number of impinged water molecules as well as the instantaneous coverage of water (governed by the dosing pressure) determines the extent of reaction.

5:00pm **SS3-TuA10 Surface and Near Surface Reactions in Aqueous Solution Exposed Na@sub 2@O-Al@sub 2@O@sub3@-SiO@sub 2@ Glasses***, **V. Shutthanandan**, S. Thevuthasan, D.R. Baer, J.P. Icenhower, M.H. Engelhard, B.P. McGrail,* Pacific Northwest National Laboratory

Glass and ceramic waste forms are proposed for the stabilization and immobilization of nuclear wastes. Recent findings show that Na ion exchange reaction control the release of radionuclides from the glass matrix. As part of understanding the processes leading to sodium release and ion exchange, the surface and near surface reaction regions on several specimens of Na@sub 2@O-Al@sub 2@O@sub 3@-SiO@sub 2@ glasses with fixed Na@sub 2@O and variable Al@sub 2@O@sub 3@ (10 mole % and 15 mole %) concentrations have been examined after exposures to isotopicaly labeled aqueous D@sub 2@@super 18@O solutions. The sodium removal and the deuterium and oxygen uptake in the glass samples were measured using Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS) and nuclear reaction analysis (NRA). The results show that the Na exchange rate is much higher than the matrix dissolution rate. Although the sodium concentration is decreased in the near surface region, it is not totally removed from the outer surface. In this same region, there is also a significant amount of @super 18@O incorporated demonstrating considerable interaction between the water and the glass. On the basis of the depth distributions of Na, D and @super 18@O, different regions including reaction, transition and diffusion zones were identified in both samples. The glass samples with higher amounts of Al content have a significantly narrower reaction zone than the low Al materials.

Surface Science
Room Exhibit Hall C & D - Session SS-TuP
Poster Session

SS-TuP1 Oriented Growth of Rod-like Second Phase Precipitate on the (1014) Calcite Surface*, **A.S. Lea**, D.R. Baer, T.T. Hurt, J.E. Amonette,* Pacific Northwest National Laboratory

An apparent epitaxial growth from solution of a Mn-rich phase on calcite (CaCO@sub 3@) has been observed by atomic force microscopy (AFM). Calcite, which is the most widely distributed carbonate mineral, interacts with and incorporates contaminants from the environment and serves as a major reservoir in the global carbon cycle. We have used an AFM equipped with a fluid cell to examine the influence of various solution contaminant ions (Mn, Sr, PO@sub 4@) on the rates of dissolution of pure calcite. Here, we report on the influence of a soluble Mn@super 2+@ impurity on the dissolution behavior of calcite. At Mn@super 2+@ concentrations well below saturation for bulk MnCO@sub 3@, the Mn@super 2+@ inhibited dissolution uniformly. However, at Mn@super 2+@ concentrations near the MnCO@sub 3@ saturation level, we observed the formation and oriented growth of rod-like precipitates on the surface. These rods grew along the [221] direction of the surface until they reached a step edge where they could grow no further. While these rods could grow many microns in length, their width was limited to 120 to 180 nm and their thickness was measured consistently at 25 Å, which is indicative of a critical thickness of growth. XPS analysis of the rod covered surfaces showed the presence of Mn with a +2 or +3 valence. EPR analysis of the bulk sample after rod formation shows an intense broad signal that is indicative of dipole-dipole alignment between neighboring Mn(II) ions and distinct from the sextuplet (commonly seen for isolated Mn(II) ions in bulk calcite) observed in the untreated sample. Together these analyses suggest formation of an epitaxial Mn(II) phase on the surface of calcite.

SS-TuP2 Photocatalytic Degradation of Self-Assembled Monolayers Anchored at the Vicinity of Titanium Dioxide Domains, as a Probe for Surface Diffusion*, **Y. Paz**, H. Haick,* Technion-IIT, Israel

The presented work demonstrates the ability of self-assembled monolayers to serve as a tool for gaining information on surface diffusion of oxidizing species formed photocatalitically on titanium dioxide. In order to study the photodegradation of molecules located at the vicinity of a titanium dioxide photocatalyst, well-defined structures comprised of alternating micro-stripes of TiO2 and silicon were prepared on silicon wafers. Onto these structures, a cross-linked self-assembled monolayer (SAM) of Octadecyltrichlorosilane (OTS) was chemisorbed. The kinetics of the photodegradation of the anchored SAM on the hybrid structure was then measured in-situ by FTIR under controlled humidity. It was found that the photogenerated oxidizing species, formed on the titanium dioxide well-defined micro-domains, are capable of inducing, within minutes, the mineralization of the aliphatic chains anchored to the inert silicon domains, even when these chains were located as far as 20 microns away from the titanium dioxide micro-zones. In contrast, no remote mineralization could be observed when the same experiments were performed with alkanethiols on gold, in Au/TiO2 hybrid systems. A mechanism, explaining these results and their dependency upon various parameters (diffusion length, temperature, humidity) is presented. The implications of these observations on the design and modeling of porous photocatalysts having "dark" pores are discussed as well.

SS-TuP3 Reactions of HCl and geminal-dichloroethylene on Pd(111) Studied by TDS, LITD, and STM*, **D.E. Hunka**,* University of California, Davis*; D.C. Herman,* University of North Carolina, Chapel Hill*; L.I. Lopez,* University of California, Berkeley*; K.D. Lormand, D. Futaba, S. Chiang, D.P. Land,* University of California, Davis

Small organic halides are common groundwater pollutants and remediation of these contaminants has become a popular field of study. Among these, chloroethylenes are the most abundant. Catalytic degradation on transition metal surfaces offers a promising method for the alleviation of this ubiquitous problem. The reactions of HCl and geminal-dichloroethylene on Pd(111) have been investigated using thermal desorption spectroscopy (TDS), laser-induced thermal desorption coupled with FT-mass spectrometry (LITD-FTMS), variable temperature scanning tunneling microscopy, as well as Auger electron spectroscopy and low energy electron diffraction. Although HCl is seen to desorb from the surface in four peaks during TDS, only three distinct surface species exist: two of which are dissociative in nature and one molecular surface species. HCl and H@sub 2@ are the exclusive desorption products from the decomposition of gem-DCE, and HCl is found to desorb in two desorption peaks at exposures over 0.33 L. These peaks occur at temperatures well above those expected for HCl on clean Pd(111) and are ascribed to a stepwise decomposition of gem-DCE. The two surface intermediates in this stepwise decomposition have been identified using FT-RAIRS. The first intermediate, which is attributed to a chlorothylidyne species, forms by 150 K and is not seen to decompose further until ~400 K. Further decomposition of this intermediate produces a chlorovinylidene species which does not decompose further until ~600 K. Variable temperature scanning tunneling microscopy has been used to observe the reactions of both HCl and gem-DCE on Pd, as well, with the results supporting the above assignments.

SS-TuP4 Lubrication Mechanisms of Tricresylphosphate, TCP, on Cr and Fe Surfaces at Elevated Temperatures: An Atomic-Scale View*, **M. Abdelmaksoud**, B. Borovsky, J. Krim,* North Carolina State University

TCP is a high-temperature vapor-phase lubricant which is known for its demonstrated anti-wear properties for macroscopic systems. Although this lubricant has been the subject of much research for over 40 years, the atomic-scale details of its lubrication mechanisms are far from being satisfactorily understood. In this study, we evaporated Fe and Cr substrates in UHV conditions onto Quartz Crystal Microbalances, (QCM), and then monitored the uptake rates of TCP on these substrates at different temperatures. Using an in-situ Auger spectrometer, the samples' surface chemistries were investigated in parallel with uptake rates at the various temperatures. Graphitic carbon was found to be the dominant surface constituent. To understand the role of oxygen in the lubrication process, some samples have been exposed to oxygen before TCP deposition. Comparing deposition rates of pure and oxide surfaces and the corresponding Auger scans allowed determination of whether or not oxygen has an effective part in the lubrication of these two metals with TCP. Our results suggest that oxygen is not a factor in controlling TCP interaction with Fe. Overall, we observed TCP to diffuse more readily into Fe than Cr, supporting recent conclusion by N. Forster.@footnote 1@ on the diffusion mechanisms underlying the lubricants effectiveness. In addition, we observed the TCP to greatly inhibit the uptake of oxygen from the gas phase. @FootnoteText@ @footnote 1@ N. H. Forster, Triboblogy Transactions, Volume 42, P. 10-20, (1999).

SS-TuP5 Density-Functional Study of NO Dissociation on the Al(111) Surface*, **B. Razaznejad**, B.I. Lundqvist,* Chalmers University of Technology, Sweden

A first-principles density-functional study utilizing the generalized-gradient approximation (GGA) for exchange-correlation effects is made for the energetics and electron structure of nitrid monoxide (NO) on the (111) surface of aluminum. The calculated adiabatic potential energy surfaces show that (i) when the molecule is kept perpendicular to the surface, with the oxygen atom down, there exist an activation barrier of 0.6 eV in the exit channel, while (ii) there exist a moleculer chemisorption state, identified as a "NO@sup 2-@" electron configuration, precursor to dissociation, when the molecule is kept parallel or perpendicular to the surface, with the nitrogen atom down. The complexity of the adiabatic potential energy surface indicates an interesting dynamics for NO dissociation on the (111) surface of aluminum.

SS-TuP6 Electrochemical Characterization and Surface Analysis of Bulk Amorphous Alloys in Aqueous Solutions at Different pH*, **D.L. Cocke**,* Lamar University*; D.G. Naugle,* Texas A&M University*; H. McWhinney,* Prairie View A&M University*; R. Schennach,* Lamar University

Bulk amorphous alloys are a new class of materials with a variety of characteristics that make them useful for applications in aqueous environments. While some bulk amorphous metals show increased corrosion resistance, there is still a lack of fundamental electrochemical studies of these materials. Three different compositions of BeCuNiTiZr bulk amorphous alloys have been studied at pH 5, 7 and 8 using Cyclic Voltammetry (CV), X-ray Photoelectron Spectroscopy (XPS) and electron microscopy. While XPS is used to determine the composition of the resulting oxide films, the CV curves are compared to the corresponding binary alloys, to pinpoint differences in the corrosion resistance of the amorphous multi-component alloy. The effect of the amorphizity, multi-component structure and the presence of elements with widely varying interfacial reactivities will be discussed.

SS-TuP8 Characterization of High Surface Area Platinum Black Electrodes for Electrochemical Sensing Applications*, **P. Neuzil,*** Institute of Microelectronics, Singapore*; B. Ilic, D. Czaplewski,* Cornell University*; T. Stanczyk,* Molex Incorporated*; J. Blough, G.J. Maclay,* University of Illinois at Chicago

The investigation of adsorbed high surface area noble metal nanoparticulates is important in medicine, nanotechnology, electrochemistry, microelectromechanical systems (MEMS) and sensors, biology, and in industry. In particular, high surface area noble metal electrodes have made a considerable impact in the field of microfabricated solid state, chemical and biological sensors. In our work, we investigate the properties of electrochemically deposited platinum black by atomic force and scanning electron microscopy. Initially the platinum electrodes were fabricated on various substrates utilizing developed silicon surface micromachining techniques. Platinum black was then electrochemically deposited on top of the microfabricated platinum electrodes. The platenized electrodes were subsequently used in an electrochemical cell for carbon monoxide detection (CO). The primary benefit of platinized electrodes is the increase in the surface area of the catalyst, which in turn causes an enhancement in the CO sensitivity by a few orders of magnitude. Deposition time and thermal conditioning were found to influence the quality and morphology of the platinum black layer. Methods of fractal analysis were employed to the acquired tapping mode atomic force micrographs in order to demonstrate the degree of roughness of the platinization. Morphological inclusions were readily observed in films deposited for duration of less than 60 seconds, at a bias of 1.5 V against a platinum counter electrode. Shorting of the microfabricated electrodes due to lateral outgrowth of high surface area platinum black was observed for various electrode geometries when current densities on the order of 100 mA cm@super -2@ were employed. We further show from out CO sensor performance that reproducibility of highly adherent platinized electrodes is achieved.

SS-TuP9 A Novel Technique for Producing Regular Nano-Channel Arrays*, **S.A. Barnett**, S. Sambasivan,* Applied Thin Films, Inc.

In this paper, we describe a simple method for producing large area nano-channel arrays with channel widths down to 1 nm. The synthetic method involves deposition of multilayers by magnetron sputtering where the width of each layer can be accurately controlled from 1-100nm. Subsequent to the deposition, one of the layers is preferentially etched to leave behind trenches of the other layer left intact. With appropriate choice of chemistry and etching technique,we have demonstrated the feasibility of this technique for a multilayer system. The residual layer and the intervening channels are quite planar for optimized film growth conditions, and thicknesses can be very accurately controlled. A number of applications can be envisioned for these channel arrays. For example, they should make good media for nano-stamping with the choice of a very hard material as one of the component layers. This should allow for imprinting of a wide range of materials. Initial results on nano-stamping will be presented.

SS-TuP10 In situ Investigation of Stage Formation of Eutectic Alloys during Annealing Amorphous and Crystalline Silicon with Metals*, **B.B. Bokhonov,** M.A. Korchagin,* Institute of Solid State Chemistry SB RAS, Russia

The in situ electron microscopic investigation of the formation of eutectic alloys in the system: amorphous film Si or crystalline thin foil (100)Si - particle Me (Me = Au, Ag, Cu, Al), showed the formation of eutectics is preceded by metal diffusion into amorphous silicon with the formation of metastable amorphous metal silicide. Supersaturation and decomposition of metastable metal silicide leads to the evolution of polycrystalline silicon. Morphological characteristics of liquid eutectic formation in system: crystalline silicon foil - metal particle are similar to well known morphological characteristics of the formation of etch pits in crystals. For the systems: crystalline silicon foil - metal particle (gold, silver and copper), oriented formation of the liquid evtectic are observed. The crystallization of liquid eutectic alloys leads to topotaxial evolution of metal silicide islands or compounds at the interface - eutectic alloy/silicon crystal.

SS-TuP11 The Study of ITO Targets Produced at Various Temperatures*, **J.H. Choi,*** Samsung Advanced Institute of Technology, Korea, R. of Korea*; H. Choi, J.S. Lee, J.Y. Won,* Samsung Advanced Institute of Technology, Korea*; J.C. Lee, C.B. Lim,* Samsung Advanced Institute of Technology, Korea, R. of Korea

ITO targets were produced by annealing of mixed powder of 90 wt% In@sub 2@O@sub 3@ and 10 wt% SnO@sub 2@ at various temperatures. The products were investigated by using TEM/EELS, XRD, XPS, and AES. The XRD results show that the phases of In@sub 2@O@sub 3@ and SnO@sub 2@ remain unchanged until 1300°C annealing. Whereas only In@sub 2@O@sub 3@ phase appears over 1400°C annealing. Further experiments with TEM/EELS demonstrate that in fact the In@sub 2@O@sub 3@ over 1400°C annealing is Sn-doped In@sub 2@O@sub 3@ which is dominant phase and there is another phase which is Sn-rich In@sub 2@O@sub 3@ . As the annealing temperature increases, the grain size increases, but the phases still remain. And many small spots exist inside Sn-doped In@sub 2@O@sub 3@ grains. It is In@sub 2@O@sub 3@ which is not Sn-doped. It is thought that the content of SnO@sub 2@ is more than proper to achieve Sn-doped ITO target completely.

SS-TuP12 Structure Analysis of Ta Films Deposited on Si(100), SiO@sub 2@, and Si@sub 3@N@sub 4@ Surface by Tapping Mode Atomic Force Microscopy*, **F. Wu,*** Medtronic, Inc.

Ta films deposited on Si(100), SiO@sub 2@, and Si@sub 3@N@sub 4@ surface during growth at different pressure and temperature were investigated using tapping mode Atomic Force Microscopy. The surface morphology of the films was found to depend on the subtrate surface, sputtering pressure and substrate temperature. Film stress and roughness of Ta/different substrate vs different deposition conditions were measured. The surface roughness of the films decreased with decreasing sputtering pressure and with increasing substrate temperature.

SS-TuP13 The Orientational Effects under Ion Grazing Incidence on the GaP(100) Surface*, **U.O. Kutliev,*** Urganch State University, Uzbekistan*; A.A. Dzhurakhalov,* Institute of Electronics, Uzbekistan*; B.C. Kalandarov,* Urganch State University, Uzbekistan

Research of laws of grazing scattering of ions begins with study of the form of trajectories of scattering particles. The forms these trajectories are rather difficult, as they are determined large by number correlated of collisions. This circumstance not allows to receive the analytical decision of the given task. By unique effective way of account of the form of trajectories grazing scattering is the modeling on the computer. In the present work the scattering processes on the GaP(100) surface under grazing ion bombardment have been investigated by computer simulation. The trajectories of incident positive ions Ne were simulated in the binary collision approximation. Energy and angular distributions of Ne+ ions scattered from the GaP (100) surface in the , directions and target orientations were calculated. The computational results show that in the energy spectrum the characteristic peaks corresponding to scattering of ions by the surface atomic chains and semichannels are observed. The situation and intensity of these peaks depend on the forms of the surface semichannels. This technique can be useful for investigations of semiconductor structures.

SS-TuP14 Tribocharging in Electrostatic Beneficiation of Coal: Effects of Surface Composition on Work Function as Measured by XPS and UPS in Air*, **S. Trigwell,** M.K. Mazumder,* University of Arkansas at Little Rock*; R. Pellissier,* RKI Instruments

The cleaning of coal by electrostatic beneficiation is based on tribocharging characteristics of pulverized (smaller than 120 µmm) coal particles. The variation in the charge distribution of electrostatically separated coal particles, as measured by an E-SPART analyzer, indicates that coal exhibits bi-polar charging. This appears to be in conflict with expectations in that the organic coal particles should charge positively, and the mineral particles, present as impurities such as pyrite, charge negatively, as predicted by the relative work functions of the particles (coal and mineral) and the metal surface (copper or stainless steel) used for tribocharging. UPS measurements in air on specimens of three different coal species showed the work function to be higher than predicted, approximately 5.4 eV. Determination of the coal surface composition by XPS showed the coal and the pyrite to be oxidized to different degrees. Studies by UPS and XPS, on copper, stainless steel, aluminium, and other commonly used tribocharging materials such as glass and PTFE, as well as pure pyrite, showed that the work function varied considerably as a function of surface oxidation. Therefore the reason for the bi-polar charging of the coal particles may be due a too small work function difference. The choice of a material for impaction triboelectric charging for coal or mineral separation should therefore depend upon the oxidized work function difference. The correlation between the charge distribution and work function is discussed.

**SS-TuP15 The Secondary Electron Emission Characteristics for Sol-Gel Based SiO@sub2@ Thin Films*, T. Jeong,* *J. Lee, S. Yu, S. Jin, J. Heo, W. Yi,* Samsung Advanced Institute of Technology, Korea*; D. Jeon,* Myongji University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

We have fabricated SiO@sub2@ thin films by sol-gel method with six different tetraethyl orthosilicate (TEOS) molarities, which were 0.116 M, 0.058 M, 0.029 M, 0.015 M, and 0.007 M. Each solution of the different TEOS molarity was coated on the Si substrate by a spin coater. The SiO@sub2@ layer was formed on the substrate by thermal heating at 450°C for three hours. From Nanospec/AFT Model 200 the thickness of the SiO@sub2@ film decreased as the concentration of TEOS decreased; the thicknesses of SiO@sub2@ were estimated to be 69 nm, 36 nm, 16 nm, 11 nm, 9 nm, and 7 nm for 0.232, 0.116, 0.058, 0.029, 0.015, and 0.007 molarity of TEOS solution, respectively. Finally, we measured secondary electron emission (SEE) yields for these SiO@sub2@ thin layers by bombarding electrons in the vacuum chamber which was maintained at around 110-7 torr. It was observed that the 9 nm thick SiO@sub2@ film exhibits the highest SEE yield (about 4) among six samples. This observation agrees well with our previous results obtained from thermal SiO@sub2@ films. The higher SEE yields for sol-gel based SiO@sub2@ films than thermal SiO@sub2@ films suggest that the sol-gel method is useful for secondary electron emission layer formation. In conclusion, the solution based SiO@sub2@ layer coating method is promising, especially for secondary electron emission layer for the electron multiplying devices, due to high secondary electron emission yield and its easy application to a porous surface such as alumina.

SS-TuP16 Absolute Determination of the Stoichiometry of Ultrathin Oxide Films as a Function of Thickness: Antimony Oxide on Gold*, K. Stefanov,* ***A.J. Slavin,*** Trent University, Canada

As the thickness of oxides in microelectronic devices decreases, it has become essential to know how oxide stoichiometry evolves with film thickness. This work uses a high-stability quartz crystal microbalance@footnote 1@ which can provide an absolute determination of stoichiometry as it evolves one molecular layer at a time. In the case of antimony films on a gold substrate, the first two monolayers of Sb oxidize as SbAuO, whereas subsequent layers oxidize as Sb@sub2@O@sub3@. @FootnoteText@ @footnote 1@ S.S. Narine and A.J. Slavin, J. Vac. Sci. Technol. A16, 1857 (1998).

SS-TuP17 Dodecanethiol on Cu(110) Studied by Low-temperature STM*, A. Kühnle,* *T.R. Linderoth, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

Monolayers of alkane thiols, primarily on Au(111), have been studied extensively as model systems for self-assembly. A number of UHV-STM investigations have been carried out at room temperature adressing the structure of different phases formed from low coverage where the molecules are lying down to higher coverage where they are standing-up.@footnote 1@ Very little is known, however, about the diffusion dynamics of the individual molecules or the quantitative details of the initial nucleation and growth of molecular aggregates on the surface. We have recently initiated a programme to investigate such questions using a home-built UHV-STM operating at variable temperatures down to 25 K. For dodecanethiol [CH@sub 3@(CH@sub 2@)@sub 11@-SH] deposited onto Cu(110) at a sample temperature of 110 K we find the formation of an ordered overlayer structure with molecules lying with their backbone parallel to the surface. There is thus considerable molecular mobility on the surface already at this temperature. We are currently extending these experiments to lower temperatures where the diffusion of individual molecules can be followed by time-lapse STM. @FootnoteText@ @footnote 1@ G.E. Poirier and E.D. Pylant, SCIENCE vol. 272, 1145, (1996).

SS-TuP18 Temperature-induced Morphology Changes for 1D Pt Islands on Pt(110)-(1x2)*, T.R. Linderoth,* *S. Horch, L. Petersen, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

The Pt/Pt(110)-(1x2) system has proven a fascinating one-dimensional model system for the study of adatom dynamics by time-resolved STM. At temperatures between 290-380 K, isolated ad-atoms and islands are restricted to the missing-row troughs where atoms show a quasi-1D diffusion behaviour@footnote 1@ while islands migrate along the troughs by a so-called "leap-frog" mechanism.@footnote 2@ Here we wish to present the results of quench-and-look experiments initiated to investigate ripening in this seemingly 1D system. When a surface with 1D Pt islands situated in the missing-row troughs is annealed at 369-395 K, we find: (a) an increase in the mean island size (coarsening) and (b) a surprising island restructuring, where adatoms move from the troughs up on top of the islands. Quantitative analysis of these findings and comparison to the known rates for island diffusion and other relevant kinetic processes interestingly reveal that the Pt/Pt(110)-(1x2) system can NOT be treated as purely 1D at the higher adatom coverages of 27±4 % used in the present experiments. Dynamic STM data, acquired at these higher adatom coverages, provides direct evidence for novel atomic-scale mechanisms leading to inter-trough mass transport. @FootnoteText@ @footnote 1@ Phys. Rev. Lett. 78, 4978 (97). @footnote 2@ Phys. Rev. Lett. 82, 1494 (99).

SS-TuP19 Friction on Diamond-Like Thin Films : Analysis by XPS*, J.M. Campbell,* *L.-S. Johansson,* Helsinki University of Technology, Finland*; J. Koskinen,* VTT Manufacturing Technology, Finland

Under humid conditions, an anomalous drop occurred in the coefficient of friction for a stainless steel ball bearing impinging on a Diamond-Like Coated (DLC) metal ring. XPS analysis of the wear area revealed minute but significant changes from the native film surface. Metal particles were present on the wear track; however, no chemical change in the DLC film was apparent. Assessment of the inelastic background shows that the metal resides on top of the DLC film. It is believed that the metal particles adsorb water from the humid atmosphere to form a lubricating layer.

SS-TuP20 Scanning Tunneling Microscopy of Single-Crystal Si@sub 3@N@sub 4@ Layer Grown on Si(111) by Nitridation*, C.-L. Wu,* *H. Ahn, Y.-C. Chou, S. Gwo,* National Tsing-Hua University, Taiwan

It has been known that ordered thin Si@sub 3@N@sub 4@ layer can be formed on Si(111) by exposing the Si surface to various nitrogen-containing gases (NH@sub 3@, NO, N, etc.) at high substrate temperatures. A variety of surface orderings ("8x8", "8/3x8/3", "4x4", and quadruplet) have been reported by previous studies using different surface-sensitive techniques, such as low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM), etc. However, until now there is no proposed structure model can satisfactorily incorporate all the observed features. In this work, by using high-resolution STM images at dual bias polarities in combination with Kikuchi electron holography (KEH), transmission electron microscopy (TEM), and ab initio total-energy calculations, we have determined an atomic model for this surface, which is capable of explaining the previously observed surface orderings.

SS-TuP21 Electron- and Photon-stimulated Desorption of Alkali Atoms from Silicon Dioxide and Ice Surfaces*, B.V. Yakshinskiy,* *T.E. Madey,* Rutgers University

To investigate mechanisms for the origin of K and Na in the tenuous atmospheres of the Moon, Mercury and Europa, we are studying the electron- and photon-stimulated desorption (ESD and PSD) of alkali atoms from model surfaces: amorphous SiO@sub 2@ and water ice films (both crystalline and amorphous) grown on a metal substrate. The measurement scheme for ESD and PSD of alkali atoms includes a highly sensitive detector based on surface ionization, and a time-of-flight technique. For PSD measurements, a mercury arc light source (filtered and chopped) is used. In the present work, we focus on ESD and PSD of K atoms, and compare with our previous studies of Na desorption from SiO@sub 2@.@footnote 1@ We find that bombardment of the alkali covered surfaces by ultraviolet photons or by low energy electrons (E>4 eV) causes desorption of "hot" K and Na atoms. The velocity distributions (VD) of K and Na desorbing from the silica surface are peaked at 650 and 1000 m/s, respectively, whereas the corresponding VD for desorption from the ice surfaces have maxima at 500 and 800 m/s. These values are consistent with the "hot" components of the lunar, Mercurian and Europian atmospheres. The mechanism of desorption is identified as an electronically excited charge-transfer from the silica or the ice substrate to neutralize alkali ion, followed by desorption of the alkali atom. We conclude that PSD by UV solar irradiation is a dominant source process for K and Na in tenuous planetary atmospheres. @FootnoteText@ @footnote 1@ BVY and TEM, Nature, Vol. 400, 642 (1999).

SS-TuP22 Using Surface-modified Embedded-atom-potentials to Simulate the Adsorption and Diffusion of Gold and Lead Atoms on the Au(111) Surface*, M.C. Robinson,* Trent University, Canada*; K. De'Bell,* University of New Brunswick, Canada*; A.J. Slavin,* Trent University, Canada

The usual embedded-atom method (EAM) typically underestimates surface energies and surface diffusion barriers on (111) surfaces. However, the EAM potentials can be modified@footnote 1@ to provide a fit to the surface energy without modifying the zero-temperature bulk properties. These modified potentials provide much more reasonable values for other surface properties. For example, they predict a surface-layer compression in agreement with that observed in the Au(111) "herringbone" reconstruction. Molecular-dynamics simulations indicate that the preferred mode of surface diffusion is incorporation of an adatom into the surface at one location with the ejection of another atom to the surface elsewhere. In the case of Pb deposited on the reconstructed Au(111) surface, they also predict an instability in the surface energy for a coverage of about 0.05 monolayers. Comparisons are made with scanning tunneling microscopy data for Pb on the Au(111) surface. Research supported by NSERC Canada. @FootnoteText@ @footnote 1@ M.I. Haftel and M.I. Rosen, Phys. Rev. B15, 4426 (1995).

SS-TuP23 The Adsorption and Trimerization of Acetylene to Benzene on Cu(110) Monitored by X-ray Spectroscopies*, **H. Öström**, K. Weiss, L. Triguero, A. Nilsson,* Uppsala University, Sweden

We have studied the adsorption of acetylene on Cu(110) and its trimerization reaction to benzene by high resolution X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS) spectroscopy and temperature programmed desorption (TPD). At liquid nitrogen temperature the XP spectra show two different C 1s peaks which correspond to two nonequivalent adsorbed acetylene species. By heating the sample one species transforms into the other. This species disappears above room temperature due to the trimerization of acetylene to benzene. The reaction has been followed by time resolved XP spectroscopy. We have been able to monitor the reaction in real time, finding that benzene leaves the surface as soon as it is formed. The adsorption geometry of the different adsorbate species has been determined by polarization dependent NEXAFS spectra and the experimental results are completed by ab-initio cluster model calculations performed in the framework of density functional theory (DFT).

SS-TuP24 Study of High and Low Work Function Surfaces for HyperThermal Surface Ionization using an Absolute Kelvin Probe*, **I.D. Baikie**, U. Petermann, B. Lägel, K. Dirscherl,* Robert Gordon University, UK

We have performed a study of high (> 6eV) and low (

SS-TuP25 A Double Quartz Crystal Microbalance Sensor for Monitoring High Pressure Heterogeneous Catalytic Reactions on Real Catalysts*, **I. Zori@aa c@**,* Chalmers University of Technology and Göteborgs University, Sweden*; P. Borchardt, C. Keller, B. Kasemo,* Chalmers University of Technology, Sweden

The quartz crystal microbalance (QCM) is a piezoelectric oscillator with a high sensitivity for micro weighing (<0.01ML of H@sub 2@) and a fast response. In this work we report a novel sensor consisting of two QCMs mounted on a single, 5 MHz, AT cut quartz crystal. The catalyst consists of metallic, highly dispersed, nanosized Pt particles on an Al@sub 2@O@sub 3@ washcoat deposited on one QCM by standard wet deposition methods. The other QCM, coated with washcoat only, was used as a reference allowing for subtraction of the frequency shift due to temperature changes, or in a constant temperature experiment, the separation of gases adsorbed on the noble metal of the catalyst from those adsorbed on the alumina support. The catalytic reaction chosen for testing of the sensor system was the high pressure H@sub 2@+O@sub 2@ reaction, catalyzed by nanosized Pt particles on alumina support. The resonant frequencies of the two QCMs, proportional to the total coverage of the reactants, were monitored. The time dependence of the frequency difference (proportional to the total coverage) reflects reaction kinetics on the Pt particles. These measurements are complemented by mass spectrometric measurements of the gas phase products, yielding wealthy information about reaction kinetics on a real catalyst at high pressure. In addition we also demonstrate the ability of the sensor for detection of kinetic phase transitions in the above reaction. The sensitivity of the sensor is estimated to about 30Hz/10@super 15@ Pt atoms. The noise level is < 1Hz thus enabling us to measure coverage changes corresponding to 2-3% ML.

SS-TuP26 Effect of Step Edges upon CO Dissociation over Ni Surfaces*, **H. Nakano**,* University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan*; J. Nakamura,* University of Tsukuba, Japan

We have studied the formation process of surface carbide on Ni(111) and Ni(977) by Boudouard reaction (2CO --> CO@sub 2, g@ + C@sub a@) using UHV-STM in order to clarify the dissociation site of CO. A reconstructed structure consisting of square units due to carbide was observed at the step-edges on Ni(111) when the carbide coverage was about @theta@ @sub c@ = 0.01. Islands of the reconstructed structure were formed on the upper terrace in the vicinity of specific step-edges. The same square units were then observed on the terrace at a carbide coverage of 0.13. This structure consisted of three domains in which one direction of the square unit corresponded to that of the Ni(111) substrate's hexagonal unit. Thus, the surface reconstruction caused by carbide formation was found to occur from step-edges. The formation rate of carbon on Ni(111) depended on annealing temperature after Ar ion sputtering. Increasing anneal temperature from 850 to 1100 K resulted in a decrease in formation rate of carbon by about 50 %. STM results showed that the number of defects on the Ni(111) surface decreased upon the annealing at 1100 K. These results indicate that Boudouard reaction or the CO dissociation occurs at defect sites. The formation rate of carbon on a stepped Ni(977) surface was promoted remarkably compared with Ni(111). The apparent activation energies of the carbon formation on Ni(977) and Ni(111) were measured to be - 36.4 and + 7.2 kJ/mol, respectively. It is considered that the formation of carbon consists of the CO dissociation at step sites and subsequent migration onto (111) terraces.

SS-TuP27 Ion Desorption from Molybdenum Oxide by Specific Core-to-Valence Resonant Excitations at the Mo L@sub 2,3@, Mo M@sub 2,3@ and O K-edges*, G. Wu, **Y. Baba**, I. Shimoyama, T. Sekiguchi,* Japan Atomic Energy Research Institute, Japan

Irradiation of X-rays on solid surface induces various chemical changes such as decomposition and desorption. Due to the localized nature of inner-shell electrons, the primary excitation localizes around specific element or specific chemical bond. The question is whether or not the primarily localized excitation leads to the specific chemical reaction. The examples for specific chemical-bond scission and ion desorption induced by core-level excitation have been reported for adsorbed molecules on solid surfaces. Here we present the results for the ion desorption from bulk material induced by a specific core-to-valence resonant excitation. Molybdenum trioxide was chosen as a sample, because this material is known to be sensitive to irradiation of X-ray or electrons. In the X-ray absorption near-edge structure (XANES) spectra, the resonance peaks corresponding to the excitations from Mo2p to 4d have two components due to the ligand-field splitting of 4d state, which are assigned as transitions from Mo 2p to triply degenerated t@sub 2g@-type orbits and doubly degenerated e@sub g@-type orbits. When we compare the desorption-yield curves with XANES spectra taken by total electron yield, the O@super +@ ion yield at the resonance from Mo 2p@sub 3/2@ into the e@sub g@-type orbits was enhanced compared to that into the t@sub 2g@-type orbits. Similar enhancements were also observed for the Mo M@sub 3@ and O K-edge excitations. Considering the antibonding character of the e@sub g@-type orbits, the enhancement of desorption is explained by the localization of excited electrons in the e@sub g@-type orbits which leads to the specific Mo-O bond breaking and O@super +@ desorption. The detailed mechanism will be presented on the basis of the results for the Auger decay spectra.

SS-TuP28 Surfactant Behaviors of Bi and As in the Growth of Ge/Si(001)-2x1 Systems Studied with Photoemission Spectroscopy*, **P. De Padova**,* Consiglio Nazionale delle Ricerche, Italy*; R. Larciprete,* ENEA, Italy*; C. Quaresima, A. Reginelli, S. Priori, E. Paparazzo, L. Moretto, P. Perfetti,* Consiglio Nazionale delle Ricerche, Italy

Heteroepitaxial Ge/Si(001)-2x1 systems show promising applications in the fabrication of infrared detectors. A layer-by-layer growth is essential for smooth films to be obtained, and this is greatly facilitated by addition of surfactant elements, such as As, Bi and Sb. Among these, Bi is a good candidate, as it little affects the Ge chemistry and has a low desorption temperature, whereas As has been generally regarded as being the ideal surfactant element. We used synchrotron radiation (SR) photoemission and XPS techniques to comparatively study the roles that Bi and As play in the growth of thin and thick Ge films on Si substrates. Angle-resolved SR core level spectra allowed us to identify two distinct growth modes in Ge/Bi/Si(001) systems as a function of Ge coverage. Sub-monolayer Ge coverages involve Ge- and Bi-atoms exchanging sites with each other, whereas greater Ge coverages involve the Ge-atoms lying both underneath Bi-atoms, as well as on top of the Si substrate. XPS depth-profiling conducted into a 15-monolayer Ge-film reveals that the Bi-atoms remain confined to the true surface. SR spectra of the Ge/As/Si(001) system show that the As-atoms lie anchored to the Si substrate, even for great Ge coverages, which is at striking variance with the expected layer-by-layer growth. Ge growth, carried out via codeposition of As and Ge on Si substrates, gives spectral evidences suggestive of the As atoms diffusing downward the Ge film, with no Ge-As site exchange taking place. We discuss our results in light of theoretical and experimental reports available in the literature, and propose an interpretation to account for the different surfactant behaviors of Bi and As.

SS-TuP29 Electron Transfer in Organic Monolayers*, **K. Raiber**, B. Zeysing, A. Terfort,* University of Hamburg, Germany

The electron transfer through organic monolayers is a field of research which is receiving an increased interest since these monolayers on conductive materials are not only used as barrier and protection materials@footnote 1,2@ but also as conductors. These new applications for the monolayers require a detailed understanding of the processes during the electron transfer through the monolayer. There are three different possible conduction mechanisms through monolayers discussed in literature:@footnote 3@ the through bond conduction, a through-bond tunneling and a through-space tunneling. To discriminate between the conduction and the tunneling mechanisms we investigated the electron transfer properties of unsubstituted aliphatic and aromatic molecules by cyclovoltammetry. To avoid problems with the match of Fermi-niveaus we attached an electrochemically active group to an aliphatic and an aromatic thiol, respectively, of approximately the same length and investigated the electron transfer within SAMs formed by these molecules on gold surfaces. The exact knowledge of the place of electron generation, which is determined by the immobilisation of the electrochemical active group on a gold electrode, allowed a better determination of the conduction mechanism. @FootnoteText@ @footnote 1@A. M. Becka, C. J. Miller; J. Phys. Chem. 1992, 96, 2657-2668. @footnote 2@ R. Haag, M. A. Rampi, R. E. Holmlin, G. M. Whitesides; J. Am. Chem. Soc. 1999, 121, 7895-7906. @footnote 3@K. Bandyopadhyay, K. Vijayamohanan, M. Venkataramanan, T. Pradeep; Langmuir 1999, 15, 5314-5322.

SS-TuP30 Reactions of Hydrazoic Acid (N@sub3@H) on Water and Gold Surfaces Characterized Using RAIRS and XPS*, S.R. Carlo, J. Torres, **D.H. Fairbrother**,* Johns Hopkins University

The chemistry of hydrazoic acid (N@sub3@H) on gold and amorphous ice surfaces was studied as a function of N@sub3@H exposure, temperature, and X-ray irradiation using reflection absorption infrared spectroscopy (RAIRS) and XPS. N@sub3@H adsorbed on ice at 100K initially led to azide production (N@sub3@@super-@), and subsequent N@sub3@H deposition. On Au, N@sub3@H adsorbed molecularly at 100K. On either surface annealing caused increased order in the film and loss of N@sub3@H correlated with N@sub3@@super-@ production. Three new IR bands were observed in the NH stretching region at T>180 K. The adsorption characteristics and thermal chemistry of N@sub3@H on ice suggest a chemisorbed state. These NH and N@sub3@@super-@ bands were stable to T>220K. Experiments were performed using N@sub3@D to elucidate the nature of these species. On both surfaces X-ray irradiation induced significant molecular desorption, increased azide concentration and production of the same three bands in the NH stretching region as observed when heating.

SS-TuP31 Adsorption and Desorption Processes of Alkanethiol Self-Assembled Monolayers on Au(111)*, **J. Noh**,* Frontier Research System, RIKEN, Japan*; T. Araki,* Saitama University, Japan*; K. Nakajima, M. Hara,* Frontier Research System, RIKEN, Japan

Adsorption and desorption processes of alkanethiol self-assembled monolayers (SAMs) on Au(111) have been examined by scanning tunneling microscopy (STM) and thermal desorption spectroscopy (TDS). New intermediate phases that are expected by a recent diffraction study from coverage-dependant SAMs prepared by a wet process were observed in a molecular level, revealing phase transitions from the striped phase to the upright phase. In addition, surface structure and molecular species desorbing from such SAM samples as a function of surface temperature were monitored by TDS and STM. TDS spectra for dimer molecules as well as alkyl groups formed after cleavage of C-S bond clearly show second-order desorption behavior implying the associative desorption of alkanethiolate adsorbed on Au(111) surface. STM images clearly show structural transitions due to desorption of molecules at elevated surface temperature. Moreover desorption process and stability of pre-covered alkanethiol SAMs in pure solvents at room temperature were investigated. In this study, it is revealed that desorption of alkanethiol SAMs under solvent and UHV conditions initiate at domain boundaries and near depressions that have weaker lateral interactions compared to close-packed domains, followed by desorption of molecules in close-packed domains. From these results, we discuss the adsorption states in alkanethiol SAMs as well as the precise model of the adsorption and desorption processes.

SS-TuP32 Hydroxymethylcyclopropane on Oxygen-covered Mo(110): A Radical Clock on a Metal Surface?*, **I. Kretzschmar**, J.A. Levinson, C.M. Friend,* Harvard University

Radical clocks are a well-established means for the determination of radical lifetimes in liquid and gas-phase organic chemistry.@footnote 1@ However, no equivalent tools yet exist for the evaluation of radical lifetimes on surfaces, although radicals are often proposed as the most important intermediates in surface reactions. In this study, the reaction of hydroxymethylcyclopropane has been investigated on clean and oxygen-covered Mo(110) surfaces. Since methylcyclopropane is the expected product upon C-O bond scission in hydroxymethylcyclopropane and represents the smallest possible model system for a radical clock, this molecule seems to be a promising system for gauging radical lifetimes in the vicinity of the surface. Changes in binding and structure of the adsorbate are monitored using a combination of temperature programmed reaction spectrometry and reflectance-infrared absorbance spectroscopy. These studies reveal that the surface species formed upon adsorption of hydroxymethylcyclopropane onto oxygen-covered Mo(110) is stable up to 400 K. Above 450 K, 1-butene, 1,3-butadiene, and ethene are produced. In addition, two new vibrational peaks develop at 1245 cm@super -1@ and 1645 cm@super -1@ in the infrared spectra obtained after heating to 450 K. Both peaks are attributed to ring-opened surface intermediates: the 1645 cm@super -1@ peak to alkoxide species and the 1245 cm@super -1@ peak to the formation of a metal-bound alkyl species after ring opening. The observation of ring-opened products points to the fact that ring opening is faster than hydrogen abstraction from the surface. The experiments are discussed in the general framework of alkyl oxidation processes. @FootnoteText@ @footnote 1@ See for example: Newcomb, M. Tetrahedron, 1993, 49, 1151.

SS-TuP33 LEED and STM Investigations of the Heteroepitaxy of Perylenetetracarboxylic-dianhydride (PTCDA) on Hexa-peri-benzocoronene (HBC) on Reconstructed Au(111) Surfaces*, T. Fritz, **F. Sellam**, T. Schmitz-Huebsch, M. Toerker, S. Mannsfeld, H. Proehl, K. Leo,* TU Dresden, Institut fuer Angewandte Photophysik, Germany

The fabrication of multilayered films and superlattices consisting of different molecules has recently attracted considerable interest because of the prospective applications of those structures as active optoelectronic components in modern integrated devices. While the epitaxy of inorganic semiconductor heterojunctions is already well established, only little is known about the growth of organic heterostructures. We present the result of the combination of two OMBE (organic molecular beam epitaxy) grown materials of planar molecules, namely perylene-tetracarboxylic-dianhydride (PTCDA) and hexa-peri-benzocoronene (HBC). As substrate the Au(111) surface was chosen. Two complementary surface analysis methods which are low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) have been applied to characterize the growth of the ultrathin organic molecular heterojunction and to determine the epitaxial relation between the two lattices. In a first step, we investigated the growth of HBC on reconstructed Au(111) surfaces. Large domains which are defect free on the molecular scale are observed by STM. The LEED investigations reveal that HBC grows on reconstructed Au(111) in a commensurate hexagonal structure. The HBC lattice is rotated by 30° with respect to the Au[110] direction and therefore it appears only in a single domain orientation. In a second step, a monolayer of PTCDA was deposited on HBC and structurally characterized. The LEED and STM measurements show the well-known herringbone alignment of the PTCDA molecules, similar to that in the (102) bulk plane with two molecules in a rectangular unit cell, indicating the p2gg space symmetry group. Besides these findings, the pronounced two-dimensional Moiré pattern in the STM images was used to determine the relative orientation of the PTCDA unit cell with respect to the underlying HBC lattice, revealing a parallel orientation between the short PTCDA lattice vector and the HBC[10] direction.

SS-TuP34 DeNOx Reactions on MgO(100): Photoemission and Density Functional Studies*, **T. Jirsak**, J.Z. Larese,* Brookhaven National Laboratory*; A. Maiti,* Molecular Simulations Inc.*; J.A. Rodriguez,* Brookhaven National Laboratory

In environmental catalysis the destruction or removal of nitrogen oxides (DeNOx process) is receiving a lot of attention. Nitrogen oxides (NO and NO@sub 2@) are formed in automotive engines and industrial combustion systems. Metal oxides can be useful in the control of environmental pollution. It has been found that MgO has the ability of trapping the NO@sub 2@ formed in automotive engines during the burning of fuels under oxygen-rich conditions. Synchrotron-based photoemission and first-principles density-functional calculations (DF-GGA) have been used to study the chemistry of NO and NO@sub 2@ on MgO(100). NO is weakly adsorbed on the oxide surface. On flat MgO(100), DF results predict an NO adsorption energy of 6 kcal/mol, which is close to the value of 5 kcal/mol observed experimentally. At steps of the surface, NO interacts with tetra- and penta-coordinated Mg atoms and the adsorption energy can increase to 9 kcal/mol. On MgO@sub 1-x@, O vacancies and defect sites enhance the bonding energy of NO, and lead to the production of N@sub 2@O at 100 K plus the deposition of N above 200 K. NO@sub 2@ is very reactive on terraces and steps of MgO(100). Adsorbed NO@sub 3@ and NO@sub 2@ are detected after exposing the oxide to NO@sub 2@ at 150 K. Strong bonding interactions between Mg sites and NO@sub 3@ favor disproportionation of adsorbed NO@sub 2@. The large differences in the reactivity of NO and NO@sub 2@ reflect the fact that nitrogen dioxide is a much better electron acceptor. The role of metal promoters (K,Cs,Cr,Ni) on DeNOx operations on MgO will be discussed.

SS-TuP35 Oxygen Loss and Recovering Induced by Ultra High Vacuum and Oxygen Annealing on WO3 Thin Film Surfaces*, M. Pssacantando, L. Lozzi, C. Cantalini,* ***S. Santucci,*** University of L'Aquila, Italy

Thin films of WO3 with thickness in the range of 150 nm have been deposited onto silicon substrates by thermal evaporation. The films as deposited and annealed at 300 and 500°C in oxygen for 24 hours were submitted to UHV annealing. XPS measurements (W4f and valence band) show for the as deposited sample annealed at 200°C in steps of 50°C a marked increase of the metallic features of the surface attributable to oxygen loss. This film extracted from the UHV ambient and annealed in oxygen at 200° shows XPS features meaningful of a renewed oxygen incorporation which is again reduced by the UHV annealing demonstrating an evident reversibility towards the oxygen loss and recovery for this kind of sample. Also the WO3 film treated by oxygen annealing at 300° shows an increase of the metallic character of the film surface due to oxygen loss as a consequence of the UHV annealing up to 300°C but the sample extracted from the UHV ambient and submitted to a second annealing in oxygen at 300°C for 24 h recovers oxygen remaining substantially stable and scarcely influenced by successive UHV annealing. Finally the surface of the sample initially annealed in oxygen at 500°C appears at the XPS measurements evidently stable after the UHV annealing up to 500°C. These results have been confirmed by Scanning Tunneling Microscopy measurements which evidenced for the as deposited sample a narrowing of the band gap when the annealing temperature in UHV overcomes 300°C. Gas sensing towards NO2 of samples with UHV annealing modified surfaces have been also investigated giving encouraging results respect to the increase of the sensitivity of the sensor.

SS-TuP36 Spectral Changes in Far and Near Field Optical Microscopy of Surface Clusters*,* ***M. Xiao,*** CCMC-UNAM

We theoretically study the spectra in far and near field optical microscopy of a group of nanoscopic scatterers such metallic and semiconductor quantum dots two-dimensionally distributed on a plane surface. Our emphasis is on the spectral changes in the far and near field spectra as compared with spectra of individual scatterers. We show that extra spectral changes can be observed when the coupling between scatterers becomes strong. If the coupling is mainly due to the evanescent field, the produced spectral changes are localized in the near field zone. The extra spectral changes include both red and blue shift, as well as deformation.

SS-TuP37 1-to-9 keV Electron-Induced Surface Chemistry in Ultra High Vacuum Systems*,* ***Q. Ma,*** Argonne National Laboratory, US*; R.A. Rosenberg,* Argonne National Laboratory

Electrons in accelerators are ubiquitous. They range in energies from MeV down to a few eV (secondary electrons). Collisions of these electrons with surfaces of accelerator components may produce reactions that will modify the properties of the surface/vacuum interface. In order to gain insight into these reactions, we have studied the interaction of 1-to-9 keV electrons with the Ar-ion sputtered surfaces of Al, TiN, and Si, under ultra high vacuum conditions using scanning Auger electron spectroscopy. Electron-induced surface chemistry takes place on all these surfaces. For both Al and Si, layer-by-layer growth of oxides was produced by electron beam bombardment. In the case of Al, a clear threshold behavior of the oxidation rate is observed for excitation energies near the Al K-core hole (1560 eV), which suggests participation of secondary electrons in the surface reaction. In the case of TiN films, surface carbonation occurred with 9 keV electron bombardment while no reaction was observed with 5 keV el ectrons. No enhancement of the surface oxidation rate was observed. It will also be shown that the deposited carbonaceous layer is graphitic in nature, resulting in a decrease of the secondary electron yield and thus an increase of the observed sample current. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38.

Biomaterial Interfaces
Room 202 - Session BI+SS-WeM

Water at Biointerfaces

Moderator: B. Kasemo, Chalmers University of Technology, Sweden

8:20am **BI+SS-WeM1 Role of Water in Biological Processes*, E.A. Vogler,*** The Pennsylvania State University **INVITED**

Water is so familiar and ubiquitous in our environment that we frequently forget, ignore, or underestimate the role its special properties play in the biological and material sciences. Likewise in the hybrid field of biomaterials, where water-surface interactions apparently control and/or moderate the biological response to materials applied in medicine and biotechnology. In fact, the behavior of water near surfaces is becoming increasingly relevant in these fields as surface-to-volume ratios increase with the ever-decreasing size imposed by micro-to-nano-scale analytical and medical devices, especially as applied in nanobiotechnology. This lecture reviews some important water properties from both a thermodynamic and molecular perspective. The occasionally forgotten biological/environmental importance of thermodynamic attributes such as heat capacity, (latent) heats of fusion/vaporization, density, and interfacial tension are briefly recapitulated, leading to the conclusion that terrestrial life simply could not and would not work the way it does without the special mediating influence of water. Molecular aspects that give rise to these important bulk-water properties will be discussed along with the impact these have on the mechanisms of water wetting. It will be suggested that current theories of wetting substantially ignore some of these unique aspects of molecular water that distinguish it from all other room-temperature fluids. Against this backdrop, evidence suggesting that the role of water in the acute biological response to materials has been underestimated will be presented, concluding that the interfacial behavior of water must be explicitly included in any comprehensive biophysical theory attempting to explain or predict performance of biology at aqueous interfaces.

9:00am **BI+SS-WeM3 Neutron Reflectivity Studies on the Interaction of Water with Biocompatible Monolayer Films*, D. Schwendel,*** University of Heidelberg, Germany*; R. Steitz,* Hahn-Meitner Institute, Germany*; J. Pipper, R. Dahint, M. Grunze,* University of Heidelberg, Germany

Since the early 1990s protein resistance has been obtained for surfaces coated with poly- or oligo(ethylene glycol) (PEG or OEG) derivatives ((CH@sub2@-CH@sub2@-O)@subn@). While the inertness of PEG has been explained by the steric repulsion theory associating the inertness of the polymer brushes with the high conformational freedom of PEG chains in the near surface region, FT-IRRAS studies related the protein resistance of OEG to its molecular conformation. Whereas the helical and amorphous conformers on Au are inert towards protein adsorption, the planar all-trans conformer on Ag does adsorb protein. In Small Angle Neutron Scattering (SANS) studies we found experimental evidence for a strongly bound water layer on helical OEG-terminated alkanethiolate self assembling monolayers (SAMs). The experimental observations have been predicted by ab initio calculations simulating the adsorption of water molecules on methoxy terminated OEG with 3 EG units (EG3-OMe) and Monte Carlo simulations of water close to the SAM surfaces. Both theoretical studies postulate easy accommodation of water at helical OEG strands and a lower density of water near the SAM surface. This strongly bound water film is identified as the physical cause that these surfaces are inert against protein adsorption and cell attachment. SANS studies showed that the data for a hydroxy terminated helical OEG-SAM with 6 EG units (EG6-OH) on Au correlate satisfactorily with the model assuming a boundary water layer of 56 Å at the solid/liquid interface with a density of 92 % of that of bulk water. Also for the investigation of amorphous EG3-OMe immobilized on Au the assumption of a 36 Å water layer with a density of 78 % compared to bulk D@sub2@O yielded a much lower @chi@@super2@ deviation between the experimental data and the fit than the assumption of no interphase water.

9:20am **BI+SS-WeM4 Hydrogen Bond of Water in Ih Ice Probed by Core-level Spectroscopies*, H. Ogasawara*,** *D. Nordlund, M. Cavalleri, L.-A. Näslund, M. Nagasono, L.G.M. Petterson, A. Nilsson,* Uppsala University, Sweden

In biological complexes, DNA, protein and so on, materials consist of two types of chemical bonds. A shorter covalent bond has the strength of a few eV to construct molecular flame, and longer hydrogen bond has the strength of a few tenth meV. This energetically weak nature of hydrogen bond gives flexibility and enables the self-organization of molecules at ambient temperature. Ice is a unique material that hydrogen and oxygen atoms in the crystal are connected both covalent and hydrogen bonds where each oxygen atom has two covalent O-H bonds and two hydrogen O-H bonds. Here we report electronic structure of water in Ih ice, a thin film grown on Pt(111), studied with combination of core-level spectroscopies, X-ray absorption spectrosocpy (XAS), X-ray emission spectroscopy (XES) and theoretical simulation (DFT calculation). The experiments were performed at MAX-LAB, Sweden. The details of the endstation is described elsewhere.@footnote 1@ The theoretical simulation of spectra was done using the deMon program@footnote 2@ XAS and XES results indicate a reconfigration of molecular orbitals of water in ice beside the binding energy shift. In O 1s XAS, 4a@sub 1@ resonance is severely suppressed indicating the enhancement of s-character of this orbital compared to that of the gas phase. In O 1s XES, 3a@sub 1@ emission is suppressed showing the strong s-character of this orbital. From these observations we conclude that a water molecule in ice has a pseudo-totally-symmetric character. This pseudo-totally-symmetric character of water in ice is confirmed by excitation profile of 3a@sub 1@ photoemission peak and theoretical simulation. @FootnoteText@ @footnote 1@ R. Denechke et al, J. Electron Spectrosc. Relat. Phenom. 101-103, 971(1999). @footnote 2@ deMon-KS version 4.0, deMon Software, (1997).

9:40am **BI+SS-WeM5 Tyrosine Derivatives Adsorbed on Gold for Surface Modification*, K. Uvdal,*** *J. Svensson, P. Konradsson, B. Liedberg,* Linköping University, Sweden

Model molecules can be very useful when searching for mechanisms of protein folding. We intend to use model molecules to study if the changed conditions for binding of water, caused by binding and cleavage of ATP, is the main reason for protein conformational changes. In this very first study we are investigating tyrosine derivatives linked to 3-mercaptopropionic acid through an amide bond. Two different tyrosine derivatives, one with the OH group free and one with the OH group phosphorylated are studied. These molecules are adsorbed on gold and studied by X-ray Photoelectron Spectroscopy (XPS), Infrared Reflection-Absorption Spectroscopy (IRAS). The techniques are used to investigate the coordination to the surface and the molecular orientation of adsorbates relative to the surface. Molecular surface interactions causing chemical shifts in the core level XPS spectra of the adsorbates on gold are investigated using multilayer films as references. IR in transmission mode is used as a reference to the IRAS results and thus the surface selection rule is used to identify the orientation of certain vibrations relative to the surface. The S(2p) core level XPS spectrum for the adsorbate of the tyrosine derivative shows only one type of sulfur. The S(2p3/2) peak is shifted about 2.5 eV to lower binding energy when compared to multilayer showing a chemical adsorption through the sulfur atom. A phosphorylated tyrosine derivative adsorbed on gold shows an enhanced signal from PO3 in surface sensitive mode in good agreement with a molecular orientation with the PO3 group pointing away from the surface. The IR spectrum of the tyrosine derivative is showing several strong bands in transmission mode (KBr). Most of these peaks are also strong in the spectrum for the adsorbate. However, some significant differences are observed which are correlated to the molecular orientation relative to the surface. In a second step these monolayers are to be used for water interaction studies.

10:00am **BI+SS-WeM6 Stretching of a Macromolecule: A First Principles Theory*, H.J. Kreuzer,*** Dalhousie University, Canada **INVITED**

The statistical mechanics to describe the stretching of a single polymer strand (in particular in an AFM experiment) is formulated. As ingredients one needs the potential energy surfaces of the various conformers of the macromolecule. These have been calculated for oligo (ethylene glycol) resulting in quantitative agreement for the force/extension curves measured for PEG, both in hexadecane and in water. The interaction of water with PEG is discussed in great detail. We also present results for the effect of strong electric fields on PEG, such as surprisingly large electrostriction.

10:40am **BI+SS-WeM8 A Fundamental Approach to Protein Adsorption: Changes in Free Energy for Adsorption of Individual Peptidyl Residues onto Functionalized SAM Surfaces*, R.A. Latour,*** Clemson University*; L.L. Hench,* Imperial College, UK

Cellular response to biomaterial surfaces has great importance for the design of bioactive substrates for implant, drug delivery, and tissue engineering applications and is greatly influenced by protein/surface adsorption. All proteins are made up of amino acids (peptidyl residues); thus protein adsorption must be fundamentally governed by the submolecular interactions between a protein's residues and surface functional groups. The objective of this research was to develop an approach to quantitatively determine changes in Gibbs free energy for individual mid-chain residue/surface (R/S) functional group interactions and apply it to selected R/S group pairs. Molecular models (MOPAC/COSMO; CAChe software, Oxford Molecular Inc.) were created of 3 residues (Ala, Ser, Lys) and 3 SAM surfaces (CH@sub 3@, OH, COO-) to represent hydrophobic, hydrophilic, and charged systems in an aqueous environment. Adsorption enthalpy for each R/S pair was determined by positioning the residues over the surfaces and calculating the system energy as they were sequentially separated from the surface. Additional enthalpy and entropy contributions due to water restructuring effects were estimated based on changes in solvent accessible surface area and experimental wetting data. This was combined with the modeling data to calculate the net @DELTA@G@sub ads@. Ala was predicted to tightly bind to the CH@sub 3@ surface with @DELTA@G@sub ads@ = -5.8 kcal/mol with Ser and Lys each having @DELTA@G@sub ads@ > 0. All 3 residues exhibited @DELTA@G@sub ads@ > 0 for adsorption to the OH surface. Lys was predicted to be attracted to the COO- surface with @DELTA@G@sub ads@ = -5.4 kcal/mol, but only through intervening water layers with a 5 - 7 Å surface separation distance. Ala and Ser had @DELTA@G@sub ads@ > 0 for their interaction with the COO- surface. Further work is planned to integrate this type of data to develop a universal model for predicting protein-surface adsorption behavior.

Organic Films and Devices
Room 313 - Session OF+EL+SS-WeM
Transport and Device Issues in Organic Thin Films

Moderator: A. Kahn, Princeton University

8:20am **OF+EL+SS-WeM1 The Transport and Injection of Positive Carriers in Conjugated Electroluminescent Polymers and their Devices***, **A.J. Campbell**,* University of Sheffield, UK, U.K.*; D.D.C. Bradley,* University of Sheffield, UK*; H. Antoniadis,* Infineon Technologies Corp. **INVITED**

Organic light emitting diodes (OLEDs) based on electroluminescent conjugated polymers are an important emerging technology with a wide range of display and lighting applications. Polyfluorene and its copolymers are considered to be amongst the most promising materials for use in commercial OLEDs. Indium tin oxide (ITO) is also the hole injecting electrode of choice in any practical device. Here we report the results of time-of-flight measurements on the transport of positive carriers in polyfluorene and its copolymers. The field and temperature dependence of the charge carrier mobility is compared to theoretical models for charge transport in disordered organic materials. We also report the results of dark injection and current density-voltage measurements on the injection of holes from differently prepared ITO contacts. The absolute injection efficiency of the contacts is calculated by comparison to trap-free, space-charge-limited current (TFSCLC). The injection efficiency is shown to vary with not only polymer ionisation potential but also with the nature of the ITO preparation (i.e. washed in solvents, exposed to an oxygen plasma, coated with a film of poly(ethylenedioxythiophene) / polystyrenesulphonic acid). The variation of the injection efficiency with temperature is also reported.

9:00am **OF+EL+SS-WeM3 Grain Boundary Effects on Electrical Transport in Polycrystalline Organic Semiconductor Thin Films***, **R.J. Chesterfield,** A.B. Chwang, K. Puntambekar, C.D. Frisbie,* University of Minnesota

The role of microstructure in electrical transport in polycrystalline thin films of organic semiconducting oligomers (e.g., pentacene, sexithiophene) has not been extensively explored. This talk describes experiments in which transport through single grain boundaries (GBs) is probed using field effect transistor (FET) structures and Kelvin probe force microscopy (KPFM). In the FET studies, closely spaced gold source and drain electrodes are connected to pairs of pentacene or sexithiophene microcrystals grown on insulating substrates, such as SiO@sub 2@. The microcrystals, or grains, share a common boundary that dominates the transport through the FET. Conduction through the GB is measured as a function of gate field and temperature, and the results are compared with a recent model by Schon and Batlogg.@footnote 1@) In the KPFM studies, a metal-coated AFM tip is used to record potential distributions across an operating microcrystal FET. The resulting images reveal where the voltage is dropped across the device and thus point to the chief bottlenecks in the current transport. In general, both the microcrystal FET and Kelvin probe experiments show that microstructure, and in particular GBs, can potentially dominate transport in polycrystalline organic semiconductor films. @FootnoteText@ @footnote 1@J. H. Schon, B. Batlogg, Appl. Phys. Letters, 74(2), 1999, 260-262.

9:20am **OF+EL+SS-WeM4 Quantum Confinement and Electron Transfer at Organic-Metal Interfaces***, **G. Dutton**, H. Wang, X.-Y. Zhu,* University of Minnesota

Electron transfer at organic-metal interfaces is important in molecule-based electronic and optoelectronic devices, such as light-emitting devices (LEDs), field-effect transistors (FETs), and molecular quantum wires (QW). We probe interfacial electronic structure and electron transfer dynamics using two-photon photoemission in model systems: thin films of hexafluorobenzene and naphthalene adsorbed on Cu(111). Electron transfer to the lowest unoccupied molecular orbitals, as well as to those mixed with image-type states, are observed. In both systems, these resonances display quantum well behavior: the electronic wavefunction is delocalized parallel to the surface but confined in the direction normal to the surface. The detailed structure and dynamics are established by dispersion measurements and by femto-second time-resolved two-photon photoemission. We believe the formation of these molecular quantum wells is a result of the strong interaction of molecular states with the metal substrate. A simple theoretical framework is developed to describe the formation of these molecular quantum wells.

9:40am **OF+EL+SS-WeM5 Chemistry and Electronic Properties at Metals (Al, Mg and Au)-Organic Molecular Semiconductor (F@sub 16@CuPc) Interfaces***, **C. Shen**, J. Schwartz, A. Kahn,* Princeton University

The fabrication of efficient and stable metal-organic contacts is exceedingly important for the optimization of organic devices such as organic light emitting diodes (OLED) and thin film transistors. Al and Mg have low work functions and are typically used as electron injecting cathode materials. Au is a mostly inert metal in contact with organic materials. F@sub 16@CuPc is a candidate for n-channel thin film transistor material because of it relatively high electron mobility. Chemistry and physical processes (e.g. interdiffusion) that take place at metal/organic interfaces have a direct impact on the electronic properties of the contacts. It is generally believed that metals deposited on organics lead to more extensive interface chemistry and broader interfaces than organics deposited on metals. In some cases, these interfaces have actually been reported to lead to drastically different electrical behavior. The interfaces fabricated in ultra-high vacuum, however, shows identical electrical behavior.@footnote 1@ We have investigated the interface chemistry, electronic structure and electrical transport in nominally symmetric metal/F@sub 16@CuPc/metal structures fabricated and tested in ultra-high vacuum. For these structures, we performed detailed ultra-violet and X-ray photoemission spectroscopy (UPS, XPS) photoemission spectroscopy measurements that suggest that the chemistry at metal-on-organic interfaces is very similar to, if not identical with, that at organic-on-metal interfaces. Using current-voltage measurements performed in vacuum, we demonstrate that carrier injection is identical from top and bottom cathodes. @FootnoteText@ @footnote 1@Role of electrode contamination in electron injection at Mg:Ag/Alq@sub 3@ interfaces, C. Shen, I.G. Hill and A. Kahn, Adv. Mat. 11, 1523 (1999).

10:00am **OF+EL+SS-WeM6 Microcontacts to Self-Assembled Monolayers with a Conducting AFM Tip***, D.J. Wold, **C.D. Frisbie**,* University of Minnesota

Molecular level electrical transport studies require innovative approaches for making electrical contacts to oriented molecules. While scanning tunneling microscopy (STM) and electrochemical methods have been used for years to study transport in surface-confined molecules, conducting probe atomic force microscopy (CP-AFM) provides an alternative approach to electrically contacting monolayer films and the formation of metal-molecule-metal junctions. In CP-AFM, a metal-coated AFM tip is placed in direct contact, under controlled load, with the material to be probed. The technique differs from STM in that the probe is positioned using normal force feedback, which decouples probe positioning from electrical measurements. Using this technique, we show that CP-AFM may be used to make mechanically stable electrical contact to SAMs of alkane thiols on Au. We have probed the current-voltage (I-V) characteristics of the resulting junctions as a function of the number of methylenes in the alkane chains and the load applied to the tip-sample contact. The ease of this technique and the fine control of the probe during measurements make CP-AFM a promising approach for studying transport through molecular junctions. Further studies of dependence on conjugation, functional group distributions, orientations, and molecular dimensions will also be discussed.

10:20am **OF+EL+SS-WeM7 White-Light-Emitting Organic EL Devices Based on Vacuum Deposited Thin Films***, **J. Kido,*** Yamagata University, Japan **INVITED**

In this paper, we describe the design and fabrication of bright and high efficiency white-light-emitting EL devices based on vacuum deposited organic thin films. In order to archive high quantum efficiency, multilayer structures are employed. White light can be generated by using two emitter layers composed of blue and yellow emitters. For the blue emitter layer, distyrylbiphenyl derivative is doped with a few percent of distyrylarylene derivative with carbazolyl groups. For the yellow emitter layer, rubrene was doped into hole-transporting arylamine derivative (NPD). Reduction of drive voltage was realized by using metal-doped electron injection layer,@footnote 1@ which is composed of electron-transporting bathophenantroline (Bphen) doped with Cs metal. Cs-doping to Bphen reduces resistivity of the Bphen film, and the contact between cathode and the Bphen layer becomes ohmic, which results in the low drive voltage. The typical device structure is ITO/NPD/yellow-emitting layer/blue-emitting/Bphen doped with Cs/Al. By optimizing the thickness of each layer and dopant concentration, the white EL devices exhibited extremely high luminous efficiency of 15 lm/W and external quantum efficiency of 4% which are the highest values reported for white organic EL devices. @FootnoteText@@footnote 1@J.Kido and T.Matsumoto, Apply. Phys. Lett, 73, 2868(1998).

Surface Science
Room 208 - Session SS1-WeM
Chemical Interactions and Surface Reactivity

Moderator: J.L. Gland, University of Michigan

8:20am **SS1-WeM1 Increased Reactivity of Strained Ni Layers on Ru(0001)***, **R.C. Egeberg**, I. Chorkendorff,* Technical University of Denmark, Denmark

Understanding the reactivity of metal surfaces and in particular how to control and manipulate this reactivity is the first step towards improved catalysts. From many surface science studies a detailed knowledge about the structures emerging from metal on metal growth has been gained whilst the link to the overall reactivity of such bimetallic structures has not been equally thoroughly investigated. We here present data showing how to utilize the growth properties of Ni on Ru(0001) to improve the ability of Ni to catalyze the reforming of methane. By growing a pseudomorphical Ni overlayer on Ru(0001) a strained Ni layer is formed with respect to Ni(111). As a result of the change in electronic configuration this procedure results in a more reactive Ni layer as it has been predicted from DFT calculations. In steam reforming catalysis the dissociation of methane is the rate-limiting step and we have therefore focused on the initial sticking of methane on this surface. Thermal experiments at 530 K show that the Ni overlayer is ca. 2 times more reactive than Ru(0001) and ca. 20 times more reactive than Ni(111). As more than 1 monolayer of Ni is deposited the sticking decreases and saturates at the value for Ni(111). The adsorption energy of CO which is used as a probe molecule follows the same trend as the CH@sub 4@ sticking. Supersonic molecular beam experiments support the picture of a lower activation barrier on the strained Ni overlayer. Finally, the ability of the surface to catalyze the partial oxidation of methane is under investigation.

8:40am **SS1-WeM2 Suppression of NO Dissociation by Adsorbed Gold on Pt(335)***, **D.C. Skelton,*** Michigan State University / General Motors*; R.G. Tobin,* Tufts University*; C.L. DiMaggio, D.K. Lambert, G.B. Fisher,* Delphi Automotive Research Labs

We have conducted a temperature programmed desorption study to compare the dissociation probabilities of oxygen and NO on a partially gold-covered stepped Pt(335) surface. NO dissociation takes place almost exclusively at step sites. It apparently requires either multiple adjacent open step sites, or special sites such as kinks, and is therefore unusually sensitive to modification of steps and defects. A gold coverage of 0.15 ML reduces NO dissociation by a factor of five compared to bare Pt, and increasing the gold coverage to 0.3 ML further reduces it to an undetectable level. Oxygen dissociation also occurs preferentially at step sites, but is far less sensitive to step blockage: At 0.3 ML gold, the saturation oxygen coverage is only 20% lower than on bare Pt. These results help explain the operation of a recently developed electrochemical NO@sub x@ sensor.@footnote 1@ An effective NO@sub x@ sensor is vital for pollution control in fuel-efficient lean-burn gasoline and diesel engines. The electrochemical sensor uses a platinum-gold alloy electrode in a pumping cell to remove oxygen from the exhaust gas without dissociating NO. For effective sensor operation, the electrode must be ~10@super 3@ more effective at dissociating oxygen than at dissociating NO. Our experiments suggest that a platinum-gold alloy electrode has this remarkable selectivity because gold blocks special sites that are needed for NO dissociation but not for oxygen dissociation. @FootnoteText@ @footnote 1@ N. Kato, Y. Hamada and H. Kurachi, SAE Paper 970858 (1997).

9:00am **SS1-WeM3 Chemical and Electronic Properties of Ni/Pt(111) Bimetallic Surfaces: Unique Surface Reactivity at the Monolayer Ni Coverage***, **J.G. Chen**, J. Eng, Jr., M.T. Buelow, H.H. Hwu, N.A. Khan,* University of Delaware **INVITED**

In a recent paper we reported the observation of an "anomalous" reactivity of Ni/Pt(111) bimetallic surfaces at Ni coverages around one monolayer (ML) [3]. For example, after a saturation exposure of D2 to a Ni/Pt(111) surface with one ML Ni, the desorption of D2 occurs at 220 K from the TPD measurements. This desorption temperature is lower than that of D2 desorption from either Pt(111) (294 K) or Ni(111) (379 K). The lower desorption temperature suggests that the D atoms are rather mobile on the one ML Ni/Pt(111) surface. We have tested this idea by investigating the hydrogenation of cyclohexene to cyclohexane, and the hydrodesulfurization of thiophene to 1,3-butadiene on the one ML Ni/Pt(111) surface. In both cases the hydrogenation reactions take place at around 220 K under UHV conditions; these two reactions do not occur on either Pt(111) or Ni(111) under similar experimental conditions. In this talk we will present these latest TPD results, as well as our characterization of the chemical and electronic properties of the Ni/Pt(111) surfaces using high-resolution electron energy loss spectroscopy (HREELS), near-edge X-ray absorption fine structure (NEXAFS), and X-ray photoelectron spectroscopy (XPS).

9:40am **SS1-WeM5 Coverage Dependent Selectivity and a New Approach to Tayloring Nanostructures on Single Crystal Surfaces***, **A.V. Teplyakov**, H. He, A.T. Mathauser,* University of Delaware

Here we report a remarkable chemistry exhibited by 6-bromo-1-hexene on a Cu@sub 3@Pt(111) surface. The dehydrocyclization reaction leading to the formation of benzene takes place at very low coverage; as the surface fills up the decomposition becomes a predominant pathway. Similar behavior was reported for other linear hydrocarbons on metals and metal alloys previously. However, further increase of surface concentration of 6-bromo-1-hexene leads to a different type of chemistry. The hydrogenation of 5-hexenyl produced as a result of C-Br bond dissociation leads to the formation of 1-hexene which is stable on a surface until the molecular desorption of this compound starts at 230 K. Molecular desorption from the monolayer becomes significant at even higher dose. All these processes occur within a specific coverage very cleanly making the 6-bromo-1-hexene on a Cu@sub 3@Pt(111) surface extremely attractive to analyze the kinetics of coverage dependent processes. Steric requirements for each of the processes described here and the availability of the adsorption sites on the alloy surface are believed to govern the predominant reaction. Thermodynamics and potential applications of these chemical processes for masking and production of nanoscale features will be discussed.

10:00am **SS1-WeM6 The Near Edge X-ray Absorption Fine Structure of n-octane Adsorbed on Cu(110): New Insights Into the Type of Chemical Interaction***, **K. Weiss**, L. Triguero, H. Öström, A. Nilsson,* Uppsala University, Sweden

Using near edge X-ray absorption fine structure (NEXAFS) spectroscopy we have investigated the electronic structure of n-octane adsorbed on Cu(110). The molecule is found to be well oriented on the surface, which is seen from the high degree of NEXAFS dichroism. The NEXAFS spectra, which display the density of unoccupied molecular states, reveal large changes in the electronic structure of the adsorbed octane relative to the free molecule. We find that the molecular Rydberg states are strongly quenched upon adsorption and that there is a significant hybridization of molecular valence orbitals with the metal bands. In order to understand these adsorption induced electronic structure changes we have performed cluster model calculations in the framework of density functional theory. The calculations show nice agreement with the experimental results. In addition to a precise interpretation of the NEXAFS spectra, we present details on the geometric structure of the adsorbed octane molecule and the molecular orbital structure. The results are complemented by calculations of the X-ray emission spectra, which provide information on the occupied valence states. Our study gives new insights into the type of chemical interaction experienced by saturated hydrocarbons adsorbed on metal surfaces, which is of importance for the understanding of the C-H bond activation mechanism.

10:20am **SS1-WeM7 Direct Experimental Measurement of Donation/Backdonation in Unsaturated Hydrocarbons Bonding to Metals***, **L. Triguero**,* Uppsala University, Sweden*; A. Föhlisch,* Universität Hamburg, Germany*; P. Väterline, J. Hasselström,* Uppsala University, Sweden*; M. Weinelt,* Universität Erlangen, Germany*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Uppsala University, Sweden

Soft X-ray emission spectra (XES) from C@sub 2@H@sub 4@/Cu(110) and C@sub6@H@sub6@/Cu(110) have been obtained for two excitation energies, resonant and non-resonant, and resolved in all three spatial components (x, y, z). The one-step theory for resonant soft X-ray spectroscopy and Raman scattering is extended to adsorbates on metal surfaces and is implemented within a density functional theory framework. A combination of these expermiental and theoretical works are used to examine the electronic structure of chemisorbed ethylene and benzene on the Cu(110) surface in order to investigate the suitability of the donation/backdonation bonding model given by Dewar, Chatt and Duncanson for the interaction of unsaturated hydrocarbons with metal surfaces. We give an experimental verification of the DCD model and find donation/backdonation to be twice as large for ethylene as for benzene. In particular, the degree of @sigma@--@pi@ mixing (rehybridization) is found to correspond to the amount of donation/backdonation, which is put into relation to the aromatic and non-aromatic @pi@ characters of benzene and ethylene, respectively.

10:40am **SS1-WeM8 Trapping-mediated Dissociative Chemisorption of Cycloalkanes on Ru(001) and Ir(111): The Influence of Ring Strain on the Activation of C-C and C-H Bonds***, **T.-W. Kim**, C.J. Hagedorn, M.J. Weiss, W.H. Weinberg,* University of California, Santa Barbara

We have measured the initial probabilities of dissociative chemisorption of perhydrido and perdeutero cycloalkane isotopomers on the hexagonally close-packed (hcp) Ru(001) and Ir(111) single-crystalline surfaces for surface temperatures between 250 and 1100 K. Kinetic parameters (activation barrier and preexponential factor) describing the initial, rate-limiting C-H or C-C bond cleavage reactions were quantified for each cycloalkane isotopomer on each surface. Determination of the dominant initial reaction mechanism as either initial C-C or C-H bond cleavage was judged by the presence or absence of a kinetic isotope effect between the activation barriers for each cycloalkane isotopomer pair, and also by comparison with other relevant alkane activation barriers. On the Ir(111) surface, the dissociative chemisorption of cyclobutane, cyclopentane, and cyclohexane occurs via two different initial reaction pathways: initial C-C bond cleavage dominates on Ir(111) at high temperatures (T > 600 K), while at low temperature (T < ~400 K), initial C-H bond cleavage dominates. On the Ru(001) surface, dissociative chemisorption of cyclopentane occurs via initial C-C bond cleavage over the entire temperature range studied, whereas dissociative chemisorption of both cyclohexane and cyclooctane occurs via initial C-H bond cleavage. Comparison of the cycloalkane C-C bond activation barriers measured here with those reported previously in the literature, suggests that the difference in ring strain energies between the initial state and transition state for ring-opening C-C bond cleavage effectively lowers or raises the activation barrier for dissociative chemisorption via C-C bond cleavage depending on whether the transition state is less or more strained than the initial state. Moreover, steric arguments and metal-carbon bond strength arguments have been invoked to explain the observed trend of decreasing C-H bond activation barrier with decreasing cycloalkane ring size.

Surface Science
Room 209 - Session SS2-WeM
Stimulated Surface Processes

Moderator: R.M. Osgood, Columbia University

8:20am **SS2-WeM1 Enhanced Adatom Diffusion Using Glancing-Angle Ions***, S.A. Barnett, **K.C. Ruthe**,* Northwestern University*; P.M. DeLuca,* Kopin

We describe the effects of glancing incidence (3°) 3-4 keV Ar ion bombardment on homoepitaxial growth on vicinal GaAs (001). The average adatom lifetime on surface terraces was measured during GaAs deposition using specular ion scattering. The lifetime was observed to decrease monotonically with increasing ion current density, e.g. from 1.8 to 0.8 s for a current density increased from 0.6 to 22 mA/cm2 at a temperature of 520C (GaAs miscut = 2.5). There was no measurable sputtering, and the results suggested that the Ga surface diffusivity was increased by the ions. The ion beam also suppressed scattered ion beam current oscillations, suggesting that the growth mode had changed from two-dimensional island nucleation to step-flow due to increased adatom surface diffusivity. The RMS roughness of 0.3 micron thick GaAs epitaxial layers, measured by atomic-force microscopy, showed a corresponding decrease from 0.5 to 0.25 nm due to ion bombardment. A simple model, involving direct momentum transfer from ions to adatoms parallel to the surface, is shown to be consistent with the measured diffusion enhancements.

8:40am **SS2-WeM2 Scattering of Hyperthermal O@super +@ Ions on a SiO@sub x@ Surface***, **C.L. Quinteros**, T. Tzvetkov, D.C. Jacobs,* University of Notre Dame

Thin SiO@sub x@ films are grown on a Si(100) surface using a low current, hyperthermal (5-200eV) O@super +@ beam under UHV conditions. Scattered products are collected as a function of incident beam energy and angle, oxygen ion dose, temperature, and surface roughness. A rotatable quadrupole mass spectrometer detector resolves the energy-, mass-, and angular-distributions of the scattered species. Incident O@super +@ is efficiently neutralized, and both positively (Si@super +@, SiO@super +@) and negatively (O@super -@, O@sub 2@@super -@) charged products are formed. The product ion yields strongly increase with O@super +@ dose, as the oxide film develops. Individual features in the energy distributions of the scattered products are assigned to scattering events occurring at particular atomic sites on the surface. Product channel contributions originating from chemical reaction with incident O@super +@ and physical sputtering are differentiated.

9:00am **SS2-WeM3 Film Growth and Surface Modification by Low Energy Polyatomic Ions***, **L. Hanley**,* University of Illinois at Chicago **INVITED**

Polyatomic ions with collision energies from 5 - 200 eV can be used to deposit films and modify surfaces in a highly controllable fashion. Low energy polyatomic ions are very surface selective, interact with surfaces via a unique collision dynamics, and can be used to transfer part or all of their chemical functionality to a surface. Ionization and mass-selection permits the facile preparation of a wide range of reactive species. Collision energy can be further used to control the final film properties. Examples discussed will include the deposition of 1) cross-linked fluorocarbon films on polystyrene by 25 - 100 eV CF@sub 3@@super +@ and C@sub 3@F@sub 5@@super +@ and 2) cross-linked organosiloxane films on Al by 15 - 100 eV Si@sub 2@O(CH@sub 3@)@sub 5@@super +@. Monochromatic x-ray photoelectron spectroscopy and contact angle measurements are used to determine film chemistry. Atomic force microscopy and x-ray reflectivity are used to determine film thickness and morphology. Oxidation and other aging processes are also examined for these films following air exposure for several weeks. Molecular dynamics simulations support the experimental results and compare the surface interaction process for different ion isomers. These results show that the size and structure of the depositing ion affects film formation via different chemical structure, reactivity, sticking probabilities, and energy transfer to the surface. These results also indicate that polyatomic ions and energetic neutrals likely play an important role in film deposition and surface modification during plasma polymerization, laser ablation of polymers, and sputter deposition of polymers.

9:40am **SS2-WeM5 Super-smooth Neutron Optical Surfaces By Gas Cluster Ion Beam Processing***, L. Stelmack,* Epion Corporation and Northeastern University*; **L.P. Allen**,* Epion Corporation*; V. DiFilippo,* Epion Corporation and Tufts University*; J.A. Greer, D.B. Fenner, R. Chandonnet, J. Hautula, A. Kirkpatrick,* Epion Corporation

The neutron scattering research community has continuing need for advancing the technology required to produce improved neutron optical components, particularly in regard to increasing efficiency and reducing non-specular scattering from substrate surfaces and coating interfaces. A novel Ar gas cluster ion beam (GCIB) process was implemented in order to determine the effectiveness of the extreme GCIB surface smoothing technique as it applies to improving neutron optical component substrates and coatings. A matrix of GCIB smoothing conditions was applied on selected optical structures. Pre- and post-GCIB processed surfaces of Si, SiO2, Ni/Si, Ta, and Ni/Ta/ SiO2/Si substrates were examined with atomic force microscopy for surface roughness and overall film morphology. Silicon substrate surfaces coated with Ni were found to be consistently smooth to Ra ~1Å. In addition, results show that the Ni and Ta coated surfaces consistently achieved smoothness capable of supporting optical requirements for advanced neutron sources. The GCIB process parameters as applied to optical (SiO2, Ni/S, Al2O3), semiconductor (Si), and metallic

(Cu, Ta, Ti, Ni) surfaces are shown to provide a predictable surface smoothness (Ra typically <3Å) for applications in a variety of material related fields.

10:00am **SS2-WeM6 Molecular Dynamics Simulation of Hyperthermal Ne@super +@ Scattering From Si(100)***, J. Camden,* ***T. Tzvetkov****, C.L. Quinteros, D.C. Jacobs,* University of Notre Dame

An understanding of ion/surface energy transfer at hyperthermal energies is important to the semiconductor industry, where low-energy ion modification of surfaces is widely employed. In this paper, we present molecular dynamics simulations of Ne@super +@ scattering from Si(100) at hyperthermal energies (below 200eV). In the trajectory calculations, we use a Ne-Si potential consisting of pair-wise additive terms describing the repulsion between the projectile and all Si atoms within a slab, and a classical image charge attraction between Ne@super +@ and the bulk dielectric. The surface reconstruction is taken into account in the Si lattice simulation. A careful analysis of different trajectory contributions to the scattering signal is applied. The calculations for different surface conditions, including scattering from surface defects (steps, adatoms and vacancies), will be discussed. The calculations are compared to experimental results for Ne@super +@ scattering from Si(100) at energies ranging from 25 to 200 eV.

10:20am **SS2-WeM7 Laser Induced Reactivity of Ammonia on Silicon Surface***,* ***T. Gonthiez****, P. Brault,* GREMI (University of Orleans-CNRS), France*; T. Gibert,* GREMI (University of Orleans), France

In the field of the growth of materials like Si@sub3@N@sub4@ or AlN, photochemical processes are of a great interest. A study of the reactivity of surface induced by laser of NH@sub3@ on Si(100) is undertaken. Laser fluence and NH@sub3@ pressure are low enough just to realize the first steps of the process. Experimental studies are performed in an ultra-high vacuum chamber. Gaz is introduce by a µ-leakage valve near the surface. A UV laser beam (266/355 nm) is used to activate reactions at gaz-surface interface or to desorb the surface for analysis. Due to initial surface contamination, reactions between NH@sub3@ and Si are self-limiting. Indeed O and C contaminant atoms tie up the surface dangling bonds leading to a passivation layer.@footnote1@ By Auger Electron Spectroscopy, we find that laser irradiation on Si cleans the surface and regenerates the dangling bonds. Analysis of the desorbed species during or after the reaction provides information on reactions at surface. The flying ionic species are directly detected by a quadrupolar mass spectrometer and the neutrals are postionized by a tunable laser. The resonant or non-resonant post-ionization techniques are useful to measure Time-of-Flight distribution of flying species by adjusting the delay between desorption and probe laser. TOF distributions can be fitted by suitable velocity distribution and this allows the determination of kinetic temperature.@footnote2@ This temperature has been shown to be the surface temperature during the laser interaction. Direct measurements of flying ions show several species and mainly Si@sub2@N, Si@sub2@NH, Si@sub2@NH@sub2@ and Si@sub2@NH@sub3@. Comparison between silicon TOF signal with and without NH@sub3@ is expected to give more insight in the nitride bond formation. @FootnoteText@ @footnote 1@Ph.Avouris, F.Bozso, RJ Hamers - J.Vac.Sci.Techno.B 5(5), Sept/Oct 1987; 1387-1392 @footnote 2@ T.Gibert, B.Dubreuil, MF.Barthe, JL Debrun-J.Appl.Phys 74, 3506 (1993).

10:40am **SS2-WeM8 Interaction of Laser Impulse with YBA@sub2@CU@sub3@O@sub7@ Target and Generation of Four Element Plasma***,* ***I.Yu. Davletov****,* Urganch State University, Uzbekistan*; M.R. Bedilov, R.M. Bedilov,* Tashkent State University, Uzbekistan

In this work the results of studies of interactions of laser radiation with HTSC-targets are presented. The experiments have been performed by using a laser mass-spectrometer and HTSC-materials in the from of tablets of 1,0 cm diameter and thickness 0,5 cm. It was established experimentally that along with heating, destroying and evaporation of the target under interaction of the laser radiation at q>10@super9@ W/cm@super2@ with HTSC-targets, the four element plasma has been formed. Mass, charge, velocity, time and energy spectra of ions emitted from HTSC-target were studied in a wide range of the laser power. It was revealed that mass-spectra of HTSC-target atom ionized by the laser radiation contained not only one-charged ion peaks of basic element of the target but also signals of multiply charged atoms of the elements. The experiment showed, that ions with Z>1 are emitted from the HTSC-target by one-electron mechanisms of ionization of the four-element target by the laser radiation in the range of 10@super8@ W/cm@super2@ - 10@super11@ W/cm@super2@ (branch feature). Note that the formation of target ions Y@super+1@ , Cu@super+1@, Ba@super+1@, O@super+1@ begins at the power density of the laser radiation q@super8@ W/cm@super2@, and Cu@super+2@, Y@super+2@ at q@super2@ W/cm@super2@. The charge and energy distributions of the multicharged ions of the HTSC-target are determined by processes of triple recombination and energy exchange of non. Coulombic collisions between them. The energety spectra of the HTSC-target ions are analogous to those of a mono-element target, but the decreasing of the maximal energy of the ions of each multiplicity resulted from energetic losses due to Coulombic collections. The influence of oxygen state in the HTSC-target is established.

Surface Science
Room 210 - Session SS3-WeM
Gas/Surface Dynamics

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

8:20am **SS3-WeM1 Rainbow Scattering of Methane and Ethane Molecular Beams from a LiF(001) Surface: Dependencies on Incident Kinetic Energy and Molecular Anisotropy***,* ***T. Kondo****, T. Tomii, S. Yamamoto,* University of Tsukuba, Japan

An experiment to measure the angular distribution of the intensity of the alkane molecular beams scattered from a highly corrugated surface of LiF(001) has been carried out in high resolution, as a step toward the understanding of the fundamental characteristics of surface chemical reactions. One of the two major findings of the experiment shows that the rainbow peaks of the molecular beam was found to depend on its incident kinetic energy. For the clarification of this dependency, we calculated the angular distribution applying the Washboard model@footnote 1@ to fit the results by changing the amplitude of the sinusoidal corrugation in each case of different incident kinetic energy, instead of fixing the amplitude once fitted for the lowest incident kinetic energy. In this way it was further confirmed that the intensity of the rainbow peaks was reduced as the incident kinetic energy increases, contrary to the result predicted with the fixed amplitude. The reason for this discrepancy is thus because the combined structure of Li and F ions weakens the corrugation of the potential energy surface for the beam with increased incident kinetic energy. As the other major finding, the ethane molecular beam shows only one peak but not the rainbow peaks, in spite of negligible difference in the molecular size between the methane and the ethane molecules. On the other hand, the Ar atom which is heavier than both the above alkane molecules shows the distinct rainbow peaks. It is then presumed that the effect of neither the size nor the mass of the molecule is essential for the rainbow peaks. Therefore, the difference in behavior between the methane and the ethane molecules can be understood as a result of the large anisotropy of the ethane molecule. @FootnoteText@ @footnote 1@J. C. Tully. J. Chem. Phys. 92, 680 (1990).

8:40am **SS3-WeM2 Probing the Extrinsic Precursor State: Methane Trapping on Ethylidyne-covered Pt(111)***,* ***A. Carlsson***[1]*, R.J. Madix,* Stanford University

Under steady state conditions in catalytic reactions surfaces may be covered with stable species that affect the adsorption kinetics. It has been well documented that the adsorption probability of many molecules is facilitated by a species which can migrate across the adsorbed layer in search of a binding site. This species is referred to as an extrinsic precursor state. In order to obtain a more general understanding of this precursor state and its effect on adsorption, we have studied the kinetics of methane trapping on ethylidyne-covered Pt(111) with supersonic molecular beam techniques at surface temperatures spanning the range in which methane desorbs from the saturated monolayer and the second adsorbed layer. Because the surface is nearly saturated with ethylidyne, in order to adsorb methane must first occupy an extrinsic precursor state and then migrate to vacant sites within the ethylidyne structure to adsorb. In accordance with a precursor model for adsorption, the dependence of the adsorption probability on surface temperature gives the difference in activation energies for desorption and migration from the extrinsic precursor and the ratio of pre-exponential factors. The temperature dependence of the steady state coverage was used to determine the activation energy for conversion of the adsorbed state back into the extrinsic precursor to be 5.7 kJ/mol, compared to the desorption energy from the extrinsic precursor of about 9 kJ/mol.

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

9:00am **SS3-WeM3 Gas-Surface Dynamics of State-Selected Reagents***, A.L. Utz, L.B.F. Juurlink, R.R. Smith, C.L. DiCologero,* Tufts University **INVITED**

We use supersonic molecular beams of rovibrationally state-selected molecules to probe methane dissociation dynamics on Ni(100). These studies reveal key features of the gas-surface potential energy surface governing activated dissociative chemisorption. Excitation of the @nu@@sub 3@ antisymmetric C-H stretching vibration enhances reactivity by a factor of 1600 relative to molecules in v=0, which points to the important role of C-H stretch excitation in methane activation. The Coriolis-coupled sublevels of the triply degenerate @nu@@sub 3@ mode differ considerably in the relative motion of the four excited C-H oscillators, but they share a similar efficacy for promoting dissociation. This observation suggests that the reactivity of @nu@@sub 3@ is likely derived from its C-H stretching character in the one C-H bond that is properly oriented for dissociative chemisorption, but not from the collective motion of all four C-H oscillators in the molecule. Rotational-state-resolved studies show that @nu@@sub 3@ reactivity varies by less than a factor of two from J=0 to 3 and provide tentative support for dynamical steering effects. Studies of other vibrational states in methane provide a dramatic example of vibrational mode specificity in a gas-surface reaction. We find that the second overtone of the @nu@@sub 4@ triply degenerate bending mode, 3@nu@@sub 4@, is at least five times less reactive than @nu@@sub 3@, despite its containing 30% more internal energy. Mode specificity establishes that a vibrationally excited molecule retains enough memory of its initial state to influence its reactivity on a metal surface. The lack of reactivity in the @nu@@sub 4@ coordinate, coupled with the absolute reactivities we measure for the @nu@@sub 3@ state, suggests that combination vibrations containing both stretch and bend excitation may be the most reactive vibrational states in a thermal sample of methane.

9:40am **SS3-WeM5 Sticking Probability Measurement of Oriented NO on Al(111)***, **A.J. Komrowski,*** University of California, San Diego*; B. Berenbak,* FOM Institute AMOLF, The Netherlands*; S. Stolte,* Vrije Universiteit Amsterdam, The Netherlands*; A.W. Kleyn,* Leiden University, The Netherlands*; A.C. Kummel,* University of California, San Diego

We report that by controlling the reactant orientation immediately prior to the interaction, we have gained new insight into the dissociative and abstractive chemisorption of NO interacting with a reactive metal surface, Al(111). In a novel experiment, we have used the beam reflectivity technique to measure the sticking probability of an oriented molecular beam as a function of incident molecular orientation and translational energy. We observe a higher sticking probability when the N-end is preferentially directed towards the Al(111) surface. The difference in sticking probabilities between N-end first and O-end first interactions increases with increasing incident translational energy. In contrast, Auger spectroscopy results from non-oriented molecular beams of NO with similar energies show initial surface coverage Nitrogen/ Oxygen ratios less than unity. The results are consistent with a two step chemisorption process for the initial reaction with the clean surface. First, an electron harpoons from the metal to the N-end of the molecule. The NO@super -@ molecular ion is attracted to the surface by its image charge. Second, the molecule may absorb another electron from the surface before the intramolecular bond breaks and Oxygen is deposited onto the surface while Nitrogen is ejected into the gas phase.

10:00am **SS3-WeM6 Speed Distribution of Ethane Molecular Beam Reflected after Temporary Trapping on a LiF(001) Surface***, **T. Tomii,** T. Kondo, S. Yagyu, S. Yamamoto,* University of Tsukuba, Japan

We have measured at various scattering angles the time-of-flight of ethane molecules scattered from a LiF(001) surface of room temperature. With a high resolution cross-correlation time-of-flight technique we have successfully separated out the component of ethane molecules scattered after experiencing a temporary trapping on the sample surface. While the major peak in the time-of-flight spectrum, which consists of rotationally excited ethane molecules after single collision, can be fairly well fitted to a shifted Maxwell-Boltzmann speed distribution function, it was found that the temporarily trapped component can be reproduced by a single Maxwellian speed distribution function with a characteristic temperature lying slightly higher than the target surface temperature. This temperature tends to increase from around 300 to 600 K with the translational energy of the incident ethane beam in the range between 260 and 700 meV. The mean translational energy of the temporarily trapped molecules is almost uniform in the scattering angle, exhibiting a strong contrast to that of the directly scattered which qualitatively follows the washboard model predictions with the appropriate parameters. Despite the strong anisotropy of the ethane molecule, the directly scattered component shows a little surface rainbow features in the angular mean translational energy distribution, revealing the corrugation of the gas-surface repulsive potential. Temporarily trapped molecules are believed to be the ones which at first couple of bounces have stored their incident translational energy in the form of rotation, either cartwheel or helicopter mode, and tangential motion on a corrugated LiF(001) surface, resulting in a Maxwell-like speed distribution as a whole.

10:20am **SS3-WeM7 Trapping Dynamics of Ethane on Si(100)-(2x1) Studied by Molecular Beam Experiments and Classical Molecular Dynamics Simulations***, **C.T. Reeves**, C.B. Mullins,* University of Texas at Austin

In order to gain insight into the dynamics of trapping, or physical adsorption, we have experimentally measured the trapping probability of ethane on a clean Si(100) surface as a function of the incident translational energy and incident polar angle of the molecule at a surface temperature of 65 K using UHV molecular beam techniques. At all incident angles the trapping probability decreases as the translational energy of the incoming ethane molecule is increased from 0.05 to 1.3 eV. As the incident polar angle, with respect to the surface normal, is increased, the trapping probability decreases. This decrease in trapping probability with increasing polar angle contradicts the idea of normal energy scaling and has been seen in very few cases. Classical molecular dynamics calculations have been employed to study the cause of this unusual angular dependence. This simulation predicts trapping probabilities in good agreement with the experimental data. Analysis of the computed trajectories indicates that the initial site of impact within the unit cell, as well as the details of energy exchange during the initial impact with the surface, is important in determining the fate of an incident molecule. Although it is difficult to experimentally measure the effect of rotational energy and surface temperature on trapping, molecular dynamics simulations offer a means to study the details of these effects. Recent experimental studies by Vattuone et al. have indicated that for trapping of ethylene on Ag(001), increasing the average rotational energy from J = 2 to J = 8 can greatly decrease the trapping probability. Our simulations of ethane trapping on Si(100) have indicated that the trapping probability does decrease with increasing J, although the effect is only significant at very high values of J (>20). We have also computationally investigated the effect of surface temperature on trapping and these results will be reported.

10:40am **SS3-WeM8 Dynamics of Atom Abstraction in the Scattering of NH@sub 3@@super +@ on Deuterated Al(111)***, **M. Maazouz,** P.L. Maazouz, D.C. Jacobs,* University of Notre Dame

From a fundamental point of view, hyperthermal energy ion-surface reactions represent intriguing systems of study. The gas-surface collision energy is often high enough to drive reactions (e.g. dissociative scattering, activated chemisorption, sputtering, and atom abstraction) that are typically not observed in the thermal energy regime. Atom abstraction has been observed by many groups, yet the detailed dynamics of such hyperthermal energy reactions remain elusive. The experiment reported here examines the influence of translational energy and initial vibration quanta on the reaction of NH@sub 3@@super +@ with D/Al(111). The Al(111) surface was predosed with deuterium at 120 K, and the coverage was calibrated by TPD measurements. Resonance-enhanced mult iphoton ionization (REMPI) prepares incident ammonia ions in a specific vibration state. The ions are accelerated toward the deuterium-covered Al(111) surface at normal incidence, and the products are measured with mass-, angular-, and velocity-resolution. Specifically, the yield and kinetic energy distribution of NH@sub 3@D@super +@ is measured as a function of incident translational energy (5-80 eV) and vibration quanta (n=0-10) of NH@sub 3@@super +@.

Organic Films and Devices
Room Exhibit Hall C & D - Session OF-WeP
Poster Session

OF-WeP1 Electrical Properties of Polyvinylidene Fluoride Films Prepared by Physical Vapor Deposition Method*, G.B. Park,* Yuhan College, Korea*; M.Y. Chung, S.W. Lee, S.H. Park, D.C. Lee,* Inha University, Korea

Poly Vinylidene Fluoride thin films were prepared by using a physical vapor deposition and high electric field applying method. Thin films were studied with DSC, FT-IR, X-ray diffraction and electrical conduction measuring system. The melting point of PVDF thin film increases with increasing substrate temperature. It is identified by FT-IR that the crystalline phase of @alpha@ type PVDF is transformed to @beta@ type with increasing electric field applied during preparation. It is found that the crystallinity of PVDF thin films increases from 49.8% to 67% with increasing substrate temperature from 30 to 80. The absorption current of @alpha@ and @beta@ type PVDF increases with increasing the electric field applied under measurement and the current increment of @beta@ type is higher than that of @alpha@ type. The ion hopping distance, derived from a relation between current density and measuring temperature, increases from 51.5 Å to 153.5 Å with increasing temperature. >From above results, the conduction mechanism of PVDF thin film is estimated as ionic.

OF-WeP2 Transport Gap and Polarization Energy at Metals (Ag, Au) - Organic Molecular Semiconductor PTCDA Interfaces*, W. Gao,* *A. Kahn,* Princeton University

The complexity of localization and polarization in molecular solids demands experimental determination of more reliable energy diagrams for charge carrier injection and transport phenomena than just from optical measurements. We use inverse photoelectron spectroscopy (IPES) and ultraviolet photoelectron spectroscopy (UPS) to investigate unoccupied and occupied electronic states of PTCDA (3,4,9,10 - perylenetetracarboxylic dianhydride) deposited on Ag. The interface shows metal-to-organic charge transfer and formation of polaron states. The relative shifts of the vacuum level and molecular levels were analyzed in the context of interface dipole model, extended to account for the evolution of polarization energy. The comparison between the splitting of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) measured via UPS and IPES, and the optical gap measured via absorption measurements leads to an estimate of exciton binding energy E@sub e-h@ to be large (0.6eV), in accordance with the highly correlated nature of this molecular solid. We also use scanning tunneling microscopy (STM) and spectroscopy (STS) for PTCDA deposited on Au(111), and find results consistent with the UPS/IPES results. Work is supported by the National Science Foundation (DMR-98-09483).

OF-WeP3 Controlled Doping of Polycrystalline and Amorphous Molecular Organic Layers: Physics and Device Prospects*, X. Zhou, B. Maennig, M. Pfeiffer, J. Blochwitz,* ***T. Fritz,*** *K. Leo,* TU Dresden, Institut fuer Angewandte Photophysik, Germany

Organic dyes with a conjugated electron system are currently investigated intensively for optoelectronic applications. In contrast to classical silicon technology, the materials used for both research and devices such as organic light-emitting diodes (OLED) are usually prepared in a nominally undoped form, leading to scattering of device parameters and higher operating voltages as compared to e.g. polymeric devices. Shifting the Fermi level towards the transport states by doping can reduce ohmic losses, ease carrier injection from contacts and increase the built-in potential of Schottky- or pn-junctions. We present here the results of a comprehensive study of controlled p-type doping of various polycrystalline and amorphous organic materials by the strong organic acceptor F4-TCNQ (tetrafluoro-tetracyano-quinodimethane). It turns out that doping is more efficient for the polycrystalline materials like the phthalocyanines where doping enhances the conductivity by up to eight orders of magnitude (10@super -2@ S/cm). Nevertheless, we could show for the first time that also amorphous phthalocyanine layers (deposited onto cooled substrates) and amorphous wide-gap materials can be doped, i.e. their conductivity increases and their Seebeck coefficient decreases indicating a shift of the Fermi level towards the hole transport state. Amorphous wide gap materials like TDATA or TPD are commonly used as hole transport materials in OLEDs because they form smooth and stable layers. We show here that controlled intentional doping of these layers strongly reduces the operating voltages of OLEDs.

OF-WeP4 Cascade-Like Hybrid Organic-CdS Quantum Particle Architectures Studied by the Attenuated Low Energy Photoelectron Spectroscopy*, A. Samokhvalov,* *M. Berfeld, M. Lahav, R. Naaman,* Weizmann Institute of Science, Israel*; E. Rabani,* Tel Aviv University, Israel

Hybrid organic/inorganic matrices containing CdS quantum particles (QP) arranged in periodic layers separated by bilayers of arachidic acid/thioarachidic acid were prepared by Langmuir-Blodgett deposition on gold substrate. Within each layer, the QP are of the same average size of about 2.5 or 5nm, and the layers are arranged in cascade-like pattern. Electronic properties of the structures above were studied by the Attenuated Low Energy Photoelectron Spectroscopy in which a "pump" laser excites QP and a "probe" laser ejects photoelectrons either from gold or from the QP. This spectroscopy provides detailed information on electronic states of the QP and shows that they depend on the specific organization of the QP within the matrix, as well as on the interaction of the QP with the underlaying gold substrate.

OF-WeP5 Photoemission Investigation of Metal/CuPc Interfaces*, L. Yan,* *Y. Gao,* University of Rochester*; M.G. Mason, C.W. Tang,* Eastman Kodak Company

Metal/organic interface play an important role in organic light emitting diodes (OLED), which has been a very active field in the past few years because of their scientific and commercial significance. Copper phthalocyanine (CuPc) has been found to improve the electron injection when it is inserted as a buffer layer between the metal cathode and Tris(8-hydroxyquinoline) aluminum (Alq@sub 3@), the mostly used light emitting material in OLED. It is intriguing that CuPc, traditionally used as a hole transport material in OLED, can enhance electron injection at the cathode. To address this question, we investigated the formation and the energy level alignment at the interface between metals and CuPc, using X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) simultaneously. We found that unlike many other organic materials, CuPc has two components in C1s, whose relative intensity varies as the interface formation progresses. This property provides a unique avenue to determine the charge transfer, dipole formation and energy level alignment at the interface.

OF-WeP6 Photoemission Investigation of Energy Level Alignment and Chemistry in Al/CsF/Alq@sub 3@ Interfaces*, L. Yan, Y. Gao,* University of Rochester*;* ***M.G. Mason,*** *C.W. Tang,* Eastman Kodak Company

Organic light emitting diode (OLED) have attract great attention in recent years since the discovery of Tris(8-hydroxyquinoline) aluminum (Alq@sub 3@) based devices. One surprising discovery is that certain kind of metal/salt complex such as Al/LiF forms excellent cathode for electron injection, which is comparable in device performance to those made from low work function metal such as Li and Ca. However, Li has very small X-ray photoelectron spectroscopy (XPS) cross section, making it hard to investigate any possible interface chemistry. We have investigated the interface formation and energy alignment between Al/CsF and Alq@sub 3@, using ultraviolet photoelectron spectroscopy (UPS) and XPS simultaneously. The experiment result indicates that charge transfer to Alq@sub 3@ had occurred at the Al/CsF/Alq@sub 3@ interface, similar to Al/LiF/Alq@sub 3@ interface. While there is no reaction is detectable by photoemission between Al and LiF, there are significant changes in core level spectra between Al and CsF. On the other hand, the energy level alignment for the two systems is strikingly similar, which is consistent to the device performance studies. Based on these observation and simplified thermodynamic calculation, possible decomposition is proposed at the Al/LiF(CsF)/Alq@sub 3@ interfaces.

OF-WeP7 Scanning Tunneling Microscopy and X-ray Photoelectron Spectroscopy of Metal(Au,Ag) Deposited Alkanethiol and Alkanedithiol Layers*, T. Ohgi,* *W.-L. Deng, D. Fujita, H. Nejoh,* National Research Institute for Metals, Japan

The self-assembled monolayers (SAMs) of thiol molecules on Au(111) substrates have been extensively studied because of their easy preparation and potential for many applications. For example, in nano-electronics studies, application of the SAMs as a tunneling barrier@footnote 1@ is one of the attractive candidates since it is very easy to obtain widely spread, densely packed, well ordered and atomicaly flat surface and moreover, the thickness of the SAMs can be easily and exactly controlled by changing the length of the molecules. Electrical property of SAMs has so far been investigated by using a metal/SAMs/metal heterostructure, and their structural analysis has been mainly carried out by XPS, UPS, and ISS.@footnote 2@ In the previous study,@footnote 3@ we reported that in the case of SAMs of thiol molecules (HS(CH@sub 2@)@sub n-

1@CH@sub 3@: C@sub n@S), evaporated gold atoms penetrate through the SAMs. They cannot support metal overlayers, but monoatomic-height Au islands grow at the interface of the Au(111) substrate and SAMs. On the other hand, in the case of dithiol (HS(CH@sub 2@)@sub n@SH: C@sub n@S@sub 2@)layers, small Au particles are formed on them. In this paper, we show the result of Ag deposited octanethiol SAMs and alkanedithiol layers and discuss the difference from Au deposited ones. Ag atoms penetrate through both layers and do not form particles on them. The temporal change of Au particles/alkanedithiol/Au(111) structure were also studied. Sequential observation shows that particles penetrate through layers in weeks and form monatomic height islands under layers. @FootnoteText@ @footnote 1@ R. P. Andres, et. al., J. Vac. Sci. Technol. A14,(1996) 1178 @footnote 2@ D. R. Jung, et.al., J. Vac. Sci. Technol. A14,(1996) 1779 @footnote 3@ T. Ohgi, H. -Y. Sheng, H. Nejoh, Applied Surface Science 130-132, (1998) 919, T. Ohgi, H. -Y. Sheng, Z. -C. Dong, H. Nejoh, Surface Science 442, (1999) 277.

OF-WeP8 Wavelength- and Time-Dependent Two-Photon Photoemission Spectroscopy of the Dye Coated Silicon Surface*, A. Samokhvalov, **R. Naaman,*** Weizmann Institute of Science, Israel

Two dye molecules of similar structure, Rhodamine B and Sulforhodamine, were adsorbed on n- and p-doped silicon. The effect of photoexcitation of the adsorbed species on electronic properties of the surface of silicon was investigated applying the Wavelength- and Time-Dependent Two-Photon Photoemission Spectroscopy (WD-TPPE). It was found that the adsorption of Sulforhodamine, but not of Rhodamine B, causes a decrease in workfunction. For both dyes, the photoemission from the dye-covered silicon is reduced upon photoexcitation. The time-dependent recovery of the photoemission gets shorter for Sulforhodamine and longer for Rhodamine B, compared to the non-covered silicon. These observations are explained based on the electron donating properties of the molecules. In the case of Rhodamine B, photoexcitation of less than 10@super-4@ of the molecules on the surface was enough to affect the photoemission yield.

OF-WeP9 Structure and Molecular Recognition Ability of Thiolated-cyclodextrin Monolayer on Au(111) Surface*, **S. Yasuda,*** University of Tsukuba, Japan*; I. Suzuki,* Tohoku University, Japan*; K. Yase,* National Institute of Materials and Chemical Research, Japan*; J. Sumaoka, M. Komiyama,* University of Tokyo, Japan*; H. Shigekawa,* University of Tsukuba, Japan

Chemisorbed monolayers of thiols and disulfides on gold, so-called self-assembled monolayers (SAMs), have been studied to develop the novel interfacial systems. Since they easily form stable and highly packed monolayers, they are considered to have high potential to fabricate the micro-morphology of materials. From the point of view to develop a molecular recognition sensor using this technique, we analyzed structure and molecular recognition ability of the LP-@beta@-CyD (@beta@-cyclodextrin modified with lipoamide residue) monolayers formed on Au(111) surfaces, by using scanning tunneling microscopy (STM) and cyclic voltammetry (CV) measurement. The detailed adsorption process was completely different from that predicted from the macroscopic analyses. According to the macroscopic analysis, the growth process was explained by the Elovich model, which is based on the repulsive interaction between adsorbed molecules. However, many island structures were formed with the immersion time, indicating that the interaction between LP-@beta@-CyD molecules is attractive. Although the structure of the LP-@beta@-CyD molecules in the adsorbed layer was disorder, formation of the monolayer structure was clearly shown by STM. In order to examine the molecular recognition ability of the LP-@beta@-CyD/Au(111), we performed CV measurement using two electroactive makers; ferrocenecarboxylic acid (FCA) and hexacyanoferrate (HCF). FCA molecules can be included into @beta@-CyD cavity, but HCF molecules can not be. Therefore, if the monolayer structure is densely formed with the CyD cavity being perpendicular to the surface, the oxidation-reduction current is expected to be observed only for the case of the FCA molecules, which in fact was clearly shown by our experiment. These results indicate that the LP-@beta@-CyD/Au(111) structure has high potential as a novel molecular recognition sensor with its selective permeability. (http://dora.ims.tsukuba.ac.jp Appl. Phys. Lett., 76 (2000).)

OF-WeP10 Growth Modes of Vacuum Evaporated Pentacene on SiO2, MoS2 and Au Substrates*, **S. Zorba,** Q.T. Toan, N.J. Watkins, Y. Gao,* University of Rochester

Pentacene is one of the most widely used active material in organic thin-film transistors because of its remarkably high mobility. We studied the growth modes of vacuum evaporated pentacene on SiO2, MoS2 and Au substrates using Atomic Force Microscopy. Pentacene films were grown side by side on SiO2 and MoS2 substrates and separately on Au substrate by vacuum evaporation at room temperature with a deposition rate of 0.6 @Ao@/s. Pentacene films grow on SiO2 substrate in a layer by layer manner with full coverage at average thickness of 20 @Ao@ and have the highest degree of molecular ordering with large dendritic grains among the three materials. Films grown on MoS2 substrate reveal two different growth modes, ice-flake like growth and granular growth, both of which seem to compete with each other. On the other hand, films deposited on Au substrate show granular structure.

OF-WeP11 Analysis of the Surface Morphology of the Initial Growth Layers of p-quaterphenyl on NaCl (001)*, **E.J. Kintzel, Jr.**[1,2], E.A. Akhadov, T.W. Trelenberg, J.G. Skofronick, S.A. Safron, D.H. Van Winkle,* Florida State University*; F. Flaherty,* Valdosta State University*; D.-M. Smilgies,* European Synchrotron Radiation Facility

We have investigated the structural properties of the initial growth layers of p-quaterphenyl (p-4P) vapor deposited on NaCl (001) using Atomic Force Microscopy (AFM), Helium Atom Scattering (HAS), and X-Ray Grazing Incidence Diffraction (GID). The series of AFM studies provides evidence of needle-like accumulations of p-4P nucleating around surface defects, a striped-phase region with a lateral spacing of approximately 25 nm, and a region which displays a transition from lying to standing orientation of the molecules. HAS investigations at ~50K for films grown at 200K reveal many diffraction peaks which do not appear at the higher temperature. The helium diffraction pattern suggests the formation of randomly oriented micro-crystallites. Our GID studies indicate self-assembly of oriented crystallites in thin films. In thicker samples the diffraction becomes isotropic, like a powder pattern, indicating a random distribution of crystallite orientations.

OF-WeP12 Preparation of Stable Organic Layers Attached to Metals via a Double Bond*, **H. Oudghiri-Hassani**, M. Siaj, E.M. Zahidi, P.H. McBreen,* Laval University, Canada

New methods for preparing inorganic-organic interfaces lead to new types of functionalized surfaces. We describe a method to attach organic layers to a conducting solid via the formation of a carbon-metal double bond. The substrate is bulk molybdenum carbide, a material displaying metallic- like conductivity and ceramic-like hardness, as well as excellent catalytic activity. Early transition metal carbides are also of interest because they may form natural electrical contacts to carbon nanotubes in molecular electronics applications. The organic layers were formed by dissociatively chemisorbing carbonyl compounds on the carbide surface. By suitable preparation of the surface, and careful coverage control, layers stable to 1000 K could be prepared. The stability, structure and reactivity of these unprecedently stable layers were evaluated using several surface spectroscopies.

Semiconductors
Room Exhibit Hall C & D - Session SC+EL+SS-WeP
Poster Session

SC+EL+SS-WeP1 Selectivity in Attachment of a Model pi-conjugated Organic Molecule to a Group IV Semiconductor Surface: Styrene on Si(001)*, **M.P. Schwartz,*** University of Wisconsin, Madison*; M.D. Ellison,* Wittenberg University*; S.K. Coulter, R.J. Hamers,* University of Wisconsin, Madison

The bonding of styrene to the Si(001) surface has been investigated as a model system for understanding selectivity in the attachment of conjugated pi-electron systems to semiconductor surfaces. Scanning tunneling microscopy images show one primary bonding configuration, slightly off-center from the middle of a dimer row. Infrared spectra using isotopically-labeled styrene establish that attachment occurs in a highly selective way, bonding through the external vinyl group and leaving the aromatic ring almost completely unperturbed. The implications for the high degree of selectivity in understanding attachment of other conjugated pi-electron systems are discussed.

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

[2] **NSTD Student Award Finalist**

SC+EL+SS-WeP2 Ferrocene and Decamethylferrocene Adsorption and Decomposition on Ag(100) and Si(111)*, **C.M. Woodbridge**, D.L. Pugmire,* University of Nebraska, Lincoln*; N.M. Boag,* University of Salford*; M.A. Langell,* University of Nebraska, Lincoln

Although metallocenes show potential as Chemical Vapor Deposition (CVD) source molecules, there is comparatively little known about their interactions with oriented substrates. We have investigated the adsorption and decomposition of ferrocene (FeCp@sub 2@) and decamethylferrocene (FeCp@sub 2@*) on Ag(100) and Si(111) using High Resolution Electron Energy Loss Spectroscopy (HREELS), Temperature Programmed Desorption (TPD), and X-ray Photoelectron Spectroscopy (XPS). For weakly-interacting systems such as those which occur with Ag(100), both FeCp@sub 2@ and FeCp@sub 2@* are adsorbed molecularly at 130 K. Monolayers of both FeCp@sub 2@ and FeCp@sub 2@* are oriented such that their molecular axes are perpendicular to the plane of the Ag(100) substrate; monolayer desorption occurs at approximately 250 K for both metallocenes. While FeCp@sub 2@ desorption is clean, FeCp@sub 2@* shows significant amounts of metallocene dissociation competing with molecular desorption. The Si(111)/metallocene systems also show molecular adsorption at 130 K but are more reactive to thermal decomposition upon heating and decompose primarily through hydrogenation and ligand-metal dissociation mechanisms. Specific information about the orientation of the adsorbed species and decomposition intermediates will be discussed.

SC+EL+SS-WeP3 Lowering of Processing Temperature due to a High Pressure Deuterium Anneal for Improved CMOS Hot Carrier Reliability*, **J. Lee**, K. Cheng, K. Hess, J.W. Lyding,* University of Illinois, Urbana*; Y.K. Kim, Y.W. Kim, K.P. Suh,* Samsung Electronics Co., Ltd.

The deuterium (D) isotope effect has been found to be very effective in reducing hot carrier induced degradation in CMOS transistors of numerous technologies. The magnitude of lifetime improvement (10x to 100x) varies from one technology to the other, but it directly correlates with D incorporation at the gate SiO@sub 2@/Si interface. Secondary ion mass spectrometry (SIMS) depth profiling has been used to make this determination. We have recently implemented high pressure D annealing to enhance its incorporation at the interface. By increasing the D pressure, the concentration at the interface can be increased for a fixed annealing temperature. Consequently, lower temperatures and shorter anneal times can achieve equivalent transistor reliability. This promises to be a technologically significant result for future CMOS production which requires a much lower thermal budget process due to the introduction of advanced materials (e.g. low k dielectrics) and increased number of metal layers. This high pressure annealing technique has been applied to one of the most recent CMOS technologies from Samsung Electronics. For these short-channel (0.18 µm) and low operating voltage (1.5V) devices, the isotope effect is substantially enhanced (700x). Rather than being scaled away, deuterium reduction of hot electron damage appears more relevant in future generations of CMOS integrated circuits. In the current work, the annealing temperature has been lowered from 450@degree@C to 350@degree@C. Although the lifetime improvement is not as great, we do observe a significant lifetime improvement (300x) just from changes in pressure. More experiments are in progress to maximize the D incorporation at the low annealing temperature. In addition, SIMS depth profiles are being determined for devices that were sintered at different annealing conditions.

SC+EL+SS-WeP4 Investigation of the Penetration of Atomic Hydrogen from the Gas Phase into a SiO@sub 2@/GaAs System*, **V.A. Kagadei**,* Research Institute of Semiconductor Devices, Russia*; E.V. Nefedtsev,* Tomsk University of Control Systems and Radioelectronics, Russia*; D.I. Proskurovsky,* Institute of High Current Electronics, Russia

Introduction of hydrogen into near-surface layers of semiconductor materials (hydrogenation) substantially varies their properties. In some cases hydrogenation improves the electrophysical parameters of the material and allows one to create devices with improved characteristics, while in other cases the penetration of hydrogen into a solid accompanies a technological process and causes unwanted changes in the parameters of the material. Therefore, it appears urgent to investigate the penetration of hydrogen into a semiconductor material, and a better understanding of this process will make it possible to optimize the technology of hydrogenation. The hydrogenation of GaAs samples coated with thin (5 nm) SiO@sub 2@ film was investigated. Samples were treated in a flow consisting of a mixture of atomic and molecular hydrogen produced by a source whose operation is based on a reflected arc discharge with a hollow cathode and a self-heating element. The hydrogenation time was 5 - 30 min, the hydrogenation temperature was 150 - 300 C, and the hydrogen pressure was varied from 10@super -1@ - 10@super -3@ Pa. It has been established that an increase in discharge current results in an increase in the concentration of atomic hydrogen in the gas phase, N, and in a decrease in the number of atoms penetrating into samples, and this is in contradiction with the usual notions about the penetration of hydrogen atoms into a solid. The data obtained suggest that the amount of hydrogen penetrating into samples is more dependent on the probability of the penetration of hydrogen atoms into a solid body, F, rather than on N. It has been proposed that F decreases substantially with decreasing the energy of the hydrogen atoms arriving at the solid surface. The energy of the atoms emerging from the reflected-arc-discharge-based source is estimated to vary between 0.1 and 10 eV. It is determined by the operating voltage of the discharge and decreases with increasing discharge current. Another possible cause of the observed phenomena is the formation of a near-surface diffusion barrier constituted by immobile hydrogen molecules, which occupy interstitials and retard the diffusion of atoms. The contribution of each of the proposed mechanism is discussed.

SC+EL+SS-WeP5 a-SiC:H Thin Films Fabricated by the High Rate Deposition Method*, **B.G. Budaguan**, A.A. Sherchenkov,* Moscow Institute of Electronic Technology, Russia*; A.A. Berdnikov, V.D. Chernomordic,* Institute of Microelectronics of Russian Academy of Science*; A.A. Aivazov,* UniSil Corp.

The a-SiC:H alloys are considered to be a perspective wide band gap material for different optoelectronic utilization. For the commercial application it is necessary to increase the deposition rate. However the increase of the growth rate results in the increase of structural inhomogeneity and in the deterioration of electronic properties of amorphous layers. Recently we have shown that deposition rate of a-Si:H films with high electronic properties can be increased with using of low frequency (55 kHz) glow discharge. In this work we investigated the growth mechanism and microstructure of a-SiC:H thin films fabricated for the first time by this method. The a-SiC:H films were deposited at different methane content from 0 to 100%, substrate temperatures T@sub s@ from 160 to 320 °C, and different discharge regimes: continuous wave and square wave modulated (SQWM). It was shown that the increase of the deposition rate of a-SiC:H films (5.3-11.1 Å/s depending on the methane content in gas mixture) in comparison with the standard deposition technology (3 Å/s for 13.56 MHz PECVD) is caused by the close position of a-SiC:H precursors formation to the growth surface. The joint analysis with using of infrared/optical spectroscopy and atomic force microscopy measurements showed that a-SiC:H films has the island type microstructure where the clustering of C atoms occurs at the island surfaces in the form of C-H@sub n@ bonds. The increase of C-H@sub n@ configurations on islands surfaces at high C content facilitate the relaxation of rigid a-SiC:H network through formation of flexible sp@super 2@-sites. The incorporation of Si-C bonds in the interior of islands determines the optical bandgap while the clustering of CH@sub n@ and SiH at the islands surface leads to the formation of graphite-like microstructure. It was shown that the suppression of formation of graphite-like microstructure at low T@sub s@ and in SQWM plasma allows to fabricate device quality alloys.

SC+EL+SS-WeP6 Mechanism for and Site of the Dissociative Chemisorption of XeF@sub 2@ on Si(100)2x1 Below 1 ML of Fluorine Coverage*, **J.R. Holt**, R.C. Hefty, M.R. Tate, S.T. Ceyer,* Massachusetts Institute of Technology

Upon exposure of a clean Si(100)2x1 reconstructed surface to a beam of xenon difluoride incident with an average kinetic energy of 0.9 kcal/mol, the XeF@sub 2@ dissociatively chemisorbs by atom abstraction solely on the Si dangling bonds up to a fluorine coverage of one monolayer (ML) before it begins to react with the Si-Si lattice bonds. This conclusion is based on the observations of scattered XeF and the preservation of the 2x1 dimer row reconstruction at 1 ML fluorine coverage. The scattered XeF is detected by a line-of-sight and differentially pumped mass spectrometer while the order of the surface is monitored by He diffraction. A clean Si(100)2x1 surface is characterized by three primary features in a He diffraction spectrum: a specular feature due to the smoothness and general order of the surface, a half-order feature due to diffraction perpendicular to the dimer rows, and a first order feature due to diffraction parallel to the dimer rows. The presence of the half-order feature at a fluorine coverage of 1 ML provides evidence that even the Si-Si sigma dimer bonds are undisturbed, preserving the original dimer rows. The reaction exothermicity of approximately 230 kcal/mol does not destroy the surface order. Molecular fluorine has previously been observed to react with a clean Si(100)2x1 surface in a similar manner by atom abstraction, saturating the Si dangling bonds at a coverage of 1 ML. The 2x1 periodicity is maintained. However, after saturation of the dangling bonds, F@sub 2@ ceases reacting with the surface while XeF@sub 2@ continues to deposit fluorine on the surface by its reaction with the Si-Si sigma dimer bonds and the Si-Si lattice bonds. The surface order is destroyed as a result of the continued fluorine deposition and ultimately etching occurs by the formation of volatile SiF@sub 4@.

SC+EL+SS-WeP7 STM Investigations of the Initial Ad- and Desorption Sites of Molecular Hydrogen on Si(001), ***M. Dürr,*** Philipps University Marburg, Germany; *A. Biedermann, Z. Hu,* Columbia University; *U. Höfer,* Philipps University Marburg, Germany; *T.F. Heinz,* Columbia University

Whereas the extremely small sticking coefficients for dissociative adsorption of H@sub 2@ on Si surfaces indicate a high, the almost thermal energy distribution of the desorbing H@sub 2@ molecules points to a low barrier in the reaction channel. Recent molecular beam experiments have shown that this apparent contradiction is in full accordance with the principle of detailed balance and can be understood in terms of phonon-assisted sticking.@footnote 1@ To shed light on the underlying microscopic mechanisms, we have adsorbed H@sub 2@ on Si(001) at temperatures below the onset of H diffusion and investigated the site distributions with scanning tunnelling micrcoscopy (STM). The STM images show configurations of 4 adsorbed H atoms indicating a two-step process with an inter-dimer rather than the commonly assumed intra-dimer adsorption path as the relevant initial step. In the inter-dimer path, H@sub 2@ interacts with two dangling-bonds on adjacent Si dimers and forms a transition state with relatively large lattice distortion. Single-shot laser-induced thermal desorption experiments from nearly perfect hydrogen monolayers reveal distributions of unsaturated dangling bonds which indicate that the reverse path is also active in desorption. The influence of coverage, minority reaction channels as well as the consequences of the results on the reaction kinetics will be discussed. @FootnoteText@ @footnote 1@ M. Dürr, M. B. Raschke, and U. Höfer, J. Chem. Phys. 111, 10411 (1999).

SC+EL+SS-WeP8 Photoemission Study on Initial Oxidation of Si(001) Surfaces with Supersonic O@sub 2@ Molecular Beams, ***Y. Teraoka,*** Japan Atomic Energy Research Institute, Japan; *A. Yoshigoe,* Japan Atomic Energy Research Institute

We made a new surface reaction analysis apparatus at a soft x-ray beamline (BL23SU) in the SPring-8 (Super Photon ring-8GeV) to study incident energy effects for reactant chemisorption on semiconductor surfaces. As the first step, initial oxidation of Si(001) with O@sub 2@ has been investigated because that is not only interesting for surface reaction analysis but also important as electronic device development. The maximum incident energy was 3 eV in calculation. The clean Si(001) surfaces were irradiated by the supersonic O@sub 2@ molecular beams with various incident energy to achieve saturated adsorption. The oxygen amount on the surface was evaluated by measuring O-1s photoemission intensity. The intensity depended on the incident energy and two thresholds of 1.0 eV and 2.6 eV were found. These values are very resemble to the predicted values of 0.8 eV and 2.4 eV from the first-principles calculation, showing potential energy barriers for dimer backbond oxidation and oxygen insertion between the second and the third layer. Si-2p photoemission spectra were obtained at room temperature and 873 K by using high resolution soft x-rays from the beamline. In the case of room temperature, the maximum silicon oxidation number increased with increasing the incident energy from Si@super 2+@ to Si@super 4+@. Whereas a peak corresponding to SiO@sub 2@ was minor even in the case of 2.9 eV at room temperature, the peak was apparent in 873 K cases. Thermal energy may drive oxygen migration to form the SiO@sub 2@ structure. Even at such high temperature, incident energy affected in sub-oxide peak composition. The sub-oxide peak for Si@super 3+@ was increased with increasing the incident energy and was dominant in the case of 2.9 eV whereas the peak for Si@super 2+@ was primary in the case of 0.6 eV. The variation may be resultant from the Si@super 3+@ increase due to oxidation of dimer and sub-surface silicon atoms depending on the incident energy.

SC+EL+SS-WeP9 The Effect of Time and Moisture on the Adhesion Bond between Silica Particle and Silicon Oxide Substrate, ***J.W. Feng,*** *A.A. Busnaina,* Clarkson University

Adhesion of silica particles to silicon wafers is a problem that affects semiconductor manufacturing processes. The particle adhesion forces are greatly affected by the environment such as humidity, temperature and adhesion induced stress between the particle and the wafer following the particle deposition. The adhesion forces considered in the process include van der Waals, capillary force, double layer force and hydrogen bonding. In this study, silica particles are deposited onto wet and dry thermal oxide silicon wafers, then the samples are aged in different relative humidity environments. Results show that the largest increase in contact area between silica particles and thermal oxide wafers occur when the particle is first deposited on wet surface then aged in relative humidity above 55%. Higher humidity, results in higher adhesion force and lower removal efficiency. Results also indicate that adhesion force increases by more than two order of magnitude after the aging process. This suggests that hydrogen and covalent bonds are responsible for the increase in the adhesion force especially in humid environments.

SC+EL+SS-WeP10 Influence of Growth Direction on Order-Disorder Transition in (GaAs)@sub (1-x)@(Ge)@sub 2x@ Semiconductors, *A.G. Rodriguez,* ***H. Navarro-Contreras,*** *M.A. Vidal,* University, Mexico

We provide direct evidence of the dependence on the growth direction of the critical concentration of IV atoms at the order-disorder transition in ternary metastable (III-V)-IV, zincblende-diamond semiconductor alloys. The excellent agreement between the experimental and model predicted critical concentrations is evidence that the atomic ordering in these alloys is ruled almost entirely by substrate geometry. We report the observation of the critical concentration dependence on substrate orientation in (GaAs)@sub (1-x)@(Ge@sub 2@)@sub x@ metastable alloys, epitaxially grown on (001), (111), (112) and (113) GaAs. A different long-range order parameter behavior with Ge concentration is obtained for each growth direction, 0.36, 0.96, 0.59, and 0.50 ± 0.03, respectively, numbers that compare well with results of a Montecarlo simulation of the growth, 0.33, 1.0, 0.64 and 0.54, respectively.

SC+EL+SS-WeP11 Surface Electronic Structure of p-type GaN(000-1), ***P. Ryan,*** *Y.C. Chao, K.E. Smith,* Boston University

Our investigation sought to describe the surface electronic characteristics of MBE grown (Mg-doped) wurtzite p-GaN (0001'). Four surface bands were mapped within the surface Brillouin zone. The peaks have been removed by atomic hydrogen exposure and three of the peaks show pz orbital configuration, the fourth an s orbital. The most interesting peak is a highly dispersing surface state which sweeps from the bulk valence band into the forbidden bulk band gap, approaches the Fermi level then returns to the bulk valence band. We compare this state to previously predicted mid-gap surface states.

SC+EL+SS-WeP12 Ultrafast Dephasing of Coherent Phonons by Lattice Defects in n-GaAs, ***M. Kitajima,*** *M. Hase, K. Ishioka,* National Research Institute for Metals, Japan; *K. Ushida,* RIKEN, Japan

GaAs is a key material for ultrafast switching and THz radiation because the carrier lifetime of low-temperature grown (defective) GaAs is ultrafast (sub-picosecond). In doped GaAs, the plasmon and the LO phonon form coupled modes through Coulomb interactions, and the frequencies of the LO phonon-plasmon coupled (LOPC) modes depend on the carrier density. We report the effect of active lattice defects on dephasing of coherent LOPC modes in He-ion irradiated n-GaAs by using a femtosecond pump-probe technique. The time-domain oscillations of the coherent LOPC modes in He@super +@ irradiated n-GaAs have been precisely measured for the different ion doses. The samples used were n-type GaAs with carrier density of ndop= 1.4x10@super 18@cm@super -3@. In order to examine the effect of point defects, 5 keV He@super +@ were irradiated to n-GaAs samples at doses of 9.4x10@super 12@ and 3.0x10@super 14@ He@super +@/cm@super 2@ in a UHV chamber with base pressure of 3x10@super -9@ Torr. The light source was a mode-locked Ti:sapphire laser with a pulse width of 25 fs. The anisotropic reflectivity change revealed coherent oscillations which shows beating pattern for the as-grown n-GaAs. This beating pattern in the time-domain data is due to an existence of the strong LO mode and the L@sub -@ mode. The mode beating changed clearly as increasing the ion dose, and the pattern of the Lmode disappeared at doses higher than 3.0x10@super 13@ He@super +@/cm@super 2@. The results suggest that defect-induced carrier trapping dominate annihilation of the coherent coupled modes. In addition we will also discuss on an anormalous behavior of dephasing of the coherent LO-phonon.

SC+EL+SS-WeP13 High Density Plasma Via Hole Etching In SiC*, H. Cho,* Miryang National University, South Korea*; K.P. Lee, P. Leerungnawarat,* University of Florida*; S.N.G. Chu,* Lucent Technologies, Bell Laboratories*; F. Ren,* University of Florida*; C.-M. Zetterling,* Royal Institute of Technology (KTH), Sweden*; S.J. Pearton,* University of Florida

Through-wafer vias ~100µm deep were formed in 6H-SiC substrates by Inductively Coupled Plasma etching with SF@sub 6@/O@sub 2@ at rates up to 0.8 µm·min@super -1@ and employing Al masks. Selectivies of @>@40 in SiC over Al were achieved. Electrical (C-V, I-V) and chemical (AES) analysis techniques showed that the etching produced only minor changes in reverse breakdown voltage, Schottky barrier height and near-surface stoichiometry of the SiC and had high selectivity over common front side metallization. The SiC etch rate and etch yield were measured as a function of plasma composition along with the selectivity over Al. This process is attractive for power SiC transistors intended for high current, high temperature applications.

SC+EL+SS-WeP14 RHEED Study of Ion-beam Induced Carbonization for 3C-SiC Heteroepitaxial Growth on Si(100)*, **N. Tsubouchi**, A. Chayahara, A. Kinomura, Y. Horino,* Osaka National Research Institute, Japan

3C-SiC heteroepitaxial film formation on a Si substrate is a very important when we consider compatibility with the silicon fabrication technology. So far, it has been reported that a carbonization process as buffer layer formation using various film-growth methods is effective for the heteroepitaxial film growth of 3C-SiC on Si while the lattice mismatch between 3C-SiC and Si is as large as 20 %. These methods reported for this reaction process, however, require high-temperatures ranging 700--1000°C, causing serious problems of redistribution of dopants and crystal defects such as dislocations and stacking faults especially at the heterointerface. In addition, carbonization reaction between provided gases including carbon atoms and Si substrates also results in promotion of defect formation in the Si-SiC interface. For solving these problems, a newly process, that is, ion-beam induced carbonization process of Si(100) with mass-separated energetic carbon ion species (e.g., @super 12@C@super -@, @super 12@C@sub 2@@super -@, @super 12@C@super +@ ions) was tried and investigated by RHEED measurements. The kinetic energies of ions and substrate temperatures were in the range 20-1200 eV and 400-700 °C, respectively. Such energetic species have possibility to lower a growth temperature inducing a decrease in defects and dislocations at the SiC/Si interface, in comparison with conventional methods. We report on the SiC growth condition during the carbonization process, i.e., ion-beam energy and substrate temperature dependence together with structural information.

SC+EL+SS-WeP15 Auger Depth Profile Analysis: Process Window Definition of 0.2 micron Aluminum RIE Interconnections*, **C. Dziobkowski**, L. Clevenger,* IBM Corporation*; M. Honda,* Toshiba, Japan*; R. Ramachandran,* Infineon Technologies

For fabrication of devices with dimensions of less than 0.2 microns, processing requirements become more demanding. New design requirements for the 256 Mbit DRAM also have higher aspect ratios. Process temperature control becomes very important because of the effects of temperature on the RIE etch, theta-Al2Cu precipitate distribution and texture. Eventually, even the electrical properties are affected resulting in device shorts and open circuits. This paper gives a description of the methodology developed to provide Auger depth profile analysis to characterize the copper distribution in the AlCu metallurgy. Copper segregation at the Al/Ti interface also affects the RIE process etching window. The information obtained from the Auger depth profiles can be used to define a window for VLSI devices with these small dimensions.

SC+EL+SS-WeP16 Epitaxial Growth of Cubic SiC Thin Films on Silicon Using New Single Molecular Precursors by MOCVD*, **J.-H. Boo**, S.-B. Lee,* Sungkyunkwan University, Korea*; K.-W. Lee, Yunsoo Kim, K.-S. Yu, S.H. Yeon, I.N. Jung,* Korea Research Institute of Chemical Technology, Korea

Heteroepitaxial cubic SiC thin films have been deposited on silicon substrates at temperatures in the range of 750 - 1000 ° C using newly developed single molecular precursors by MOCVD method. Single-crystalline, crack-free stoichiometric cubic SiC films were successfully grown on both Si(001) and Si(111) substrates without surface carbonization at as low as temperature of 920 ° C with 1,3-disilabutane (DSB), H@sub 3@Si-CH@sub 2@-SiH@sub 2@-CH@sub 3@, as a liquid single source precursor which contains silicon and carbon in 1:1 ratio. Cubic SiC thin films highly oriented in the [001] direction were also obtained on Si(001) using either a liquid mixture of 1,3,5-trisilapentane (TSP), H@sub 3@Si-CH@sub 2@-SiH@sub 2@-CH@sub 2@-SiH@sub 3@, and 2,4,6-trisilaheptane (TSH) at 980 ° C or 2,6-dimethyl-2,4,6-trisilaheptane (DMTSH), H@sub 3@C-SiH(CH@sub 3@)-CH@sub 2@-SiH@sub 2@-CH@sub 2@-SiH(CH@sub 3@)-CH@sub 3@ at 950 ° C without carrier gas. These growth temperatures were much lower than conventional CVD growth temperatures, and this is the first report of cubic SiC film growth using the single molecular precursors of trisilaalkanes.

SC+EL+SS-WeP17 Optical and Contact Properties of Indium Tin Oxide on p-GaN*, **D.W. Kim**, Y.J. Sung, J.W. Bae, G.Y. Yeom,* Sungkyunkwan University, Korea*; H.S. Kim,* University of Strathclyde, Scotland

Because Gallium nitride(GaN) is an attractive material which has an wide direct band gap, GaN-based optoeletronic devices such as light emitting diodes(LEDs) and laser diodes(LDs) in blue and ultraviolet wavelength regions have been studied intensively and fabricated successfully. However, the contacts to GaN-based LEDs are currently made by depositing metal layers on the top of GaN-based LEDs, therefore, significant optical loss is inevitable. In this study, we applied multilayers containing transparent conducting oxide such as indium tin oxide(ITO) to p-GaN and the effect of the optically more transparent contacts to p-GaN on the electrical and optical properties were investigated. As substrates, Mg-doped p-GaN layers were used. ITO thin films were deposited on p-GaN at room temperature using an oxygen radical assisted electron beam evaporator system. To improve the contact properties to p-GaN, various ITO/very thin metal multi-layer contact systems were also attempted and their electrical, structural, and optical properties were investigated. A semiconductor parameter analyzer and a four point probe were used to measure contact and electrical properties of ITO and mutilayer films on p-GaN. X-ray diffractometry(XRD) and Auger electron spectroscopy(AES) were used to investigate the structural properties of the contact during the annealing process, and an optical spectrophotometer was used to investigate the optical properties. The deposited ITO thin films showed the optical transmittance above 80 % at 420 nm(blue) with the sheet resistance of 40 ohm/sq. With ITO contact to p-GaN alone, Schottky contacts were generally obtained. However, depending on the applied very thin metal inter-layer and followed annealing conditions, different electrical and contact properties, which could be applicable to GaN devices, were obtained.

SC+EL+SS-WeP18 Visible Emission from Electroluminescent Devices using an Amorphous AlN:Cu, Mn, and Cr Thin Film Phosphor*, **M.L. Caldwell**, V.I. Dimitrova, M.E. Kordesch, H.H. Richardson, P.G. Van Patten,* Ohio University

Electroluminescence (EL) studies of AlN:Cu, Mn, and Cr alternating-current thin-film electroluminescent (ACTFEL) devices were performed at 300 K. Thin films of Cu, Mn, and Cr doped AlN, ~ 200 nm thick, were grown on p-doped silicon (111) substrates using RF magnetron sputtering in a nitrogen atmosphere. A transparent layer utilizing indium tin oxide was employed as the top layer contact. A strong bluish-green emission from the AlN:Cu films was observed under reverse bias due to electron impact excitation of the Cu atoms. The emission spectrum consisted of one broad peak in the visible region of 475 nm. a strong red emission from the AlN:Mn films was observed also under reverse bias due to electron impact excitation of the Mn atoms. There were two sharp emission peaks in the visible region at 680 nm and 700 nm. Studies of incorporationg the Cr@super +3@ ion will be performed to try to overcome the charge compensation problem. Temperature-dependent cathodoluminscence (CL) and photoluminscence (PL) studies will be performed between 30 - 450 K to determine the relationship of them to the EL results and show the optimum conditions for device performance.

SC+EL+SS-WeP19 Organic Contamination Removal on Silicon Substrate by Low Temperature Remote Plasma*, **H. Kang**, H. Soh, H. Seo, Y.C. Kim,* Hanyang University, Korea*; H. Jeon,* Hanyang University, Korea, South Korea

Organic contamination on silicon substrate deteriorates the film adhesion and forms deleterious decomposition during heating process. Organic impurities absorbed on the Si substrate surface generally desorbes in the form of volatile compounds by radio frequency (RF) remote oxygen and hydrogen plasma at relatively low temperatures. In this study, organic contamination removal and Si substrate surface microroughness by RF remote oxygen and hydrogen plasma will be described. The remote plasma system and analysis systems were connected by ultrahigh vacuum transfer system to avoid recontamination such as carbon absorption in the air. Organic impurity were intentionally contaminated and removed by hydrogen and oxygen remote plasma system. Surface contamination concentration and bonding state changes were analyzed by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). Surface morphology and microroughness were observed by scanning tunneling microscope (STM) and atomic force microscope (AFM). After remote hydrogen and oxygen plasma cleaning, carbon impurity was significantly reduced below detection limit of AES and the Si-C peaks of XPS were not observed. The surface microroughness generally degraded with increasing plasma power and exposure time.

SC+EL+SS-WeP20 Studies of the Surface Morphology, Chemical and Structural Changes of Ion Bombarded Silicon Carbide*, **P. McCarty,*** University of Alabama, Huntsville*; C.I. Muntele, I. Muntele,* Alabama A&M University*; M.A. George,* University of Alabama, Huntsville*; D. Ila,* Alabama A&M University*; D.B. Poker, D.K. Hensley,* Oak Ridge National Laboratory

Silicon carbide is gaining increasing interest for high temperature/harsh environment applications including miniature integrated sensors. In the past few years, efforts have been made toward controlling the defects and impurification that occur during various growth and fabrication processes. This work is intended to analyze the surface damage that occurs during ion implantation of silicon carbide, and the evolution of these defects. In order to correlate the effects that surface damage has on the sensing properties of ion implantation based silicon carbide gas sensors we have characterized these sensors under various conditions. We present the results of our investigation of the morphological, electrical and spectroscopic characteristics of ion implanted silicon-face 6H-SiC. In this work we have used He, O, Pd, and Au at energies between 100 keV to 8 MeV at fluences between 1 x 1015/Cm2 to 3 x 1017/Cm2. The ion bombardments were performed at both room temperature (300oK) and at elevated temperature (773oK). Atomic force microscopy, surface potential measurements and electric field microscopy was performed before and after ion implantation, as well as after the post-implantation high temperature annealing. This study is correlated with results obtained using micro-Raman, FTIR and Rutherford Backscattering Spectrometry. @FootnoteText@ We would like to thank Dr. David Larkin, NASA Glenn Research Center. Research sponsored by the NASA Grant No. NG3-2302, and partially by the Center for Irradiation of Materials, Alabama A&M University and the Division of Materials Sciences, U.S. Dept. of Energy, at the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy under contract DE-AC05-00OR22725

SC+EL+SS-WeP21 Gallium Oxide Deposition and Radical Oxidation on GaAs(001)-(2x4) Investigated with STM*, **S.I. Yi,** P. Kruse, M. Hale, A.C. Kummel,* University of California, San Diego

Growth of metal oxide on GaAs with a low interface defect density is necessary for development of GaAs based metal oxide semiconductor field effect transistor (MOSFET). Vapor deposition of gallium oxide on GaAs(001) is emerging as a viable method for this objective. Using STM, we have investigated deposition of gallium oxide on GaAs(001)-(2x4) during the initial period and oxidation of the surface by atomic oxygen. Deposition of gallium oxide results in an atomically abrupt interface with the GaAs(001)-(2x4) surface, without disrupting the (2x4) surface order. In contrast, oxidation of GaAs(001)-(2x4) by atomic oxygen results in disordering of the surface characterized by formation of undimerized As surface atoms with half filled dangling bonds and As@subGa@ antisites. The stark difference in these two methods of oxide preparation has a profound implication for development of GaAs based MOSFET devices.

SC+EL+SS-WeP22 Density Functional Theory Studies of Semiconductor Surfaces*, G.S. Hwang,* California Institute of Technology*; **C.B. Shin,*** Ajou University, South Korea

Density functional theory (DFT) simulations have been proven to be a reliable and tractable tool in condensed matter physics. Indeed, these simulations are now successfully used to treat not only simple ordered solids but also complex systems such as surfaces and point-like/extended defects. We present the results of our recent pseudopotential based DFT studies which included: (i) the dynamics and configurations of Si(100) and (ii) the adsorption of hydrogen molecules on the surface. It is now rather well known that dimers on Si(100) are alternatively buckled at the ground state. However, the details of their geometry and dynamics at room temperature are still an issue of controversy. Our studies illustrate a tied flipping behavior of two consecutive dimers: the buckling of adjacent outer dimers becomes stronger while two inner dimers switch their orientations. Contrary to popular speculation, in most cases, the dimers undergo thermal fluctuations between two unequal energy minima, thereby preserving the 2x anticorrelation of dimer buckling along a row even at room temperature. Based upon such understanding of the dynamical behaviors of Si(100) at finite temperature, we have looked into dissociative adsorption of H@sub 2@ on Si(100), which is still ambiguous. This study reveals that intradimer @pi@-bonding disruption caused by thermal induced dimer stretching is mainly responsible for the anomalously strong surface temperature dependence of H@sub 2@ adsorption on the clean Si(100) surface.

SC+EL+SS-WeP23 Investigation of Polycrystalline Silicon Grain Structure by Single Wafer Rapid Thermal Chemical Vapor Deposition (RTCVD)*, **H. Bu**, C. Hu, M. Bevan, L. Tsung,* Texas Instruments*; L. Luo,* Applied Materials

It is known that the grain structure in poly-Si gate electrode can directly affect dopant activation and gate electrode depletion (GED). It is highly desirable to control the grain size and orientation during processing for improved IC device yield and reliability. This paper demonstrates the capability of tuning and generating a specific poly-Si grain structure with a lamp based and a heater based single wafer rapid thermal chemical vapor deposition (RTCVD) reactor at reduced pressure regime. Nitrogen gas is used as the carrier gas. The deposition temperature is varied from 650°C to 700°C. The effect of the concentration of intentionally added hydrogen during deposition is examined. Films deposited at various process conditions are characterized by TEM and XRD analysis. The results show that poly-Si grain size and orientation are sensitive to the hydrogen concentration. With a carefully selected process temperature and hydrogen concentration combination, the RTCVD technique is able to engineer the poly-Si grain size and orientation. The effect on poly-Si grain structure on electrical parameters such as electrical oxide thickness (EOT) and gate electrode depletion (GED) will be discussed.

SC+EL+SS-WeP24 Buried Low-Temperature (T@sub s@ <500 °C) Lateral Epitaxial Overgrowth of Si on SiO@sub 2@ Using Solid-Metal-Mediated Epitaxy*, **T. LaFave Jr.**, N. Lakshminarayana, A. Faik, M.-A. Hasan,* University of North Carolina

Buried lateral epitaxial overgrowth of Si on thin SiO@sub 2@ layers (<100 nm) using a thick solid Al layer as growth mediator was demonstrated using a newly developed solid-metal-mediated molecular beam epitaxy (SMM-MBE) method. The experiments were carried out at growth temperatures T@sub s@ < 500 °C using electron beam evaporation for Si and thermal evaporation of Al from an effusion cell. Si(100) wafers were thermally oxidized and patterned to provide seed/oxide strips ranging from 2/2 to 50/500 microns. Each seed/oxide strip was repeated within an area of ~ 1.25x2.00 cm@super 2@ and all patterns were placed on the same wafer. The wafers were then thermally etched at T@sub s@ = 900 °C under UHV conditions to desorb the remnant native oxide from the seed areas followed by deposition of Al at room temperature. Si deposited on the resulting structure at T@sub s@ < 500 °C re-grew epitaxially at the buried Al/Si interface and growth was extended laterally over the oxide layer. Initial TEM results demonstrated lateral growth of single crystalline Si over the oxide layer. This SOI method described above is based on SMM-MBE. In SMM-MBE, silicon grows epitaxially at a buried Al/Si interface during thermal evaporation of Si. Si atoms diffuse through the Al overlayer to the interface where low-energy atomic Si sites act as sinks for the diffusing Si atoms. This process is fundamentally different from surfactant assisted growth in which a small concentration of a metal (typically a fraction of a monolayer) is used to enhance epitaxial growth. In SMM-MBE, the Al layer can be thousands of monolayers thick (solid). The new findings may lead to new silicon-on-oxide fabrication method. Also, it provides a procedure for combined metallization and heavy p-type doping, e.g. in MOS device structure. Applications of this method in device fabrication will be discussed.

SC+EL+SS-WeP25 Field-Assisted Metal-Induced Crystallization of Amorphous Silicon Films*, **A. Khakifirooz**, S.S. Mohajerzadeh, S. Haji,* University of Tehran, Iran

Recently, metal-induced crystallization has gained special attention for low-temperature fabrication of polysilicon thin-film transistors. Metal-induced lateral crystallization, has been successfully utilized for obtaining high-performance TFTs. Very large silicon grains, free of metal contamination, are formed as a result of this lateral growth, providing a high carrier mobility. However, the lateral growth rate is still low and very long time annealing is required for practical applications. It has been reported that applying an electric field may enhance the growth rate. We have also observed this effect and the obtained results will be reported. Amorphous silicon films with a thickness of 1000Å are deposited on 50µm thick glass substrates via e-beam deposition. A 1000Å thick passivation oxide layer is subsequently deposited with e-beam and windows are opened for metal pads. A 1000Å thick nickel film is then deposited and patterned using photolithography. Samples are annealed on a hot plate while a DC voltage up to 100 V is applied between the pads. Growth rate is monitored using optical microscopy. SEM, TEM, and XRD are also used to investigate the crystalline structure of the films. A 300 µm crystallization was observed in samples annealed at 400°C for 30 min. when a 100 V/cm field applied. This is much higher than the previously reported growth rates. This may be explained by the fact that we have applied the field directly to metal pads, allowing a considerable current to pass through the a-Si film. Three regions with different crystalline structure are clearly observed in the laterally crystallized area when a high voltage is applied. The mechanism behind these phenomena will be discussed. In addition to filed-enhanced diffusion of Ni atoms, which has been supposed to be responsible for enhanced growth rate, we study the role of energetic electrons. Effect of impurities on the growth kinetics will be also reported.

SC+EL+SS-WeP26 Medium Range Order in Amorphous Silicon Films as a Function of Low-Energy Particle Bombardment During Growth*, J.E. Gerbi,* *J.R. Abelson,* University of Illinois at Urbana-Champaign*; P.M. Voyles,* University of Illinois and NEC Research Institute*; M.M.J. Treacy,* NEC Research Institute*; J.M. Gibson,* Argonne National Laboratory

Medium range order (MRO) refers to atomic correlations on a length scale of 1-2 nm. The recently developed TEM fluctuation microscopy technique@footnote 1@ is directly sensitive to MRO, as opposed to diffraction-based methods which are notably insensitive. In this work, we quantitatively compare the MRO in nominally amorphous hydrogenated Si thin films grown by significantly different vapor phase methods: plasma enhanced CVD, hot-wire (HW) CVD, and reactive magnetron sputtering (RMS). All films show significant MRO in the as-deposited state; the MRO decreases upon light soaking or thermal annealing, indicating the existence of a metastable state in the starting material. We investigate the roles of various particle bombardments in producing MRO with the RMS and HW-CVD growth processes. In previous work, we showed that bombardment by ions or neutrals promotes the formation of nanocrystalline or polycrystalline Si, depending on hydrogen addition and substrate temperature. We compare the MRO of a-Si:H, a-Si:D, and a-Si grown by RMS under high argon ion flux with that of a-Si:H grown by HW-CVD, which involves essentially no particle bombardment. We discuss how these bombardments affect the "structure" of a-Si in terms of MRO, and explain how this structure evolves during growth using the model of a frustrated polycrystalline growth surface which yields a highly strained, fine-grained "paracrystalline" structure. Such a structure looks amorphous in conventional diffraction methods, but is topologically crystalline. By contrast, the model of a continuous random network structure, as usually assumed for amorphous films, does not fit the data for as-deposited material. @FootnoteText@ @footnote 1@ J.M. Gibson, et al. Appl. Phys. Letts. 73 3093 (1998).

SC+EL+SS-WeP27 Cluster Deposition Study by Molecular Dynamics Simulation: Al Cluster and Cu Cluster*, J.-W. Kang,* *K.-S. Choi, E.-S. Kang, K.-R. Byun, H.-J. Hwang,* Chung-Ang University, Korea

Ionized cluster beam deposition for semiconductor interconnection technology has attracted much attention as a promising method for growing high-quality films at low substrate temperature. Therefore, it is important to understand the interaction between energetic cluster and substrate. In this work, we investigated energetic copper and aluminum clusters deposition and cluster-surface interactions. In the work, we used copper and aluminum clusters with the face centered cubic structure, a classical molecular dynamics simulation, and the second-moment approximation of tight-binding scheme. We simulated cluster deposition and investigated the variations of substrate temperature and the number of disordered atom as a functions of time, energy, and cluster size. The maximum substrate temperatures after energetic cluster impact on surface had linear relationship with total cluster energy and energy per atom, but we could not find any specific relationship with time taken for substrate temperature to reach its maximum. In this work, the correlated collisions between atoms in the cluster played a very important role in the impact on substrate surface and the correlated collision effect was proportional to the cluster size and kinetic energy per atom. For each impact angle and energy, we calculated the average properties such as sputter yield, sticking probability, average reflection angle of the impact cluster, and average emission angle of the sputter products. The calculated properties were compared with that of single atom deposition.

Surface Science
Room Exhibit Hall C & D - Session SS-WeP
Poster Session

SS-WeP2 Substrate-Dependent Interaction of Carbon Monoxide and Ammonia on Metal Carbide Surfaces*, S.S. Perry,* ***L.C. Fernández-Torres,*** *R.L. Guenard, O. El-bjeirami,* University of Houston*; S.V. Didziulis, P.P. Frantz,* The Aerospace Corporation

A study of the interaction of carbon monoxide (CO) and ammonia (NH@sub 3@) with titanium carbide (TiC) and vanadium carbide (VC) is presented. The interaction of CO and NH@sub 3@ with the (100) face of the single crystal carbides was studied over the temperature range of 100-400 K. The adsorption states of CO and NH@sub 3@ were probed with high resolution electron energy loss spectroscopy (HREELS) and photoelectron spectroscopy. The desorption of CO and NH@sub 3@ was followed with temperature programmed desorption (TPD). Together, these measurements indicate that both CO and NH@sub 3@ adsorb molecularly on TiC and VC. However, HREELS measurements show CO adsorbs more strongly on VC than on TiC, and NH@sub 3@ adsorbs similarly on TiC and VC. TPD supports these observations; CO has a higher desorption temperature on VC than on TiC while NH@sub 3@ has a similar desorption temperature from the two surfaces. Strong evidence of @pi@-backbonding for CO on VC is seen in the vibrational data, as well as in the core and valence level photoelectron spectra. This mechanism, which is not active on TiC, differentiates the interaction of CO with these two substrates. Similar interaction mechanisms and adsorption energies are observed for NH@sub 3@ on TiC and VC, where @pi@-backbonding would not be expected to play a role. These results are discussed in terms of the difference in electronic structure between the two metal carbides.

SS-WeP3 Effects of Film Morphology on the Electron Stimulated Desorption of O@super -@ from O@sub 2@ Deposited on Benzene*, A.D. Bass,* ***L. Parenteau****, L. Sanche,* University of Sherbrooke, Canada

Low energy electron impact techniques can be used to study thin molecular solids under ultra high vacuum (UHV) and have already provided valuable information on the electronic interactions underlying phenomena such as radiation damage to biological materials, dielectric aging and surface mediated photo-chemistry.@footnote 1@ Experiments measuring the electron stimulated desorption (ESD) of ionic and neutral fragments have been of considerable value, yet only recently have researchers considered how factors such as film porosity or morphology affect ESD measurements.@footnote 2,3@ In this article we investigate the effects of film phase and porosity on the ESD of O@super -@ from O@sub 2@ molecules deposited onto the surface of multilayer benzene. Benzene films deposited at temperatures below 30 K are amorphous@footnote 4@ and appear porous so that O@sub 2@ molecules diffuse into their surface. When benzene is deposited at temperatures near 100 K, a non-porous film is formed which severely limits the penetration of O@sub 2@ into the benzene layer. The results are compared with measurements of O@super -@ production from O@sub 2@ covered water ices.@footnote 5@ @FootnoteText@ @footnote 1@See for example L. Sanche, IEEE Trans. Dielec. Elec. Insulat. 4, 507 (1997) @footnote 2@ W.C. Simpson M.T. Sieger T.M. Orlando L. Parenteau K. Nagesha L. Sanche J. Chem. Phys., @footnote 3@ E. Vichnevetski, P. Cloutier, and L. Sanche, J. Chem. Phys. 110, 8112 (1999) @footnote 4@ P.Swiderek and H. Winterling Chem. Phys. 229, 295 (1998) @footnote 5@ R. Azria, Y. Le Coat, M. Lachgar, M. Tronc, L. Parenteau, L. Sanche, Surf. Sci. 436, L671 (1999).

SS-WeP4 Electron Transfer Reactions on Layered Transition Metal Sulfide Surfaces+*, K. Park,* Baylor University

Recent advances in high resolution X-ray photoemission spectroscopy (HRXPS) have enabled one to directly probe an electron transfer reaction between adsorbates and model catalyst surfaces. For example, on cesium adsorbed molybdenum disulfide surface it has been observed that deposition of submonolayer cesium onto the basal plane of clean MoS2 introduces a new electron density of states at 1.25 eV above the MoS2 valence band maximum (VBM). Combined density functional theory and angle-resolved HRXPS indicate that the new VB state originates mainly from the bottom of the MoS2 conduction band, mixed to a small extent with the Cs 6s orbital. It has been further demonstrated that the supra-valence electrons in MoS2 can be captured and reacted with electron acceptor molecules forming surface ionic species. On the other hand, the interface between Li and MoS2 exhibits a quite different behavior - a reductive reconstruction. In this talk, I will review recent findings from alkali metal adsorbed, layered transition metal sulfide surfaces and discuss the on-going effort to understand the underlying principle for the adsorbate-substrate interaction.

**SS-WeP5 Alloy Formation at the Co-Al Interface for Thin Co Films Deposited on Al(100) and Al(110) at Room Temperature*, R.J. Smith,* *N.R. Shivaparan, M.A. Teter,* Montana State University

High-energy ion backscattering spectroscopy and channeling (HEIS), combined with x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) were used to characterize the evolution of the Co-Al interface for thin Co films deposited on Al(001) and Al(110) surfaces at room temperature. This interface is of particular interest because of the possible applications for tunneling magnetoresistive junctions and the associated fabrication processes such as oxidation of Al films deposited on magnetic thin films. For the Al(001) surface, measurements of the backscattered ion yields from Al and Co show that substrate Al atoms are continuously displaced for Co coverages up to about 3 ML as the interface alloy forms. Cobalt metal eventually covers the mixed interface. Based on XPS intensity analysis, we conclude that a CoAl-like phase forms at the interface. A very diffuse LEED pattern with large spots and high background was observed after a deposition of 7.6 ML of Co coverage. For the Al(110) surface, intermixing of Co and Al atoms was observed up to 5 ML of Co deposition, where Co metal begins to cover the surface. No LEED spots were observed for any Co coverage exceeding 0.2 ML on the Al(110) surface. A Volmer-Weber type growth model for these interfaces was used with the XPS intensity data to characterize the morphology of the interfaces in both cases. In neither case was Co diffusion into the bulk Al substrate observed at room temperature. These results are briefly compared with similar measurements for Ni and Fe films on Al surfaces. Work supported by NSF Grants DMR9409025 and DMR9710092.

**SS-WeP6 Defect Structures on the Si(5 5 12)-2x1 Surface*, A.S. Sun,* *K.M. Jones, E.S. Bowman, A.A. Baski,* Virginia Commonwealth University

Scanning tunneling microscopy (STM) studies of the high-index Si(5 5 12)-2x1 reconstructed surface show that it forms a single domain of row-like structures. It has therefore been proposed as a viable template for metallic nanowire growth. In this work, we use STM to characterize two common surface defects that may influence its application as such a template. The most commonly observed surface defects are disruptions in the periodicity of the Si(5 5 12) unit cell. The Si(5 5 12) unit cell can be considered as a combination of one (7 7 17) and one (337) unit cell. In up to 20 percent of the (5 5 12) units, an extra or missing (337) subunit appears, resulting in a non-uniform surface periodicity. Because there is a dominance of either extra or missing (337) units on a given sample, sample preparation conditions appear to play an important role. Another type of defect observed on the Si(5 5 12) surface is the presence of adsorbed dimers. These dimers have a typical coverage of 10-15 percent, and exist as single dimers or in clusters up to ~10 dimers long. Statistics taken from STM data indicate that as the dimer cluster size increases, the number of clusters decreases exponentially. A Monte Carlo model of 1D clusters has been used to correlate the distribution of these dimer defects with their relative "hopping" probabilities on different surface sites.@footnote 1@ We find that single dimers have a strong preference to remain attached to the ends of existing clusters. A better understanding of both the adsorbed dimer and (337) unit cell defects should lead to a more controlled preparation of Si(5 5 12) as a growth template. @FootnoteText@ @footnote 1@ E. S. Bowman, M. F. Bishop, T. McMullen, and A. A. Baski, Cluster and Nanostructure Interfaces, edited by P. Jena (World Scientific, New York, 2000), p. 569-574, in press.

**SS-WeP7 Growth of a Group-IV Metal on Si(5 5 12)*, I. Samanta,* *A.A. Baski,* Virginia Commonwealth University

Recently, we have used scanning tunneling microscopy (STM) to study the growth behavior of noble metals (Ag, Au) on the row-like Si(5 5 12) surface.@footnote 1@ In this study, we explore the different growth modes for a Group IV metal such as Sn, where we expect more intermixing of the tetravalent Sn and Si atoms. Our STM studies show that, unlike for the noble metals, Sn forms adsorbed dimers on the Si(5 5 12) surface at low coverage (< 0.5 ML) and moderate annealing temperatures (~450C). These dimers appear as bright protrusions in the trenches between Si rows, and in fact intermix with existing Si dimers on the surface. At higher coverages, Sn forms relatively large protrusions with a 4x periodicity along the underlying Si tetramer rows. Such strongly corrugated features have never been observed for the deposition of noble metals, indicating a significantly different growth behavior for this group-IV metal. As the coverage is increased (>1 ML), Sn creates a disordered surface with only remnants of the row-like surface morphology remaining. At higher annealing temperatures (700C+), however, the surface undergoes a large-scale rearrangement with sawtooth facets being formed. We are presently exploring the optimal conditions to produce such sawtooths, because such a corrugated surface provides yet another interesting template for growth. @FootnoteText@ @footnote 1@ K. M. Jones, K. M. Saoud, and A. A. Baski, Cluster and Nanostructure Interfaces, edited by P. Jena (World Scientific, New York, 2000), p. 49-54, in press.

**SS-WeP8 Cyanogen Iodide Adsorption on Si(100)*, N.F. Materer,* *T. Watt,* Oklahoma State University

The adsorption of cyanogen iodide (ICN) on a silicon (100) surface is studied by X-ray photoelectron spectroscopy (XPS). At room temperature, ICN chemically adsorbs on the surface. The C 1s photoelectron peak indicates that the carbon nitrogen triple bond is intact. The triple bond remains until approximately 400C. Initial experiments suggest a sticking coefficient at room temperature of 0.1 for ICN. Experiments are in progress to quantitatively determine this number. In addition, thermal desorption measurements are proceeding to further complementing the XPS studies.

**SS-WeP9 Effects of Al/Si(111) Surface Phases on the Wandering of the Single-Height Steps@footnote 1@*, I. Lyubinetsky,* *D.B. Dougherty, H.L. Richards, T.L. Einstein, E.D. Williams,* University of Maryland, College Park

The thermally-induced wandrering of single-height steps have been studied by STM on a vicinal Si(111) surface, miscut by 0.5° in the [2,-1,-1] direction, after aluminum deposition at elevated temperatures (500-700°C). From direct measurement of the step-correlation function, the step diffusivity, b@super2@/a, is shown to increase strongly as Al coverage @Theta@ in the surface phases increases: b@super2@/a ~ 0.4 Å for the a(7x7) phase (@Theta@ = 0.12 ML), ~ 1.5 Å for the (@sr@3x@sr@3) phase (@Theta@ = 0.3 ML), and ~ 4.6 Å for the @gamma@ phase, also referred to as the (9.4x9.4) phase, (@Theta@ = 0.68 ML), implying corresponding systematic decrease in the kink energy. An increase of the step diffusivity compared to a clean Si(111)-(7x7) surface has been observed even at the very initial stages of the a(7x7) reconstruction formation, at @Theta@ as low as 0.02 ML. For the least stable phase of (@sr@7x@sr@7) (@Theta@ = 0.43 ML), which coexists with the @gamma@ phase on the same terrace, the wandering of the phase boundaries between (@sr@7x@sr@7) and @gamma@ phases will also been discussed. @FootnoteText@ @footnote 1@Work supported by the UMD-NSF-MRSEC.

SS-WeP10 Oxide and Nitride Film Growth on Microfabricated Cantilevers by Pulsed Mode DC Magnetron Sputtering*, P. Cao, M.-S. Lim, S.S. Perry,* University of Houston*; **K.P. Wiederhold**, Y. Yamaguchi, E.J. Mitchell, D.C. Koeck, H.C. Galloway,* Southwest Texas State University

We have investigated the growth of TiN and Al@sub 2@O@sub 3@ films on microfabricated atomic force microscopy (AFM) probes. These films are grown using a pulsed mode DC Magnetron sputtering technique. This method allows us to extend the range of traditional DC magnetron sputtering to a wider range of conductivities for oxide and nitride film growth. The TiN thin films tend to grow in a highly stressed manner which can cause severe deformations of the microfabricated cantilevers. The deposition of a thick interfacial Ti layer, increased growth temperature, and the use of pulsed mode deposition are effective in producing usable cantilevers. The Al@sub 2@O@sub 3@ films have been produced with both Ti and Al interfacial layers with less cantilever deformation than the TiN coating, indicating only moderate stress of the Al@sub 2@O@sub 3@ films. These studies indicate that an interfacial layer is essential for adhesion and that Al layers result in lower interfacial stress as compared to Ti layers. Resistivity, XPS and AFM measurements have been used to characterize blanket films grown by the same methods. Specialized samples are used to measure the tip shape and the conductive tips are used as point contacts to characterize the electrical properties.

**SS-WeP11 Vibrationally Activated Dissociative Adsorption of CO@sub2@ on Ni(100)*, C.L. DiCologero,* *A.L. Utz,* Tufts University

We will present recent results from our study of the dissociation of vibrational-state-selected CO@sub2@ on Ni(100). Previous studies@footnote 1@ have shown that the reaction is enhanced by increasing the average thermal vibrational population of the CO@sub 2@ molecules. In our study, infrared laser excitation of CO@sub 2@ in a supersonic molecular beam produces molecules with a well-defined translational energy in a particular vibrational and rotational state. Quantifying the efficacy of energy in a specific rovibrational coordinate reveals key aspects of the potential energy surface governing the interaction. @FootnoteText@ @footnote 1@ M.P. d'Evelyn, A.V. Hamza, G.E. Gdowski, R.J. Madix, Surface Science, 167,451,(1986).

SS-WeP12 W-Si(111) Force Interaction Measurements with Force-feedback Force Sensor, *R. Erlandsson,* Linkoping University, Sweden*;* ***V. Yakimov,*** McGill University, Canada

We have investigated the tungsten-silicon contact in ultrahigh vacuum using an atomic force microscope equipped with a force-feedback force sensor. The operation of the sensor is based on balancing the tip-sample interfacial force by an electrostatic actuator. The measurements show that the force changes in discrete steps both upon approach and retraction, and the magnitude of the steps indicate that these events can be attributed to neck formation and relaxation phenomena involving only a few atoms. The data is in good agreement with previously published molecular dynamic simulations of the behaviour of sharp tips interacting with surfaces. It is shown that the commonly used calculation of the long-range van der Waals force using a spherical tip approximation is inadequate for measurements on this scale. Curves obtained using force-feedback method are compared with conventional force curves, and the role of the dynamic behaviour of the force-feedback sensor in the interpretation of force spectroscopy data will be discussed.

SS-WeP13 CC Bond Breaking Before CH Bond Breaking on a Metal Surface*,* ***S. Lavoie,*** *A. Adnot, P.H. McBreen, M. Castonguay,* Université Laval, Canada

CC bonds are very rarely broken before CH bonds in the same molecule, despite the fact that they are weaker. Intense research in organometallic chemistry is aimed at the selective activation of CC bonds, however examples of selective CC bond scission are usually restricted to strained ring molecules. In contrast, this RAIRS and SSIMS study shows the selective CC bond scission of methyl pyruvate on Ni(111) leading to the formation of adsorbed methoxycarbonyl and acetyl groups. The novel surface chemistry revealed in this study is also of interest due to the fact that the hydrogenation of methyl pyruvate is a test case reaction in heterogeneous chiral catalysis.

SS-WeP14 Rovibrational State-Selected Studies of CD@sub 3@H on Ni(100)*,* ***R.R. Smith,*** *A.L. Utz,* Tufts University

Previous results in our laboratory have demonstrated the effects of rovibrational excitation in the dissociative chemisorption of methane on Ni(100). In an effort to further probe the dynamics of this system, we have recently begun state-selected experiments of the molecule CD@sub 3@H on this surface. Replacing three hydrogen atoms with deuterium removes the spherical top symmetry and changes the nuclear motions of the normal modes. This gives us access to a nearly pure C-H stretching vibration (@nu@@sub 1@) and, by using polarized laser light, allows us to investigate the effects of the incident molecular orientation. This provides us with a method to more accurately probe the transition-state and may shed light on the role that dynamical steering plays in this reaction. In a related study, we have also been investigating the collision-induced absorption and collision-induced recombinative desorption of hydrogen on this surface. Our most recent results of these topics will be presented.

SS-WeP15 Conformation of Model Self-assembled Monolayers Studied by Sum-frequency Generation Spectroscopy*,* ***M.B. Raschke,*** *P.B. Miranda, X. Wei, Y.R. Shen,* University of California, Berkeley

Potential technological applications of self-assembled monolayers (SAM) as lithography resists, lubricants or biosensors make detailed surface strucural analysis of these materials highly desirable. In this respect chemisorbed films of model self-assembling n-alkyl monolayers have been investigated by means of infrared-visible sum-frequency generation spectroscopy providing information about chain orientation and internal molecular conformation. The trans-gauche transformation behavior of n-Octadecyltrichlorosilane (OTS) and Octadecyldimethyl(3-trimethoxysilyl-propyl)ammonium chloide (DMOAP) adsorbed on quartz with different surface molecular densities has been studied in vacuum for temperatures between 100 and 450 K. Whereas tight packing sterically prevents low energy excitations (e.g. molecular tilt, gauche defects), for low chain-densities large number of gauge conformations are found even at low temperatures. This corresponds to an observed increase in the onset temperature for chain melting with increasing surface density. For high chain densities metastable conformations (e.g. entanglement with neighboring molecules) can persist even at T=300 K and may be annealed at elevated temperatures. The observed behavior will be discussed in terms of the thermodynamics describing linear chain molecules.@FootnoteText@ Work supported by DOE.

SS-WeP16 X-ray Photoelectron Spectroscopy Measurements of Mid-gap Density of States in Amorphous Hydrogenated SiC Thin Films*,* ***F.S. Ohuchi,*** *M.-H. Lee, D.A. KuKuruznyak,* University of Washington

Optical properties of amorphous Si-C thin films are directly related to electronic structure. The most significant optical parameters in amorphous systems are the optical band gap, E@sub g@, and the steepness parameter of the exponential absorption edge called Urbach energy, E@sub u@. In amorphous materials such as amorphous hydrogenated SiC (a-Si@sub 1-x@C@sub x@:H) thin films, the absorption edge is not clearly defined, and the Urbach tails further complicate the electronic band structure due to the mid-gap energy states. By fabricating metal-semiconductor junctions, electrons can be externally supplied to the mid-gap states. When an insulating layer further exists between the metal and a-Si@sub 1-x@C@sub x@:H thin film, occupied electrons in the mid-gap states will induce charges in the insulator, resulting in a shift in the electron binding energy at the interface, thus the density of mid-gap states can be measured by X-ray photoelectron spectroscopy (XPS). In this talk, a new method to evaluate the mid-gap density of states is proposed and applied to a-Si@sub 1-x@C@sub x@:H thin films. Experimentally, a-Si@sub 1-x@C@sub x@:H was deposited on the top of Au surface on Si by DC plasma enhanced chemical vapor deposition. Very thin oxide (SiO@sub 2@) and Au layers with the thickness of below electron penetration depth were grown subsequently. The shift in difference between Au 4f and Si 2p core-level binding energies was measured by XPS as a function of the bias voltage. The energy distribution of mid-gap DOS was obtained from analyzing the amount of the bias-induced binding-energy shift, and the measured mid-gap DOS was further compared to optical absorption measurements in an attempt to elucidate the relationship between the optical property and electronic structure in a-Si@sub 1-x@C@sub x@:H thin films.

SS-WeP17 CO Adsorption on Au{110} and Au/TiO@sub 2@*,* ***D.C. Meier,*** *V. Bukhtiyarov, D.W. Goodman,* Texas A&M University

A great deal of interest has been generated by the catalytic properties of gold nanoclusters on metal oxide supports. These complex systems will be better understood if they are first dissected into their simplest components and studied separately. After comparing and contrasting the behavior of the components to the behavior of the system of interest, conclusions can be drawn as to the function of the catalytic system. With this information, steps can be taken to optimize those properties with the most desirable catalytic effects. IRAS studies of the dynamics of CO adsorption on the Au{110}(1x2) and Au{110} unreconstructed surface were performed as a function of CO pressure and sample temperature. The CO IRAS absorption shifted from 2118 cm@super -1@ to 2108 cm@super -1@ with increasing coverage on the reconstructed surface while the unreconstructed sample exhibited no shift, remaining at 2108 cm@super -1@. Clausius-Clapeyron data analysis yielded a E@sub a@ for CO adsorption of 12 kcal/mole at low coverages and 9 kcal/mole at elevated coverages, where the phase change appears at approximately 0.17 monolayers. These results are compared and contrasted to CO adsorption on Au/TiO@sub 2@ systems, which exhibit similar wavenumber shifts, but at higher adsorption energies.

SS-WeP18 Adsorption, Decomposition and Stabilisation of 1,2-dibromoethane on Cu(111)*,* ***A.S.Y. Chan,*** University of Nottingham, UK*;* *R.G. Jones,* University of Nottingham, UK, U.K.

The molecular adsorption and thermal reaction of 1,2-dibromoethane (DBE) on Cu(111) has been studied using Ultraviolet Photoelectron Spectroscopy (UPS), work function change (@Delta@@Phi@) measurements, Low Energy Electron Diffraction (LEED) and Line-of-sight Temperature Programmed Desorption (LOSTPD). At 100 K, DBE adsorbs molecularly, exhibiting a decrease in work function of 0.86 eV at the completion of the monolayer. Layer-by-layer growth is observed up to two molecular layers, with further adsorption leading to the growth of tower crystallites. The first layer of DBE undergoes thermal decomposition at 120 K to give gaseous ethene and chemisorbed bromine in a (@sr@3x@sr@3)R30° structure, which increases the work function of the surface by 0.58 eV. Chemisorbed bromine from partial decomposition of the first layer is found to stabilise the remaining DBE molecules in the decomposing layer, thereby arresting complete decomposition until a higher temperature, leading to the emission of ethene at 140 K and 160 K for decomposition of the surface DBE layer in the submonolayer and multilayer regime respectively. The possibility of the ethene product being stabilised by co-adsorption adjacent to the chemisorbed bromine is discussed.

SS-WeP19 Methyl Nitrite: Potential Intermediate in Methane-assisted Reduction of Nitric Oxide*, **L.J. Deiner**,* Harvard University*; S.W. Wilke,* California Institute of Technology*; C.M. Friend,* Harvard University

Reactions of methyl nitrite (CH@sub 3@ONO) on O-covered Mo(110) were studied in order to determine if methyl nitrite is a possible intermediate in the methane-assisted reduction of NO. The product distribution in temperature programmed reaction studies depends on the coverage of CH@sub 3@ONO. At saturation coverage, there is low temperature desorption of CH@sub 3@ONOand NO (160 K)and high temperature desorption of methyl (CH@sub 3@) radicals (650 K). At low coverage, the only products detected in temperature programmed reaction are CH@sub 3@ radicals at 650 K. Isothermal reaction experiments performed at 100 K and 300 K indicate that N@sub 2@O and NO are evolved directly into the gas phase. At both temperatures, N@sub 2@O evolution occurs first and then decreases rapidly as NO production rises. NO continues to desorb until saturation coverage of CH@sub 3@ONO. Fourier transform infrared spectroscopy confirms the results of the temperature programmed reaction and isothermal experiments. The infrared spectrum of the low coverage surface displays only one band corresponding to the C-O stretch of methoxy. The infrared spectrum of the saturation coverage surface possesses bands corresponding to intact CH@sub 3@ONO, NO, and methoxy. Upon heating the surface to 450 K, only the methoxy bands remain.

SS-WeP20 Technique for Optical Lever Calibration for Surface Stress Measurements*, **P.J. Williams**, M. Godin, V. Tabard-Cossa, P. Grutter,* McGill University, Canada

The atomic force microscope (AFM) is increasingly being used not just to image surfaces of interest but also to probe the mechanical properties of the surface, using force spectroscopy for example. In addition, AFM cantilevers are being used as the basis of nanosensors to measure a variety of signals, including surface stress, temperature etc. In all of these applications, it is important that the relationship between the output of the position sensing detector (PSD) and the deflection of the cantilever be well known. In this poster we present a new technique for determining this relation. We attach a small resistive heater to the cantilever chip to induce a bending through the bimetallic effect. We simultaneously monitor the deflection of the beam with a fibre optic interferometer that is brought up to the backside of the cantilever and with a PSD. The interferometer fibre is positioned to be at the focus of the laser beam and hence we are measuring the deflection of the cantilever at the same position that the laser spot is focused. By computing the power spectrum of the interferometer output versus the PSD output, the PSD can be accurately calibrated. We have employed this calibration technique in a measurement of the surface stress associated with the formation of a self assembled monolayer of alkanethiol on gold.

SS-WeP21 The AFM Study of the Growth Process of a-Si:H Films Deposited by Low Frequency PECVD*, B.G. Budaguan, **M.N. Meytin**,* Moscow Institute of Electronic Technology, Russia*; A.A. Aivazov,* UniSil Corp.

In this work the growth process and surface morphology of a-Si:H films fabricated by the low frequency (55 kHz) PECVD at substrate temperatures from 40°C to 325°C was investigated.The results of the mass-spectra measurements of LF plasma have shown the presence of SiH3 and Si2Hx radicals.We detected large powder particles in plasma by laser beam scattering.The intensity of Si2Hx mass spectra peaks as well as the intensity of laser beam scattering decrease with the Ts increase, indicating on the decreasing of the probability of polymerization processes. The AFM analysis of a-Si:H surface reveals the island type morphology. The average diameter of islands increases with Ts, while the concentration of islands decreases. The dependence of the RMS roughness,w, on the thickness of the films,d, is w~d^b,where b~6. The high value of b (b>0.5 for a conventional 13.56MHz PECVD) and the dependence of islands diameter on Ts are proposed to be due to the participation of powder particles in the film growth. In that case the formation of a-Si:H surface morphology is controlled by two types of precursors-SiH3 radicals and powder particles. We performed computer modeling of the growth process. The initial diameter of islands formed from the powder particles and the rate of islands formation,Ci, were determined by the fitting of simulated RMS and islands diameter distribution to the experimental data. It was found that Ci decreases with increase of Ts,which correlates with the experimental data. The dependence of the island diameter on Ts is explained by the participation of SiH3 radicals in the growth process. The sticking of the SiH3 radicals to the film surface leads to the growth of island diameter, which is restricted by the boundaries of the neighbor islands. So,the higher the number of islands the lower their diameters and vice verse. This mechanism of island growth allows to explain the increase of the island diameter with the substrate temperature.

SS-WeP22 Effects of Low Dose Ion Bombardment Upon the Hg-distribution in a CeO2-layer in a TL-lamp*, **C. Van der Marel**,* Philips Electronics, The Netherlands*; V.H. Hildenbrand,* Philips Research, The Netherlands

Experiments have been done with a TL-lamp of which the inside was coated with CeO2. After a long time of operation the Hg vapor pressure in the lamp was too low to sustain the plasma. ARXPS was applied to determine the chemical state of the Hg and to obtain information about the depth-distribution of the Hg in the upper few nm of the CeO2-layer. Additionally experiments were done with a low flux, low energy ion beam (0.5 kV). The dose was chosen such that, even when a sputter yield of 1 is assumed, much less then 1 ML might be removed. The influence of successive ion bombardments upon the Hg-distribution was investigated. It is found that even low dose ion bombardment, in which only a small fraction of the surface is directly hit by the ions, has an important influence upon the depth distribution of the Hg within the layer.

SS-WeP23 Electron-Stimulated Desorption of Europium Atoms from Oxidized Tungsten Surfaces*, **V.N. Ageev**, Yu.A. Kuznetsov,* A. F. Ioffe Physico-Technical Institute, Russia*; T.E. Madey,* Rutgers, The State University of New Jersey

We have measured the electron-stimulated desorption (ESD) yield for neutral europium (Eu) atoms from Eu layers adsorbed on oxidized tungsten surfaces, as a function of electron energy, europium coverage, degree of oxidation of tungsten and surface temperature. The objective is to compare ESD of multivalent Eu with ESD of monovalent alkali atoms, studied previously. The measurements have been carried out using a time-of-flight method and surface ionization detector. The Eu ESD desorption yield is a complicated function of Eu coverage, electron energy E@sub e@ and substrate temperature. In the coverage range 0.05 to 0.35 monolayers (ML), thresholds for Eu desorption are observed at electron energies E@sub e@ of 25 and 37 eV, and are associated with Eu 5p and 5s excitations. Additional features (resonant-like peaks) are seen at E@sub e@ = 50 eV and 80 eV; these are associated with W 5p and 5s, respectively, and are observed even for Eu coverages > 1 ML. The Eu yields at 25 and 37 eV vanish above 330K, whereas the yields at 50 and 80 eV persist above 500K. This is the first report of ESD of metal atoms in which threshold features correlate both with adsorbate excitation energies and substrate excitation energies.

SS-WeP24 Optical and STM-based Excitation of Adsorbed Molecules: Elucidating their Elementary Mechanisms and Novel Experiments*, **L. Bartels**,* University of California, Riverside*; E. Knoesel, D. Moeller, T.F. Heinz,* Columbia University*; S.W. Hla, G. Meyer, K.H. Rieder,* Free University Berlin, Germany*; D. Velic, A. Hotzel, M. Wolf,* Fritz-Haber-Institute, Germany*; P. Saalfrank,* University College, England

Photodesorption and other photochemical reactions have been studied for a long time and lately using femtosecond laser pulses extremely detailed measurements could reveal an astonishing amount of their underlying elementary steps in the time domain. The scanning tunneling microscope, initially invented as a tool to image surfaces at atomic resolution, has in the meantime developed into a highly precise and powerful means to manipulate them. It could be shown that some of the excitation mechanisms relied elementarily on electron attachment to a molecular resonance. This is very similar to photoelectron attachment, but while STM has poor inherent temporal resolution, its superior spatial resolution can trace down reactions to specific adsorption sites and molecular arrangements. In this contribution a comparison of both excitation methods is given and for the induced lateral movement of CO on copper the results are compared. Further results from STM induced measurements are shown.

SS-WeP25 Atomic Resolution Imaging of Si(100)2x1-H Surface with Non-contact AFM*, **A. Yoshimoto**, Y. Sugawara, S. Morita,* Osaka University, Japan

Noncontact Atomic Force Microscopy (NC-AFM) have achieved true atomic resolution in 1995. NC-AFM is one of the most promising tools for surface analysis of materials including insulators on an atomic scale. In fact, many experimental groups reported atomically resolved images on various surfaces. NC-AFM imaging mechanism which contributes to the image contrast is still in progress. Although NC-AFM imaging mechanism has been investigated mainly on a chemically reactive surfaces such as semiconductor surface (Si(111)-7x7, Si(111) r3xr3-Ag etc.), there is no report on a comparative study between a reactive surface and an inactive surface using the same tip. In the present experiments, we performed the NC-AFM imaging on reactive Si(100)-2x1 reconstructed surface with dangling bond and inactive hydrogen- terminated Si(100)-2x1-H surface without the dangling bond. As a force sensor, we used a silicon tip with dangling bond, which was cleaned by Ar ion sputtering. As a result, by using the same tip, we succeeded in obtaining atomic resolution images on Si(100)-2x1 reconstructed surface and Si(100)-2x1-H monohydride surface. We found that the distance between bright spots of AFM images increased by the hydrogen termination. This suggests NC-AFM has capability for hydrogen atom imaging of Si (100) 2x1-H on an atomic scale.

SS-WeP26 Desorption Induced Change in Surface Stress of Self-assembly Alkanethiol Monolayer on Gold*, **A.N. Itakura,*** National Research Institute for Metals, Japan*; T. Narushima,* University of Tsukuba, Japan*; M. Kitajima,* National Research Institute for Metals, Japan*; R. Berger,* IBM SSD GmbH, Germany

Self-assembled monolayers such as alkanethiol, -HS-(CH@sub 2@)@sub n-1@-CH@sub 3@ for n=4,6,8,12, on metal surface have been well studied because they have potential use in the wide range of technological applications such as molecular recognition and nanofabrication. The alkanethiol monolayer on gold induces a compressive surface stress during the self-assembly and the saturation value of the compressive stress is directly proportional to the alkyl chain length. There are few papers on the stress induced by the desorption. Here we present the evolution of surface stress during adsorption and desorption of self-assembly alkanethiol monolayers (SAM). The adsorption of SAM (n=12) produces a compressive stress of 0.18 N/m in air. An exposure to an argon plasma, in a UHV system, induces a rapid decrease of the compressive stress. This is because of the desorption of SAM, and if the adsorption and desorption are a reversible reaction then the final stress should be zero. But actually, the final value of the stress is tensile : -0.12 N/m. After the stress experiment we examined the surface with Auger electron microscope and detected S remaining on the surface. It suggests that the removing of dodecanethiol is not as a molecule but a part of alkyl chain which is cut from adsorbed molecule. The tensile stress should be due to the remaining part.

SS-WeP27 HREELS on CO/Rh(111): Lateral Interactions in Adsorbate Layers and Vibrational Frequency Shifts*, **R. Linke,*** Eindhoven University of Technology, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

Lateral interactions in CO adlayers on Rh(111) were studied by HREELS and TDS. At low coverage CO adsorbs only on-top. From about 0.5 ML also the 3-fold hollow site becomes populated. The occupation of the second adsorption site is accompanied by the development of a low temperature shoulder in the TDS peaks indicating increasingly repulsive interactions in the adsorbate layer. A continuous shift to higher frequencies of the internal C-O vibration is observed over the whole coverage range. At low coverage the on-top Rh-CO frequency hardly shifts but undergoes a shift to lower frequencies upon the emergence of the 3-fold hollow. To assess the origin of the frequency shifts we measured isotopic CO mixtures. HREEL spectra of 12CO and 13CO mixtures at total CO coverage of 0.33 ML proof that the frequency shifts arise purely from dipole-dipole coupling. We also used a fixed low 13CO coverage to monitor the frequency shifts in a changing 12CO matrix. The internal 13C-O frequency remains at its singleton frequency until 0.5 ML total CO coverage, then a pronounced shift to higher frequencies begins. This testifies that at low coverage (<0.5 ML) frequency shifts arise from dipole-dipole coupling while at high coverage (0.5 - 0.75 ML) also chemical effects contribute to a large extent.

SS-WeP28 Evidence for Two Chain Length Distributions in the Polymerization of Formaldehyde on Cu(100)*, **T.R. Bryden,** S. Garrett,* Michigan State University

The adsorption of formaldehyde on Cu(100) has been studied using electron energy loss spectroscopy (EELS) and temperature programmed desorption (TPD). At 85 K, formaldehyde (H@sub 2@CO) spontaneously polymerized to form a monolayer of poly(oxymethylene) (POM). Thermal decomposition/desorption of the polymer monolayer occurred via two kinetically different routes, producing two peaks in TPD that can be attributed to molecular H@sub 2@CO generated via depolymerization of the polymer. The presence of two polymer desorption peaks has not been previously observed in studies of formaldehyde adsorption on metal surfaces. The zero and first order features observed are attributed to chain length differences present between the species and can be explained using rate equations describing the production of monomer. Our data seems to indicate the number of chains, for the zero order species, is fixed while the degree of polymerization is changing as the amount of POM formed increases. EELS spectra, taken as a function of anneal temperature, indicate the two species are similar and show losses due to POM. However, the losses due to POM for the second species are lower in intensity and new modes are identified that are attributed to the end groups of the polymer, which is consistent with shorter chains. Additionally, the second species is more ordered relative to the mixture, which could account for the enhanced production of the first species during dosing experiments where the surface is covered with the second species during exposure to H@sub 2@CO.

SS-WeP29 Photon-stimulated Ion Desorption from Mono- and Multi-layered Silicon Alkoxide on Silicon by Core-level Excitation*, Y. Baba,* Japan Atomic Energy Research Institute, Japan*; **G. Wu**, T. Sekiguchi, I. Shimoyama,* Japan Atomic Energy Research Institute

Photo-induced processes at semiconductor surface are of great importance for the fabrication of semiconductor devices, because surface modification at low-temperature is possible using photons as a driving force of the reaction. For the deposition of silicon dioxide on silicon, silicon alkoxide is widely used for the source material. Synchrotron radiation (SR) has advantages as light source of photo-induced deposition, because of the potentiality of the element-selective and site-selective reactions due to the localized nature of inner-shell electrons. Here we present the results for the fragment-ion desorption from tetramethoxylsilane (TMS) on silicon using monochromatized SR beam around the Si K-edge. In order to separate the photochemical processes induced by substrate excitation and adsorbate excitation, we have prepared well-defined monolayer, bilayer and multilayer of TMS on Si (100). In the X-ray absorption near-edge structure (XANES) spectrum taken by total electron yield, the peak energy of the resonant excitation from Si 1s to unoccupied @sigma@* orbits for TMS was shifted to higher energy by 6 eV than that for silicon substrate. For monolayer, the desorbed fragment was only CH@sub 3@@super +@ ions. Although the XANES spectrum of monolayer was almost the same as that for silicon substrate, the photon-energy dependences of the CH@sub 3@@super +@ yield followed the XANES spectrum for TMS. The results show that the secondary electrons produced by Auger decay in silicon substrate scarcely contribute to the CH@sub 3@@super +@ desorption. And it was elucidated that the core-to-valence resonant excitation in adsorbed molecule is the main cause of the molecular-ion desorption.

SS-WeP30 Formate Synthesis on Cu(111) by an Eley-Rideal Mechanism*, **M. Sano,*** University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan*; J. Nakamura,* University of Tsukuba, Japan

We have studied the kinetics and the mechanism of the formate synthesis by the hydrogenation of CO@sub 2@ over a Cu(111) model catalyst. The pressure dependence of H@sub 2@ and CO@sub 2@ upon the formation rate of the formate suggested that this reaction proceeds by an Eley-Rideal (E-R) mechanism. We thus examined the formate synthesis by the reaction of gaseous CO@sub 2@ and adsorbed hydrogen on Cu(111), where the experiments were carried out by an in-situ IRAS apparatus with a closed high pressure (1 atm) reactor. The Cu(111) sample was first exposed to 380 Torr H@sub 2@ to prepare a H/Cu(111) surface. Then, the formate synthesis was performed by exposing H/Cu(111) to CO@sub 2@ (380 Torr), where the sample temperature was constant at 308 K while the gas temperature was varied from 310 to 328 K. It was clearly shown that the bidentate formate species was formed on Cu(111) from the reaction of gaseous CO@sub 2@ and adsorbed hydrogen by IRA spectra. Moreover, the initial formation rate of the formate species increased with the heating temperature of gaseous CO@sub 2@ , indicating that the gaseous CO@sub 2@ temperature affects the formation rate of the formate synthesis. The activation energy and the pre-exponential factor of the rate constant were in good agreement with those of formate synthesis from CO@sub 2@ and H@sub 2@ at 760 Torr (P@sub CO2@ /P@sub H2@ = 1). The results mean that the formation rate of the formate synthesis only depends on CO@sub 2@ temperature, further indicating that the formate synthesis proceeds by the direct reaction between gaseous CO@sub 2@ and adsorbed hydrogen. We thus concluded that formate synthesis proceeds by an E-R mechanism.

SS-WeP31 Surface Treatment and Characterization of PMMA, PHEMA, and PHPMA*, **H. Lim,*** Korea University*; Y. Lee,* Korea Institute of Science and Technology*; J. Cho,* Hanyang University, Korea*; S. Han,* Korea Institute of Science and Technology*; K.-J. Kim,* Korea University

Poly(methyl methacrylate)(PMMA), poly(2-hydroxyethyl methacrylate)(PHEMA), and poly(2-hydroxypropyl methacylate)(PHPMA) were modified to improve the wettability using two methods: plasma treatment and Plasma Source Ion Implantation(PSII) treatment. The modified surfaces were characterized to investigate the dependence of polymer structure on the treatment conditions and hydrophobic recovery behaviors. The contact angle measurement was used to calculate the surface free energy. The polar component of surface energy is a dominant factor to improve the wettability. The changes of surface functionality were observed with XPS and ATR-IR. PSII treatment has provided much more various functional groups on the surface and deeper modified layer than plasma treatment during the same treatment time. The surface morphology was investigated by SEM and AFM after treatment. However, the severe surface alteration was not observed. The difference of experimental conditions among the polymers was interpreted by the glass transition temperature which is related to the structure of each polymer.

SS-WeP32 Coadsorption of CO and O@sub 2@ on W(110) Surface, *K.-H. Lee, H.-S. Han, H.-G. Yun,* ***T.S. Yang****, J.-H. Boo, S.-B. Lee,* Sungkyunkwan University, Korea; *H.T. Kwak,* Kookmin University, Korea

The coadsorption of CO and O@sub 2@ on W(110) surface was studied by LEED, TDS, and photoelectron spectroscopy. In the TDS for the coadsorption of CO at RT on O@sub 2@ precovered W(110) surface, two CO desorption states were observed at about 400 and 1150 K, called @alpha@ and @beta@, respectively. The @beta@-CO spectra with second order desorption kinetics were shifted to lower desorption temperature as increasing the amount of preadsorbed atomic oxygen on the W(110). Moreover, the @beta@-CO spectra were gradually increased with increasing the amount of preadsorbed oxygen to 0.5 ML. Even though a (2x1) LEED pattern appeared during oxygen adsorption at RT and 1-3 L oxygen exposures, we didn't observe any new pattern induced by CO in this study. Only the structure of c(11x5) was obtained at temperature in their range of 800-1100 K. These results indicated that there were interaction between CO and O and thereby the @beta@-CO might not be dissociated even at the higher temperature than 800 K. By using the XPS and UPS, it was also confirmed that the coadsorbed @beta@-CO at 950 K doesn't dissociate as the experimental results of the adsorption of pure CO on W(110) surface at the same temperature. According to the valence band spectra, two CO peaks at near 10.7 eV(4@sigma@) and 7.0 eV(5@sigma@+1@pi@) were observed, indicating molecular CO adsorption on the oxygen preadsorbed surface at RT. Even heating the coadsorbed surface to 950 K, we could also detect the CO 4@sigma@ peak that can be an important factor for identifying a contribution of the CO 4@sigma@ molecular orbital to the CO-metal bond. To our best knowledge, this is the first report and quite contradictory result to that reported previously.

SS-WeP33 Effect of the Sample Topography on the Adhesive Force in Atomic Force Spectroscopy Measurements in Air, ***N. Nakagiri***, Nikon Corporation, Japan; *L. Sirghi,* Nagoya University, Japan; *K. Sugisaki,* Nikon Corporation, Japan; *H. Sugimura, O. Takai,* Nagoya University, Japan

It is widely recognized that water thin films formed on probe and sample surfaces greatly affect the atomic force microscopy (AFM) measurements in air. Generally, the interaction between the probe tip and sample surface is a result of superposition of van der Waals, electrostatic, capillary and interfacial tension forces. The latter two forces arise due to water thread usually formed at tip-sample contact region in air and their contribution to the tip-to-sample adhesive force is dominant The effect of local curvature of sample surface on the capillary and interface tension adhesion force of water meniscus formed between AFM tip and sample in air is demonstrated both, theoretically and experimentally. An analytic solution for capillary and tension adhesive force is founded under approximation of thermodynamic equilibrium of a symmetric water meniscus formed at the tip-sample contact region. It is shown that the sample local curvature strongly affects the water meniscus geometry and the adhesion force. Compared to the force computed for a null local curvature of the sample surface, the theoretical model predicts larger/smaller adhesive force for concave/convex local curvature. The theoretical predictions were confirmed by experiment. Atomic force spectroscopy measurements were performed for a silicon nitride cantilever and a standard sample of quartz patterned with 3x3 mm2 in area and 20 nm in depth grooves and platinum covered. Maps of sample surface topography and adhesive force have shown a much small/large force on the high/low part of groove edges, where the sample local curvature is convex/concave.

SS-WeP34 Surface Electronic Structure of Rare Gas Xe on Cu(111): A Scanning Tunneling Microscope Study, ***J.-Y. Park***, *U.D. Ham,* Seoul National University, Korea; *S.-J. Kahng,* University of Illinois at Urbana-Champaign; *Y. Kuk,* Seoul National University, Korea

A newly built ultrahigh vacuum cryogenic scanning tunneling microscope (STM) was used to study the modified surface state and image state on an adsorbate-covered surface, one monolayer (ML) Xe on Cu(111). Electron standing waves were observed on 1 ML Xe-covered Cu(111) as well as on bare Cu surface. By carefully controlling the Xe coverage, standing waves on both bare Cu surface and 1 ML Xe-covered Cu surface could be observed simultaneously in one STM image. Therefore, any possibility of artifact due to different conditions of the tunneling tip can be ruled out. The wavelength of standing waves on Xe layer is ~15% longer (~17Å) than that on Cu surface at sample bias as low as 10meV. By performing scanning tunneling spectroscopy on this surface, dispersions of the surface state both on Xe layer and bare Cu surface are determined. It was found that the onset of the surface state is shifted towards Fermi level by (130±20) meV and the effective electron mass is slightly larger on Xe layer than on bare Cu surface. The electronic lifetime, the multilayer effect, and the effect of image states will also be discussed.

SS-WeP35 STM Barrier-Height Imaging of Alkali Adsorbed Si(111)7x7, ***S. Kurokawa****, A. Sakai,* Kyoto University, Japan

The chemisorption of alkali metals on silicon is one of the most studied adsorption systems, and a large number of theoretical and experimental investigations have been carried out to understand its atomic and electronic structures. However, little has been known on atomic-scale properties of the K adsorption on Si(111)7x7. Hashizume and his coworkers have investigated the initial stage of K adsorption on Si(111)7x7 by STM, and identified some adsorption geometries of K. They also concluded that the bonding between K atoms and Si(111)7x7 surface atoms changes from ionic when K atoms adsorb individually to weakly covalent when they form clusters. We have performed STM imaging and local barrier-height (BH) measurements upon adsorbed K atoms and clusters. The K coverage is about 0.01ML, which corresponds to a very initial stage of adsorption. We found that the local BH decreases at K cluster and each single K atom. The average BH reduction at the K adsorbed site is -1.9 eV under positive sample bias where the electronic structure of tip has little influence on the BH. According to recent photoemission experiments, the reduction of the work function at the saturation coverage of K is -2.9 eV. The measured BH reduction at K sites is smaller than this value but can be a plausible value since the K-Si bonding at the initial stage of adsorption may be different from that in a K overlayer at the saturation coverage. @FootnoteText@ @footnote 1@ T. Hashizume, K. Motai, Y. Hasegawa, I. Sumita, H. Tanaka, S. Amano, S. Hyodo and T. Sakurai, J. Vac. Sci. Technol. B9, 745 (1991).

SS-WeP36 Laser Etching of Si with NF3 using CuBr Laser, ***B. Ivanov****, K. Woynov,* University of Chemical Technology & Metallurgy, Bulgaria; *M.P. Tarassov,* Central Laboratory of Mineralogy and Crystallography, Bulgaria; *L. Zambov, V. Shanov,* University of Chemical Technology & Metallurgy, Bulgaria

Laser induced thermal etching of Si using focused copper bromide vapor laser beam with wavelengths of 510 and 578 nm on monocrystalline Si (100) with NF3 gaseous phase was presented. The laser average power was in the range 4-10 W with repetition rate - 20 kHz and pulse duration - 60 ns. The process parameters were varied in the ranges: scanning speed from 10 to 1000 microns/s, substrate temperature from 100 to 400 C and partial pressure in the range of 100 - 1000 mbar. The etching products were estimated on the base of thermodinamcal calculation. The width, depth and cross section of the etched channels were investigated by Scanning Electron Microscopy (SEM). Some residues on the side wall are removed by subsequent thermal wet etching in KOH solution. In some cases we find evidence for waveguiding effect of laser radiation during the laser etching. The etching rate increases with the scanning speed and is in the range of 2.10^5 - 5.10^6 micron^3/s for the scanning speed of 10 micron/s to 1 mm/s. The aspect ratio of laser etched groves are in the range of 5 - 40 for all structures and reaches 100 for waveguiding part of the trench. This very high etching rate allows using of such process for micromachining of Si. Application of this approach for production of square rods array and field emission like tips was presented.

SS-WeP37 Reactivity of CO over Au Surfaces at Elevated Pressure, ***K.F. Peters****, P. Steadman, O. Robach, J. Alvarez, S. Ferrer,* European Synchrotron Radiation Facility, France

The "Pressure Gap" in surface science separates the well-studied UHV regime from the near-atmospheric pressure regime, where gas-phase catalysis is typically employed. We present first results from a new UHV/HiP surface x-ray diffraction chamber that is capable of spanning the pressure gap over 13 orders of magnitude up to 5 bars or higher.@footnote 1@ The UHV/HiP chamber is employed here to study gas-surface reactivity of carbon monoxide over metals. The Au(111) and Pt(111) surfaces are investigated because of their known inertness to carbon monoxide in vacuum studies. Moreover, CO/Pt(111) is an archetypal model of catalysis, whereas gold is among the most inert metals and is only known to adsorb CO at cryogenic temperatures. The observed gas-surface reactions are unexpectedly strong, owing to the elevated pressures. Both CO/Au(111) and CO/Pt(111) become reactive at near-atmospheric pressures and elevated temperatures. On Au(111), the Herringbone reconstruction can be lifted under certain conditions.@footnote 2,3@ The Pt(111) surface reacts with CO to form a new structure that has never previously been observed in vacuum studies. An important feature of these two examples is that the metal atoms are displaced significantly from their natural positions, which is uncommon in traditional examples of gas adsorption. @FootnoteText@ @footnote 1@P.Bernard, K.F.Peters, J.Alvarez, S.Ferrer, Rev.Sci.Instr., 70, 2, 1999, 1478-1480. @footnote 2@Steadman et al, accepted to Phys.Rev.B @Footnote 3@Peters et al, submitted.

Semiconductors
Room 306 - Session SC+EL+SS-WeA
Semiconductor Alloys

Moderator: P. Desjardins, Ecole Polytechnique de Montreal

2:00pm **SC+EL+SS-WeA1 Si-Ge Heterostructures***, **K.L. Wang**,* University of California, Los Angeles **INVITED**

PLEASE SEND US AN ABSTRACT. Thank you.

2:40pm **SC+EL+SS-WeA3 Critical Behavior of Epitaxial Si@sub 1-x@Ge@sub x@/Si(001) Islands***, **R.A. Budiman**, H.E. Ruda, D.D. Perovic, B. Bahierathan,* University of Toronto, Canada

We study the island size distributions of three-dimensional Si@sub 1-x@Ge@sub x@/Si(001) islands of varying Ge fractions (x = 0.4-0.7) and thicknesses grown by ultrahigh vacuum chemical vapor deposition. The size distributions of the percolating islands obey the dynamic scaling hypothesis due to random percolation process, only in the small island limit. Morphologies of the islands strongly suggest a presence of Smoluchowski ripening mechanism, in which islands collide and ripen. We therefore combine random percolation and Smoluchowski ripening to analyze the size distributions. To understand the critical behavior of the islands as exhibited by their size distributions, we formulate a mean-field theory of coherently strained island formation by incorporating surface energy and strain relaxation. The resulting phase diagram shows that the island formation in Si@sub 1-x@Ge@sub x@/Si(001) is located near the critical region. Order parameter fluctuations can be estimated by calculating the curvature energy for such a system and we find that the strain fluctuation is indeed relevant to properly describe the island formation in the Si@sub 1-x@Ge@sub x@/Si(001) system.

3:00pm **SC+EL+SS-WeA4 Growth of Coherent Three-dimensional Si Islands on Ge(111)***, **A. Raviswaran**, C.P. Liu,* University of Illinois, Urbana-Champaign*; J.M. Gibson,* Argonne National Laboratory*; D.G. Cahill,* University of Illinois, Urbana-Champaign

We study the evolution of three-dimensional islands during Si/Ge(111) epitaxy. The strain due to lattice mismatch (4.2% tensile) and the difference in the surface energies (@gamma@@sub Si@>@gamma@@sub Ge@) contribute to the formation of the three-dimensional Si islands. We grow Si islands on pseudomorphic Si@sub 0.15@Ge@sub 0.85@ buffer layers (deposited on Ge(111) substrates) in the temperature range 500°C - 650°C using MBE; the (111) orientation is used because the critical thickness of Si layers on Ge(111) is larger than that on Ge(001). We characterize the morphology and relaxation of the Si islands using ex situ AFM, TEM and SEM. Islanding occurs at 1 BL Si coverage, i.e., without the formation of a wetting layer. We observe high densities (~ 10@super 12@ cm@super -2@) of coherent, circular base islands for growth temperatures 500°C - 600°C and low Si coverage (< 2 BL Si). The density and shape of the islands is insensitive to the growth temperature. Beyond a critical width the islands relax plastically, by the nucleation and glide of misfit dislocations; this critical width is ~ 16 nm at 550°C and ~ 25 nm at 600°C. We observe large, incoherent, irregularly shaped islands at higher temperatures (> 600°C) and coverages (> 4 BL Si). As the islands transform from coherent to incoherent, coarsening occurs which results in an increase in the island width and a reduction in the island density. The high temperature (> 600°C) growths show a secondary maximum in the island density near 4 BL Si coverage.

3:20pm **SC+EL+SS-WeA5 Adatom Assisted Stabilization of Ad-dimers on Ge(001)***, **E. Zoethout**, H.J.W. Zandvliet, B. Poelsema,* University of Twente, The Netherlands

Studies of the early stage of near room temperature growth of silicon on Ge(001) have revealed an inconsistency between experimental@footnote 1@ and theoretical@footnote 2@ work. Experimentally a stable cluster has been labeled to be a trough dimer oriented perpendicular to the substrate dimer bonds (D-dimer). The same type of cluster is found in the early stage of near room temperature homoepitaxial growth on Ge(001). Theoretically such a D-dimer is predicted to be energetically unfavorable. It turns out that the apparent D-dimer is actually comprised of three rather than two atoms. The three-atom cluster of Ge or Si on Ge(001) is shown to differ from a trough dimer orientated along the substrate dimer bonds, from a small epitaxial island and also from a three-atom Si cluster on Si(001). The three-atom cluster of Ge or Si on Ge(001) is composed of an ad-dimer in the D-configuration and an adatom on the neighboring substrate dimer row. @FootnoteText@ @Footnote 1@W. Wulfhekel, B.J. Hattink, H.J.W. Zandvliet, G. Rosenfeld, and B. Poelsema, Phys. Rev. Lett. 79, 2494 (1997). @Footnote 2@S.V. Khare, R.V. Kulkarni, D. Stroud and J.W. Wilkins, Phys. Rev. Lett. 60, 4458 (1999).

3:40pm **SC+EL+SS-WeA6 C Incorporation during the Growth Of Ge@sub 1-y@C@sub y@/Ge(001) from Hyperthermal Beams***, **J. D'Arcy-Gall**, D. Gall, P. Desjardins, I. Petrov, J.E. Greene,* University of Illinois, Urbana

C-containing group-IV semiconductor alloys are of interest due to the potential they offer for both band gap and strain engineering in microelectronics. This investigation focuses on the effects of incident particle energy and film growth temperature T@sub s@ on the distribution of C lattice configurations in Ge@sub 1-y@C@sub y@ epitaxial layers grown on Ge(001) from hyperthermal beams obtained by ultra-high vacuum ion-beam sputtering using Kr@super +@. All Ge@sub 1-y@C@sub y@ (y @<=@ 0.03) layers, grown at T@sub s@ = 245-415 °C, are fully-coherent and free of extended defects as judged by high-resolution x-ray diffraction, reciprocal lattice mapping, and transmission electron microscopy. The strain-state of epitaxial Ge@sub 0.99@C@sub 0.01@ alloys grown at T@sub s@ = 300 °C changes from in-plane tension to compression as the Kr@super +@ energy E@sub Kr@ is increased from 300 to 900 eV. This results from an increasing fraction of C incorporated in Ge-C split interstitial sites as a result of the trapping, by substitutional C, of Ge self-interstitials formed due to irradiation by the increasing fraction of sputtered Ge atoms in the high energy tail of the energy distribution. These results are supported by TRIM simulations which show that the number of displaced lattice atoms per incident hyperthermal Ge increases from 0.10 with E@sub Kr@ = 300 eV to 0.24 at 900 eV, and ab initio calculations of layer strain for different C lattice configurations. All Ge@sub 1-y@C@sub y@ alloys grown at E@sub Kr@ = 900 eV are in a state of in-plane compression, which decreases with increasing T@sub s@. Raman scattering results show that the substitutional C concentration in these layers is negligible. Comparison of experimental results with ab initio calculations reveals that an increasing fraction of C incorporates as C pairs as T@sub s@ is increased due to the higher C-C encounter probability on the growth surface.

4:00pm **SC+EL+SS-WeA7 Growth and Characterization of Metastable Ge@sub1-x@C@subx@ Thin Films on Si(100) Substrate.***, **W. Li**, D. Guerin, S.I. Shah,* University of Delaware

The Ge-C system is of interest due to the possibility of band gap engineering on Si. For strain free deposition of Ge@sub1-x@C@subx@, a carbon concentration in excess of 10% is required, assuming that the system obeys Vegard's law. The maximum equilibrium solubility of C in Ge, however, is only 10@super8@/cm@super3@. Molecular beam epitaxy and chemical vapor deposition have been used to grow metastable Ge@sub1-x@C@subx@ thin films with x up to 2.5%. We have used a bias assisted sputter deposition using Ge and C magnetrons to obtain the epitaxial Ge@sub1-x@C@subx@ films with extended carbon solubility. Without any applied substrate bias and C flux, a Ge epitaxial layer on Si(100) substrate was obtained at 750°C with proper substrate preparation. Based on the results of pure Ge epitaxy, C was systematically added. Without the substrate bias, x-ray diffraction analyses show that the films were polycrystalline. With the application of a substrate bias, we were able to obtain epitaxial Ge@sub1-x@C@subx@ films. The Ge (400) XRD peak shifts to higher 2@theta@ were observed indicating C incorporation in the Ge lattice. Extended x-ray absorption fine structure (EXAFS) analyses confirmed that the C was indeed incorporated on the substitutional sites in the Ge lattice. C concentration was determined from XRD, X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS). A C concentration of up to 5 at.% was obtained. Depth profiles of samples by XPS show that carbon is uniformly distributed in the film. Experiments are underway to study the effects of bias and thickness on the epitaxial deposition of Ge@sub1-x@C@subx@ with even further extension of the concentration of substitutionally situated C in germanium lattice.

4:20pm **SC+EL+SS-WeA8 Electrical and Optical Properties of Silicon : Germanium Alloys prepared by DC Magnetron Sputtering***, **A. Subrahmanyam**, S. Karthikeyan, J. Asbalter,* Indian Institute of Technology, Madras, India*; P. Amirtharaj,* National Institute of Standards and Technology

The Silicon: Germanium (Si:Ge) alloys are being used in various semiconductor devices. As is well known, these alloys offer advantages in band gap engineering, and can integrate well with the existing silicon technology. Several studies have been made on these alloys. In the present paper, we report the electrical and optical properties of Si:Ge alloys prepared by DC Magnetron sputtering technique. A 7.5 cm diameter circular magnetron cathode has been designed and fabricated. The balanced magnetron cathode is operated at low pressures (4.0 x 10@super -3@ mbar). Argon is the sputter gas. The target is prepared by bonding commercially available Silicon wafer to the water cooled copper backing plate. A small portion of the erosion area on the magnetron cathode is covered with pure germanium wafer. The alloys of Si:Ge (undoped) are prepared (at room temperature 25°C) on glass and Si substrates. The growth parameters in the present study are : flow rate of argon (180 - 250 sccm), Magnetron power (80 - 225 watts) and germanium content in the alloy. The thickness and refractive index of the films is measured by ellipsometer in the wavelength range 300 - 700 nm. The thickness of these alloy films is about 150 nm. The alloy films have been found to be amorphous. The germanium content in the alloy films is varied between 15 - 30 atomic % and is estimated by EDAX and RBS analysis. The optical absorption and photo conductivity measurements have been made on these alloys. The optical band gap of these alloys is in the range 1.45 - 1.6 eV. The dark conductivity is in the order 10@super-@ mho cm@super-1@. The deposition rate is observed to be linear with the magnetron power till 120 watts.

4:40pm **SC+EL+SS-WeA9 Preparation and Characterization of Highly Li-doped a-Se Alloy Films for Thermal Neutron Detectors***, **K.C. Mandal**, B. Dille, R.D. Rauh,* EIC Laboratories, Inc.*; A. Burger,* Fisk University*; R.N. Bhattacharyya,* National Renewable Energy Laboratory

This paper describes our recent research in developing highly Li-doped a-Se alloys and thin films for thermal neutron detector applications. The grown Li-doped (35 a/o) a-Se alloy thin films have shown high promise for this application due to the presence of Li in high concentrations, high dark resistivity (2x10@super 14@@ohm@. cm), good charge transport properties (mu-tau@sub e@ = 3.2x10@super -6@ cm@super 2@/V), low cost and relatively easy scale up. Highly Li-doped a-Se alloy has been synthesized in controlled ambient and used for making large area films up to 4x4 sq. inch. The vacuum evaporated a-Se alloy films have been characterized by X-ray diffraction (XRD), atomic absorption (AA), differential thermal analysis (DTA), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The detectors fabricated from these films have demonstrated potential for thermal neutron detection for the first time. Details of various steps involved in detector fabrication and testing of these devices will also be presented.

5:00pm **SC+EL+SS-WeA10 Instability in Atomic Step Morphology during the Sublimation of Si(111)***, **Y. Homma**, P. Finnie,* NTT Basic Research Laboratories, Japan

A morphological instability has been predicted to occur during step-flow crystal growth.@footnote 1@ Recently we experimentally demonstrated transitions between stability and instability@footnote 2@ during epitaxial growth on an ultra-flat Si(111) terrace - a terrace which is atomically flat on a 100 µm scale. In this paper, we show that such instability can also occur during step-flow sublimation at high temperatures. Step motion due to sublimation was tracked with in situ scanning electron microscopy. When the size of a terrace becomes comparable to the adatom diffusion length, a new step is nucleated, forming the edge of a new, monolayer-deep crater at the center of an ultra-flat terrace. As a result of successive expansion and nucleation, steps become distributed in a concentric circular pattern. The spacing between steps can be controlled by varying the annealing temperature. When the spacing is less than about 20 µm, the innermost step is typically smooth and nearly circular. For larger spacings, the innermost crater is irregularly shaped while it is still relatively small. The crater becomes smoother as it expands. The instability is manifest when the width of the lower terrace is much smaller than that of the upper terrace. Since the adatom flux from a step to a neighboring terrace depends on the terrace width, by reducing the size of the stabilizing terrace the instability can be initiated. The behavior of a subliming surface is thus similar to that of the growing surface. @FootnoteText@ @footnote 1@ G. S. Bales and A. Zangwill, Phys. Rev. B 41 (1990) 5500 @footnote 2@ P. Finnie and Y. Homma, Phys. Rev. Lett. to be published.

Surface Science
Room 208 - Session SS1+MC-WeA

Oxide Surfaces, Interfaces and Defects

Moderator: R.L. Kurtz, Louisiana State University

2:00pm **SS1+MC-WeA1 Metal/Metal-Oxide Interactions and Structures in Bulk Truncated and Thin Film Systems --The Theoretical View***, **D.R. Jennison**,* Sandia National Laboratories **INVITED**

Using DFT with up to hundreds of atoms per slab unit cell, I use several sources to illustrate basic principles concerning metal-oxide surfaces, interactions with adspecies and metal overlayers, and ultrathin (<1nm) oxide films on metals and adsorption thereon: 1) Metal oxides vary greatly in relaxation to adsorbates, with those of alumina among the largest. This surface becomes so locally oxidizing that multiply charged metal adatoms can occur. 2) The interface between an oxide film and a basal-plane metal substrate can differ fundamentally. Most metals prefer O(1x1), but the nobel metals prefer cations, which convert to a somewhat positive metallic layer with O-ions above. 3) Point defects can nucleate metal islands and alter growth and adhesion. However, common Fs and Vs centers destabilize metal dimers (the first step in nucleation), while another common defect, ad-OH, does the opposite. In fact, 1/3 ML of ad-OH on sapphire reverses the growth mode and more than doubles the adhesion of Cu metal. These results are simply due to geometry and electrostatics. 4) Ultrathin film adsorbate response depends on the substrate: While alumina on Ru is rather inert to a Pd overlayer, the film on Al(111) reacts strongly, drawing substrate metal into the oxide and extruding Al from the top to form a Pd/Al interface. Such is explained by cohesive energy differences between Al and Ru. 5) While complex mixed structures of oxides and metals cannot be predicted by simulation, proposals from STM data can be tested. In addition, model calculations expose basic factors such as interface preference, near-interface oxide film structure, and the resulting film stress, explaining the presense and variety of relief mechanisms. In this active field, examples, including experimental results, are drawn from alumina, magnesia, and titania. My valued collaborators are several. @footnote 1,2@ @FootnoteText@ @footnote 1@www.sandia.gov/surface_science/drj/. @footnote 2@Supported by US DOE.

2:40pm **SS1+MC-WeA3 Ultrathin Fe Oxides on Cu(001): a Search for Half-Metallic Films***, **R.H. Madjoe**, A.N. Koveshnikov,* Louisiana State University*; J. Karunamuni,* University of South Carolina*; R.L. Stockbauer, R.L. Kurtz,* Louisiana State University

Half-metallic oxides such as CrO2 and Fe3O4 may provide opportunities for new magnetic devices since their single spin orientation at the Fermi level gives rise to spin-dependent transport. However, these films are most often grown on oxide substrates which are not currently incorporated in GMR devices. We report a study of the electronic and geometric structures of Fe3O4 films grown on copper, which is currently used in commercial heterostructures. A broad array of techniques including ARUPS, NEXAFS, LEED and STM were used to characterize these films. They were grown by depositing Fe on Cu(001) at room temperature and oxidizing at 810K in 10-6 Torr O2 ambient. The particular oxide phase that forms depends on the initial Fe thickness. For Fe films less than 2 ML thick, LEED and STM measurements show that oxidation produces an FeO(111) bilayer. The oxide forms long, narrow strips with two mutually-perpendicular orientations aligned along Cu[110] and [110]. Oxidation of thicker Fe layers give crystallites of Fe3O4(111) of micron dimensions, which are oriented 15Â° from the [010] directions and highly lattice-matched to the Cu substrate. Both core level and valence band photoemission data will be presented. Difference spectra show that the interfaces of these films have a metallic density of states at EF, unlike any of the bulk phases of iron oxide. Near-edge x-ray absorption fine-structure (NEXAFS) at both the oxygen K- and Fe L2,3-edges will be presented in addition to magnetic linear and circularly-polarized dichroism (MLD, MCD) data. These data will be discussed in the context of the evolution of the electronic structure to that of thicker bulk-like oxide films.

3:00pm **SS1+MC-WeA4 Low Temperature Microcalorimetric Heats of Adsorption and Sticking Probabilities of Metals on Oxide Surfaces***, **D.E. Starr**, C.T. Campbell,* University of Washington

Single crystal adsorption microcalorimetry is a powerful method to study the heats of adsorption of gaseous atoms or molecules onto single crystal surfaces. The technique has been utilized to study the energetics of metal film growth from the initial stages of growth through the multilayer regime. Results for metal deposition onto metal oxide substrates all indicate an initial heat of adsorption much lower than the bulk heat of sublimation of the metal. This indicates a weaker interaction of the metal atoms with the substrate than with themselves, providing insights into the energetic driving force for the three dimensional islanding of the metal film in the submonolayer regime. Recent advances in this technique has allowed the first low temperature measurements (~ 160 K) to be performed. Low temperature results for the deposition of Pb onto a MgO(100) thin film grown on Mo(100) will be presented. These measurements have similar sensitivities to room temperature measurements. The changes in the heat of adsorption versus coverage from room temperature measurements to low temperature result from the kinetic factors governing the film morphology. In conjunction with the calorimetric measurements, the metals sticking probability as a function of coverage at a variety of temperatures allows kinetic parameters to be extracted from the model fit to the sticking probability curves. This results in deeper insights into the microcalorimetrically measured heats of adsorption.

3:20pm **SS1+MC-WeA5 Electronic Structure of Grain Boundaries in TiO2 from Ab-Initio Calculations***, **Z. Mao,** S.B. Sinnott, E.C. Dickey,* The University of Kentucky*; R.F. Wood,* Oak Ridge National Laboratory

It is well known that the properties of grain boundaries have important effects on the electronic and chemical properties of polycrystalline materials. In this work, we apply first principles electronic structure calculations to study the structure of TiO@sub 2@ grain boundaries and compare the results to experimental data. Specifically, the density functional method within the local density approximation is used to determine the structure of several tilt grain boundary structures in TiO@sub 2@. In addition, intrinsic defect formation energies at these boundaries are calculated by examining the stability of various individual defects within the bulk and at the grain boundary. These results provide information about the atomic basis for grain boundary space charge segregation and its dependence on grain boundary structure. This work is supported by the National Science Foundation (DMR-9976851).

3:40pm **SS1+MC-WeA6 Surface Defects on MgO Thin Films: Formation, Detection, Electronic and Chemical Properties***, **A.A. Kolmakov,** X. Lai, J.A. Stultz, D.W. Goodman,* Texas A&M University

Surface defects play a significant role on metal oxide surfaces since they determine its electronic structure, chemical reactivity and adsorbate kinetics. There is great interest in studying surface defects on thin-film metal oxides to understand the properties of supported catalysts and gas sensing devices at the molecular level. Because of the low density of these oxide defects and sample charging, experimental studies of oxide surface defects still remain a challenging task. Using an ultrathin film deposition methodology and high surface sensitive capabilities of metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS) and temperature programmed desorption (TPD) along with scanning tunneling microscopy (STM), the properties of surface and near-surface defects were probed. A comparative study of morphology and electronic structure with reactivity of low-defect MgO(100) films was undertaken. Defect-ridden films exhibited occupied levels located ~2 eV above the top of the valence band, observed as a separate band in MIES, unlike defect-free thin films. This additional feature was attributed to the emission of electrons from point defects (F-centers) created on the surface and subsurface regions. Initially unseen in MIES, extended defects became detectable via NO titration. These defects manifest themselves as strong, reactive centers. MIES and TPD data indicate that at ~100 K, NO adsorbs dissociatively on surface defects and produces N@sub 2@O. Differences in electronic and chemical properties between these two films were further evidenced from their morphological differences as observed by STM.

4:00pm **SS1+MC-WeA7 Metallic Electronic States on SrTiO@sub 3@ (110) Surface -- An In Situ Conduction Measurement***, **H. Bando,*** Electrotechnical Laboratory, Japan*; Y. Ochiai,* Ibaraki University, Japan*; Y. Aiura,* Electrotechnical Laboratory, Japan*; Y. Haruyama,* Himeji Institute of Technology, Japan*; T. Yasue,* University of Tsukuba, Japan*; Y. Nishihara,* Ibaraki University, Japan

In our previous works we detected metallic electronic states on the SrTiO@sub 3@ (110) surface after annealing in ultra high vacuum (UHV) at relatively low temperature, @<=@ 800 °C, based on a sharp Fermi edge detected by ultraviolet photoemission spectroscopy and finite zero-bias differential conductance by scanning tunneling spectroscopy. In order to verify the metallic feature of the surface as a macroscopic property, electric conductance is measured in situ. For the measurement, a sample holder is designed which enables both annealing in UHV by electron beam and 4-probe electric conduction measurement with uniform electric field. Conductance contributed by bulk is separated by measuring the decrease of total conductance by adsorption of oxygen at room temperature, which is supposed to modify only the surface electronic states. Surface conductance is deduced between 150 K to 300 K and showed a metallic feature. Comments will be presented on the effects of surface anisotropy and photo-induced carriers. Moreover, the surface conductance during exposure to oxygen is monitored in situ, and showed a reversible-like change depending on the oxygen pressure. This possibly evidences that the oxygen molecules which temporarily stay on the surface suppress the conduction by surface electrons.

4:20pm **SS1+MC-WeA8 First-Principles Calculations on Al@sub 2@O@sub 3@/TiC Growth and Interface***, **C. Ruberto,** B.I. Lundqvist,* Chalmers University of Technology and Göteborg University, Sweden

First-principles calculations based on density-functional theory are performed to understand the first steps in the growth of alumina on TiC(111). The alumina/TiC interface is theoretically very interesting, being an example of interface between an oxide, ionic and insulating, ceramic and a covalent transition-metal ceramic with metallic and ionic character. The TiC(111) facet is furthermore a highly active and polar surface. Technologically, the interface is of high importance in wear-resistant cutting tools used in industrial high-speed applications. Different phases of alumina (mainly the @alpha@ and @kappa@ phases) are used as chemically-inactive coatings on cemented-carbide tools. These coatings are grown on TiC(111), TiN(111), or Ti(C,N)(111) through chemical-vapor deposition (CVD). It is known that the coating quality and phase content are determined by the nucleation on the substrate surface. For example, a region of @gamma@ alumina is sometimes observed between TiC and @kappa@ alumina. This work is the first step towards establishing a fundamental understanding of the interfacial structure and of the growth of alumina on TiC(111). This is done in several steps. We investigate the adsorption energies of the different atomic species present in the CVD reactor on the TiC(111) surface. The energetics for the different atomic configurations of an aluminum layer at 2/3 coverage on TiC(111)-O are studied and the observed structural stability is understood on the basis of bonding character. The influence of thermal lattice expansion is discussed. The stability and bonding character of a layer of stoichiometric Al@sub 2@O@sub 3@ in different structural configurations on TiC(111)-O are then examined. Finally, the structure and stability of all different atomic terminations of the @kappa@-Al@sub 2@O@sub 3@(001) and (00-1) surfaces, the preferred CVD growth direction, are presented and discussed.

4:40pm **SS1+MC-WeA9 Self-Diffusion in Ceria***, **C.L. Perkins,** M.A. Henderson, G.S. Herman,* Pacific Northwest National Laboratory

Ceria, an oxygen storage material vital to the proper functioning of automobile three-way catalysts, is typically viewed as an anion conductor. In light of mounting evidence that in the prototypical oxide rutile TiO@sub 2@ the mobile species are Ti cations rather than O anions, the diffusivities of both cerium and oxygen in ceria were explored via temperature programmed static secondary ion mass spectrometry (TPSSIMS). The 500 Å thick CeO@sub 2@(111) film was heteroepitaxially grown by molecular beam epitaxy on a yttria stabilized zirconia substrate. Although high quality LEED patterns and Auger spectra free of signals from elements other than cerium and oxygen were obtained after just a few sputtering and annealing cycles, further cleaning was necessary to remove intense alkali and alkaline earth signals observed in SSIMS. The CeO@sub 2@(111)surface was slightly enriched in @super 18@O by first annealing the film in UHV at 830 K and then exposing the 130 K crystal to @super18@O@sub 2@. TPSSIMS data in conjunction with temperature programmed desorption (TPD) data demonstrate that surface oxygen begins to diffuse into the bulk around 550 K. Physical deposition in an @super18@O@sub 2@ background of submonolayer amounts of isotopically enriched cerium (@super 136@Ce) allowed the simultaneous study of the diffusivity of both cerium and oxygen. Surface cerium cations were found to be immobile with respect to diffusion into the bulk up to the highest temperature studied, 900 K.

5:00pm **SS1+MC-WeA10 Defect Characterization on MgO(100) Using Adsorption of Small Molecules***, **Z. Dohnálek**, G.A. Kimmel, R.S. Smith, S.A. Joyce, B.D. Kay,* Pacific Northwest National Laboratory

MgO(100) films with controlled defect densities are grown epitaxially on Mo(100). The crystalline order is probed using both low energy electron diffraction (LEED) and the adsorption of small probe molecules such as N@sub 2@, Ar, CO, CH@sub 4@, H@sub 2@O, NH@sub 3@ and CH@sub 3@OH. Significant changes in the LEED beam profiles are observed for films grown at various substrate temperatures, deposition rates, and film thicknesses. Thick films grown at high temperatures yield the sharpest

LEED profiles. While the quality of the LEED pattern is related to the presence of morphological defects, it is difficult to quantify and characterize the defects by LEED alone. Temperature programmed desorption (TPD) of physisorbed molecules deposited at 20K reveals a wide distribution of binding sites on the highly-defective films. Analysis of the TPD spectra yields the binding energies and concentrations of these defect sites for various adsorbates. Both the LEED and TPD from the highest quality epitaxial films are indistinguishable from highly-ordered bulk MgO(100). Even on the best surfaces, a well resolved minority desorption channel related to defects is observed, thereby demonstrating the high sensitivity and quantitative nature of TPD in characterizing defects. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

Surface Science
Room 209 - Session SS2+VT-WeA
Adsorption and Desorption Phenomena I

Moderator: C.M. Friend, Harvard University

2:00pm **SS2+VT-WeA1 The Role of Two-dimensional Compressibility in Physisorption, Competitive Adsorption and Dynamic Displacement***, **G.A. Kimmel**, Z. Dohnálek, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory **INVITED**

We have investigated the physisorption of gases (Ar, N@sub 2@, CH@sub 4@, etc) on Pt(111) with modulated beam techniques, beam reflection measurements and temperature programmed desorption (TPD). The kinetics of adsorption and desorption for systems where the coverage is larger than ~0.8 monolayer (ML) is dominated by the two-dimensional compression of the adsorbate layer. In particular, at coverages near 1 ML the repulsive interaction between adsorbates increases causing an approximately linear decrease in binding energy as the coverage increases. The formation of the first monolayer is complete when the binding energy of the adsorbates in the compressed first layer is equivalent to the binding energy of an adsorbate in the second layer (i.e. when the chemical potential of the first and second layers are equal). Evidence for this compression arises in the TPD of physisorbed gases from Pt(111) which reveal a non-zero, nearly constant desorption in the temperature range between the desorption peaks of the "first" and "second" monolayers. Modulated beam experiments also support this interpretation. In that case, the Pt(111) surface is pre-covered with ~1 ML of gas and then exposed to gas pulses of varying duration (~0.05 s - 1.0 s) and the desorbed/reflected flux is monitored. Another example where the two dimensional compression of the adsorbate layer is important occurs when the "competitive" adsorption of two gases is examined. In these experiments, an adsorbate can be displaced/desorbed when the surface is exposed to a gas which has a higher binding energy to the substrate. We will present a simple model for the binding energy as a function of coverage which explains the observed adsorption/desorption kinetics for a variety of systems.

2:40pm **SS2+VT-WeA3 Molecular Adsorption and Growth of n-butane Adlayers on Pt(111)***, **J.F. Weaver,*** University of Florida*; M. Ikai, A. Carlsson, R.J. Madix,* Stanford University

The molecular adsorption of n-butane and the growth of n-butane adlayers on Pt(111) have been investigated using molecular beam techniques, temperature-programmed desorption and low-energy electron diffraction. Our results indicate that four adlayer phases develop sequentially as the n-butane coverage increases from the submonolayer to second layer ranges at surface temperatures near 98 K. The structural properties of the adlayer and the kinetics for adlayer growth will be discussed in detail. Interestingly, although the changes in adlayer structure significantly affect the rates of n-butane desorption and surface diffusion, the adsorption probability of n-butane on Pt(111) is found to increase smoothly with increasing coverage. This finding indicates that the long-range arrangements and orientations of molecules in the n-butane adlayer have a negligible influence on the intrinsic adsorption dynamics, suggesting that the energy transfer processes that facilitate adsorption are highly localized.

3:00pm **SS2+VT-WeA4 Optical Effects of Monolayer and Multilayer Adsorption: Formic Acid and Methanol on Cu(100)***, **C.-L. Hsu,** E.F. McCullen, R.G. Tobin,* Tufts University

We have studied the adsorption of formic acid (HCOOH) and methanol on epitaxial Cu(100) films at 125 K in both the monolayer and multilayer regimes, using infrared reflectance and dc resistance measurements and visible-light ellipsometry. The results are analyzed using an electron scattering model for reflectance changes due to chemisorbed monolayers, and a macroscopic three-layer model for physisorbed multilayers. For methanol, which is only physisorbed on Cu, the infrared reflectance increases linearly with film thickness (determined ellipsometrically) in agreement with the three-layer model. For formic acid the first monolayer is chemisorbed and scattering of conduction electrons from the adsorbates leads to an initial decrease in reflectance, together with an increase in the electrical resistance of the Cu film. At higher formic acid exposures physisorbed multilayers form, leading to a reflectance increase similar to that observed for methanol. This behavior is qualitatively consistent with expectations, but there are some surprising features. As formic acid exposure increases, the initial reflectance drop continues even after the resistance change is largely complete, even though both effects are believed to result from the same process. The subsequent rapid rise in reflectance suggests that the sticking coefficient is much lower for the first layer than for subsequent layers. Possible explanations for these effects will be discussed.

3:20pm **SS2+VT-WeA5 Precursor-mediated Dissociation and Trapping Desorption of Oxygen on Cu(001)-2@sr@2x@sr@2-O***, **M. Yata,** Y. Saitoh,* National Research Institute for Metals, Japan

The adsorption and desorption of oxygen on Cu(001)-2@sr@2x@sr@2-O has been studied by molecular beam method. Angular and time-of flight distributions have been measured for scattering oxygen from the surface. The time-of flight distributions can be fitted by nonshifted Boltzmann distributions. This means that the oxygen molecules are trapped at the surface in a precursor state and subsequently desorb from the surface. The translational temperature of the desorbing oxygen is lower than the surface temperature, which suggests that there is no barrier for desorption from the precursor state. The dissociative sticking probability of oxygen increases as the translational energy of incident oxygen decreases. This probability also increases with increasing surface temperature. These results suggest that the adsorption of oxygen on the Cu(001)-2@sr@2x@sr@2-O surface proceeds via a precursor-mediated dissociation process rather than by a direct activation process. This is contrast to the dissociative adsorption of oxygen on clean Cu(001) in which the dissociation occurs by direct collisional activation. There exists a competition between dissociation reaction and desorption once the oxygen molecule is trapped in the precursor state. We have estimated the difference in activation energies between the dissociation and desorption of 330 meV. The effect of tensile stress on the dissociative adsorption reaction of oxygen on the Cu(001)-2@sr@2x@sr@2-O surface will be also discussed.

3:40pm **SS2+VT-WeA6 The Effect of Deposition Pressure on Adsorbate Structure and Coverage: Oxygen on W(110)@footnote 1@***, D.E. Muzzall,* University of California, Davis*; C.S. Fadley,* University of California, Davis and LBNL*; **S. Chiang**,* University of California, Davis

In most prior surface science studies, it has been assumed that total exposure, rather than pressure and time as independent variables, controls the types of adsorption structures formed. The importance of deposition pressure as a variable, however, was recently suggested in a study of the kinetics of the low pressure adsorption of oxygen on W(110) using X-ray photoelectron spectroscopy (XPS)and diffraction.@footnote 2@ As a more quantitative measure of such effects, we have used ultrahigh vacuum scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and XPS to explore the adsorbate structures and the coverage dependence of O/W(110) as a function of deposition pressure at room temperature. For the same total adsorbate exposure in Langmuirs (L), we find that changes in deposition pressure of as little as a factor of 3 cause significant changes in the apparent structures, domain sizes (e.g., of (1x2)O), and adsorbate coverage in monolayers. Total coverages derived from STM data using a software thresholding technique indicate that a critical dosing pressure exists for both the (2x1) and (2x2) structures, 1 x 10@sup -9@ and 3 x 10@sup -9@ torr respectively, below which coverage does not increase with increasing exposure time. This indicates that an equilibrium condition has been reached, from which surface free energies for both of these structures can be derived.@footnote 3@ Finally, in addition to the ordered (1x2), (2x2), and (1x1) structures for O/W(110), we have characterized a new fourth ordered structure by LEED and STM. The structure formed for oxygen exposure of 3 to 6 L and coexisted with the (1x2) structure. The primitive unit cell is a rectangle, 0.77nm x 1.37nm, with 15 W and 6 O atoms and has the matrix notation ((3,-1),(0,5)) relative to the W(110) substrate. @FootnoteText@ @footnote 1@ Supported by NSF

DMR-9522240. @footnote 2@ Y. X. Ynzunza et al, Surf. Sci., in press. @footnote 3@ P. Liu et al, Surf. Sci. 417 (1998) 53.

4:00pm **SS2+VT-WeA7 STM Investigation of Benzene Adsorption on Ag(110)***, **K.F. Kelly**, J.J. Jackiw,* Pennsylvania State University*; J.I. Pascual, H. Conrad, H.-P. Rust,* Fritz Haber Institute, Germany*; P.S. Weiss,* Pennsylvania State University

We have investigated the adsorption of benzene on Ag(110) using the scanning tunneling microscope. We found that the molecules preferentially adsorb above step edges at 66 K. The preference for step edge adsorption is attributed to the Smoluchowski effect enhancing the empty states to which charge is donated from the @pi@ orbitals of the benzene. However, there is no adsorption at the [001] steps. A lack of free charge due to a gap in the Ag Fermi surface along that direction reduces the Smoluchowski effect and thus the adsorption at these steps. After further deposition at 4 K, we find that benzene forms a weakly adsorbed hexagonal monolayer. The monolayer is imaged at large tip-sample separations and is transparent upon closer approach. The interaction of benzene molecules with steps and point defects reduces this transparency.

4:20pm **SS2+VT-WeA8 Scanning Tunneling Microscopy and Spectroscopy of Metal Tetraphenylporphyrins on Au(111)***, K.W. Hipps, **D.E. Barlow**, L. Scudiero,* Washington State University

STM images of metal(II) tetraphenylporphyrin monolayers on Au(111) are presented for several transition metal ions. The constant current images clearly reflect the electronic nature of the metal ion used. Scanning tunneling spectroscopy (dI/dV curves) also allows one to differentiate between the metal complexes. The primary electroactive states, as shown by tunneling spectroscopy, are those involving both occupied and unoccupied molecular orbitals close to the Fermi energy of the Au(111) substrate. Scanning tunneling spectroscopy results for the negative sample bias region are compared to Ultra-violet photoelectron spectra of these same compounds on Au.

4:40pm **SS2+VT-WeA9 Theory of Oxygen Adsorption on Ag(111): A DFT-GGA Investigation***, W. Li,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; **C. Stampfl**,* Northwestern University*; M. Scheffler,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

O/Ag(111) is an important system with unique catalytic behavior for several large-scale industrial processes, e.g., ethylene epoxidation and partial oxidation of methanol to formaldehyde. In spite of its importance, very little is known about the behavior of O at Ag(111) (which depends sensitively on pressure and temperature) on the microscopic level, and the precise atomic location and chemical nature of the various O species that form, e.g. on-surface, subsurface, in-surface. Using density-functional theory within the generalized gradient approximation, we investigate the interaction between oxygen and Ag(111). We found that the interaction between silver and oxygen is very weak. Adsorption becomes unfavorable for coverages between 0.33 and 0.50, with respect to the gas molecule O@sub 2@. Compared to hcp site, the fcc site is preferable, and the difference in adsorption energy differs by less than 0.17 eV/atom for the whole range of coverage considered. Strong charge transfer from silver to oxygen has been found due to the large difference in electronegativity between oxygen and silver, and results in a significant change in work function, which increases monotonically with oxygen coverage. Experimental studies report that at elevated temperatures two ordered phases form: a (4x4) structure (T@>=@400K),@footnote 1@ and a high-temperature (@sr@3 x @sr@3)R30° (T@>=@800K)@footnote 2@ structure. With respect to the latter, a surface substitutional site has been proposed. Our results show that this structure is unfavorable. For subsurface adsorption we find that oxygen prefers the octahedral site, but at coverage 0.33 it is also endothermic with respect to free O@sub 2@. We discuss alternative geometries for this phase. @FootnoteText@ @footnote 1@ G. Rovida et al., Surf. Sci. 43, 230 (1974); C. I. Carlisle et al., Phys. Rev. Lett. 84, 3899 (2000). @footnote 2@ B. Pettinger et al., Phys. Rev. Lett. 72, 1561 (1994); X. Bao et al. Phys. Rev. B 54, 2240 (1996).

5:00pm **SS2+VT-WeA10 Adsorption of Propylene on Clean and Oxygen Covered Au(111) and Au(100)***, **K.A. Davis**, D.W. Goodman,* Texas A&M University

The adsorption of propene on Au(111) and Au(100) was investigated using temperature programmed desorption (TPD) and high resolution energy loss spectroscopy (HREELS). A desorption activation energy of 9.4 kcal/mol and very small (< 25 cm@sup -1@) shifts of the vibrational frequencies from their gas phase values indicate that the interaction of propene with the surface is weak. Energy loss spectra suggest that propene adsorbs with its molecular plane tilted slightly with respect to the surface plane. Atomic oxygen, chemisorbed on the gold surfaces, was characterized using TPD and low energy electron diffraction (LEED), and its interaction with propene investigated. HREEL spectra of propene on the oxygen covered surfaces show shifts in the intensities and frequencies of the -CH@sub 2@ related vibrational features. Small amounts of product with masses 56 and 58 amu were observed for propene adsorbed onto a 0.4 ML oxygen-covered surface.

Surface Science
Room 210 - Session SS3-WeA
Surface and Interface Structure I

Moderator: B.P. Tonner, University of Central Florida

2:00pm **SS3-WeA1 Adsorbate Structure Determination on Surfaces using Normal-Incidence X-ray Standing Waves***, **D.P. Woodruff**[1],* University of Warwick, UK **INVITED**

X-ray standing waves (XSW) provide a particular simple way of obtaining quantitative information on adsorption geometries on well-characterised surfaces, and working a normal incidence (NIXSW) to the Bragg scatterer planes offers some specific advantages. In particular, under these conditions the experiment is extremely tolerant of crystal mosaicity and can be applied routinely to metal crystals. Normal incidence also implies lower photon energies, typically around 3 keV, making photoemission detection of the photoabsorption straight-forward. Photoemission detection offers two important advantages, namely easier access to low atomic-number species, and the possibility of obtaining chemical-state specific structural information through the use of 'chemical shift' in the photoelectron binding energies. On the other hand, photoemission detection requires the use of a modified interpretational scheme to take account of non-dipole effects in the angular dependence of the photoemission. These various aspects of the technique will be illustrated with recent results including: the direct measurement of non-dipole angular parameters; the use of chemical-shift NIXSW to determine the local geometries of coadsorbed molecular fragments (e.g. PF@sub 3@ species produced by X-ray fragmentation on Ni(111) and CH@sub 3@SH, CH@sub 3@S- and S on Cu(111) following surface reaction), and determinations of the temperature-dependent local structure of CO adsorbed on Ni(111).

2:40pm **SS3-WeA3 Oriented Quantum Dots By Buffer Layer Growth Process***, **A.P. Baddorf**, J.F. Wendelken,* Oak Ridge National Laboratory*; C.T. Venkataraman, T. Gog,* Argonne National Laboratory

Quantum dots of Fe formed by a multi-step growth process are shown to be highly oriented on a Cu(100) substrate. Growth involved deposition of Fe on a buffer of 200 layers of condensed Xe. The Xe buffer layer, which promotes clustering, was subseque ntly removed by heating. In situ scanning tunneling microscopy results reveal formation of 3-D Fe clusters averaging 10 nm in diameter. An additional 20 nm thick cap of Cu was deposited over the Fe to allow ex situ x-ray studies at the Advanc ed Photon Source. Fe clusters were found to be highly oriented, with the close-packed [110] direction normal to the Cu(100) surface and with two in-plane orientations. The first in-plane structure has Fe \{-112\} planes aligned with Cu \{001\} and the se cond has Fe \{-110\} planes aligned with Cu \{001\}. These orientations are not observed in molecular beam epitaxy of Fe directly onto Cu(100) or in precipitate growth. Buffer layer growth bypasses the intermediate fcc Fe phase formed by direct deposition on fcc Cu and brings bcc Fe immediately into contact with fcc Cu. Sidestepping the fcc Fe phase may allow the newly observed orientations.@footnote 1@ @FootnoteText@ @footnote 1@ORNL is managed by UT-Battelle, LLC, under US DOE contract DE-AC05-00OR22725. The APS is supported by US DOE contract W-31-109-Eng-38.

3:00pm **SS3-WeA4 Direct Observations of Ordered Domain Structures and their Dynamics : Pb on Cu(111)@footnote 1@***, **R. Plass**, N.C. Bartelt, G.L. Kellogg,* Sandia National Laboratories

There is considerable scientific interest in the spontaneous formation of two-dimensional periodic domain structures due to long-range interactions in two-phase systems. Theoretical investigations of the stability of periodic structures due to dipolar interactions predict a progression of droplet and striped phases as a function of area fraction@footnote 2@ but experimental verification has been elusive. Using low energy electron microscopy (LEEM), we find that the growth of Pb on Cu(111) reproduces

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

this domain evolution with surprising accuracy. Above 25C, Pb on Cu(111) follows the SK growth mode@footnote 3@ with a disordered surface alloy saturating at 0.4 ML Pb and an incommensurate (incom. hereafter) overlayer covering the surface at 1.0 ML Pb. As Pb deposition proceeds on the surface alloy held at 385C, the density of incom. structure droplets (about 90 nm in diameter) increases steadily. The droplets clearly repel each other, and pack together into a fairly well ordered lattice. They achieve maximum density near 0.3 area fraction (incom.) after which there is an abrupt transition to a striped phase characterized by lengthening bands of surface alloy and incom. regions. The stripes completely cover the surface at 0.5 area fraction, after which another abrupt transition occurs between the striped phase and a conjugate droplet phase where the surface alloy forms droplets in the incom. matrix. The conjugate droplet maximum density is near 0.7 area fraction. The domain structures' spatial dimensions, as well as the size of their thermal fluctuations are temperature sensitive. We use this sensitivity to probe the energetics responsible for the domain structures. @FootnoteText@ @footnote 1@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the U.S. Dept of Energy, contract #DE-AC04-94AL85000 @footnote 2@ K.-O. Ng and D. Vanderbilt, PRB 52 (95) 2177. @footnote 3@ C. Nagl, et al., Surf. Sci. 321 (94) 237.

3:20pm **SS3-WeA5 Normal Incidence X-ray Standing Wave and Medium-energy Ion Scattering Investigation of the Structure of Ultra-thin Films on Cu(111)***, **M.D. Crapper**, M.T. Butterfield,* Loughborough University, U.K., UK

Many of the techniques available for surface structural determination fall into two broad categories. The first of these is the family of diffraction techniques, where long-range order is required to allow investigation of a structure. In samples that are not completely ordered, a diffraction based technique will often preferentially reveal information about the regions of the sample that are ordered. The second category is the so-called local probes, which sample the environment around a particular species but do not reveal information about the long-range order. Two techniques that do not clearly fall into either category, but have aspects of each are medium energy ion scattering (MEIS) and the normal incidence X-ray standing wave method (NIXSW). Both of these methods can yield valuable information where imperfect order is present, but on a scale larger than merely local. We report the novel application of a combination of these methods to investigate the structure of ultra-thin overlayers of Co, Fe and Mn on Cu(111). In the case of Co on Cu(111), pure fcc growth does not continue after the first two layers, but there is no one single growth mode. Instead there is a gradual inclusion of stacking faults with evidence of both hcp and fcc twinning. The initial growth of Fe on Cu(111) is also fcc but with a transition of the entire film to bcc at around 5-8 ML rather than a gradual transition. Overlayers of Mn show no site coherence, even below one monolayer. Upon annealing, however, an alloy is formed to a depth of around five layers that has an effective fcc structure but with increased d-spacing over that found in Cu(111) and with Mn substituting some Cu sites.

3:40pm **SS3-WeA6 Low Energy Dynamics for S/Cu***, **C.J. Hirschmugl**,* University of Wisconsin, Milwaukee*; M.V. Pykhtin, S.P. Lewis,* University of Georgia

Dissociated H@sub 2@S on Cu(100) at 300K has been studied by a combination of AES, LEED, and Far-IRAS in the 200-2200 cm@super -1@ frequency range using synchrotron radiation. Density functional theory (DFT) calculations for a p(2x2) ordered overlayer of S on Cu have also been completed. In the Far-IRAS experiments, diffusive scattering of substrate electrons from the adsorbates gives rise to a broadband infrared absorption. This behavior was induced by sulfur coverages up to and including the p(2x2) overlayer (0.25 monolayers (ML)). DR/R at high frequency (2200 cm@super -1@) changes monotonically with increasing coverage up to 0.125 of a monolayer, and then remains constant. For the low-coverage linear regime, we calculate a scattering cross section @sigma@ of sulfur for the substrate free electrons and the e-hole pair damping rate @eta@ for the S hindered translation. We apply expressions arising from a "friction" model proposed by Persson to determine these parameters from the broadband infrared absorption data. In addition, we determine both @sigma@ and @eta@ for the ordered overlayer from previously published inverse photoemission results and DFT calculations, using a complementary theory proposed by Persson. The scattering cross section for the disordered overlayer (below 0.125 ML coverage of S) is determined to be approximately 20 Å @super 2@ from the infrared results. The scattering cross section for the ordered overlayer is dramatically smaller, approximately 3 Å @super 2@ as determined from both the photoemission results and DFT calculations. The non-linear behavior in the background change for S adsorption is attributed to a changing cross section, or a disorder to order effect.

4:00pm **SS3-WeA7 Does Adsorbed Oxygen Change the Electron Density in Cu?***, **E.F. McCullen**, C.-L. Hsu, R.G. Tobin,* Tufts University

We present new evidence that thin Cu films can have significantly lower conduction electron density n than pure bulk Cu, and that the resistivity increase caused by oxygen adsorption is due in part to a further reduction in n. This finding contradicts the prevailing model of adsorbate-induced resistance, which attributes the resistance increase to electron scattering. In a series of experiments we measured simultaneously the infrared reflectance and dc resistance changes of epitaxial Cu(100) films during oxygen dosing. Earlier experiments challenged the scattering model by showing that the reflectance-resistance change ratio is adsorbate-dependent.@footnote 1@ Adsorbate-induced changes in n could account for the results, but only if n in the films was significantly below the bulk value. The present work shows that the films indeed have reduced electron density. We find that the reflectance-resistance change ratio for adsorbed oxygen depends upon the clean-film conductivity, which varies from sample to sample. This dependence can be understood if the variations in clean-film conductivity are due in part to variations in n. We use these data to set limits on the films' electron density. The results are consistent with a model in which the resistance change produced by oxygen is caused by equal contributions from scattering and reductions in n, and in which each oxygen atom localizes about two conduction electrons. @FootnoteText@ @footnote 1@ E.T. Krastev, D.E. Kuhl and R.G. Tobin, Surf. Sci. Lett. 387, L1051 (1997); C.-L. Hsu, E.F. McCullen and R.G. Tobin, Chem. Phys. Lett. 316, 336 (2000).

4:20pm **SS3-WeA8 Soft X-ray Photoelectron Spectroscopy Studies of Faceting and Alloying for Ultra Thin Films of Ruthenium on W(111) and W(211)***, **G.J. Jackson**,* Rutgers University*; J.E. Rowe,* North Carolina State University*; T.E. Madey,* Rutgers University

High resolution soft X-ray photoelectron spectroscopy (using synchrotron radiation) and low energy electron diffraction (LEED), have been used to study alloying and faceting of Ru dosed onto W single crystal surfaces. W 4f core-level photoemission spectra and valence band spectra have been measured at various photon energies for W(111) and W(211), this photoemission being collected along the surface normal and at shallow grazing angles. The ultrathin film growth and evolution before and after annealing, on both W surfaces, has been investigated for coverages ranging from 0 to greater than 3 physical monolayers. After annealing multilayers of Ru on W(211) at low temperature (600 K), core-level shifts in the W 4f photoemission indicate formation of a Ru/W alloy that may be subsurface. Upon annealing to higher temperatures (600-1600 K), the core-level shifts reveal a concentrated Ru/W alloy. For the W(111) surface, previous studies from several other 4d and 5d dosed metals have shown that the ultrathin film covered surface forms nanoscale pyramidal facets with (211) faces. However, our LEED observations provide no evidence that Ru induces faceting of W(111). W 4f core-level shifts and their relative photoelectron intensities have indicated that clustering may occur on the W(111) surface after annealing. The results from studies of the Ru investigations are closely compared with previous studies from Pt,Pd,Ir,Rh dosed onto W(111) and W(211). In these cases it has been shown that fractional monolayer coverages do not form alloys and that for coverages exceeding 1 ML, the W atoms can dissolve into the adsorbed layer. Our results indicate some differences in the thermal stability of Ru/W, compared with Pt,Pd,Ir, Rh on W.

4:40pm **SS3-WeA9 Oxygen Induced Faceting of Ir(210)***, **I. Ermanoski**, K. Pelhos, T.E. Madey,* Rutgers, The State University of New Jersey

As a part of a larger program to study the morphological stability of adsorbate covered metallic surfaces, we have investigated the adsorption of oxygen on fcc Ir(210) and the oxygen induced faceting of Ir(210). The techniques we used include low energy electron diffraction (LEED), temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and scanning tunneling microscopy (STM). The atomically rough Ir(210) surface, when exposed to more than ~0.9L of oxygen and annealed to temperatures higher than 600K, experiences significant morphological restructuring: pyramid-like structures (facets) are formed on the initially planar surface. Our high temperature LEED measurements show that these pyramidal facets exhibit a quasi-reversible behavior upon annealing to higher temperatures. The surface reverts to its planar state at temperatures above 850K but, provided the maximum annealing temperature is below the desorption temperature of oxygen, facets reappear upon cooling to temperatures below 800K. LEED measurements show that these facets have a different structure than the original ones. Furthermore, we are able to remove the oxygen from the surface via catalytic oxidation of CO at 480K, while preserving the faceted structure. TPD and AES have shown that residual adsorbed oxygen and CO are negligible after this procedure. The faceted clean surface is stable up to 600K, but irreversibly reverts to the planar state when annealed above 600K. These experiments indicate that the clean, faceted, metastable Ir(210) surface provides an ideal substrate to study thermal relaxation of nanometer-scale surface features.

5:00pm **SS3-WeA10 Evolution of Ni(110) Surface with Low Energy Ion Sputtering**, ***S.-J. Kahng***, *B.-Y. Choi, J.-Y. Park, Y. Kuk,* Seoul National University, Korea

We have studied the spatio-temporal evolution of the Ni(110) surface structure induced by the low energy ion sputtering with scanning tunneling microscopy. In order to have better understanding of the sputtering kinetics, we performed sputtering and homoepitaxial growth experiments at 295 K. In the early stage of sputtering, erosion pits and adatom islands, elongated along the [110], are present with asymmetric adatom kinetics. They become seeds for the ripple structure under the strong diffusion bias along the [001] direction. The surface roughness increases linearly with sputtering time. In the late stage of sputtering, however, symmetric mounds replace the ripple structure and the surface roughness saturates to certain point, showing good agreement with the recent numerical simulation on the basis of nonlinear Kuramoto-Sivashinsky equation.

Organic Films and Devices
Room 313 - Session OF+EL+SS-ThM
Organic Thin Films

8:20am **OF+EL+SS-ThM1 Highly Ordered Layers of Large Conjugated @pi@-systems on Cu(111): A Novel Preparation Method**, ***G. Beernink***, *K. Weiss, A. Birkner,* Ruhr-Universität Bochum, Germany; *F. Dötz, K. Müllen,* Max-Planck-Institut für Polymerforschung, Germany; *C. Wöll,* Ruhr-Universität Bochum, Germany

With regard to applications in molecular electronics and the fabrication of nanoelectronic devices, polycyclic aromatic hydrocarbons (PAH), e.g. the graphite segment hexa-peri-hexabenzocoronene (HBC), have recently received considerable attention. For such large PAHs, however, the low solubility in organic or polar solvents and the rather large sublimation temperatures make the application of the commonly used deposition methods, namely adsorption from solution or evaporation in a vacuum system (CVD, OMBE) difficult or even impossible. In this work, we present a direct way to synthesize one particular polycyclic aromatic hydrocarbon, namely hexa-peri-hexabenzocoronene (HBC) by using a surface as a template. A modified precursor molecule, 1,2,3,4,5,6-Hexakis(4-dodecyloxyphen-1-yl)benzene (HPB), which is not planar, is evaporated on a Cu(111) surface. Heating of the substrate leads via thermally induced cyclodehydrogenation to the product HBC, which is characterized by XPS, X-ray absorption spectroscopy (NEXAFS) and STM. The NEXAFS-data directly demonstrate the formation of flat, graphite-like segments which interact only weakly with the substrate, whereas the STM data reveal a high of lateral order.

8:40am **OF+EL+SS-ThM2 The Effect of Conjugation Length on the Frontier Orbital Position of Oligothiophene Derivatives at Metal-organic Interface**, ***A.J. Makinen***, *I.G. Hill,* Naval Research Laboratory; *T. Noda, Y. Shirota,* Osaka University, Japan; *Z.H. Kafafi,* Naval Research Laboratory

We report an ultraviolet photoelectron spectroscopy (UPS) study of a novel family of end-substituted oligothiophene derivatives with a varying conjugation length, BMA-nT (n=1-4), where n indicates the number of thiophene rings. These new oligothiophene derivatives are thermally and morphologically stable, and unlike unsubstituted oligothiophenes, which undergo luminescence quenching due to the polycrystalline nature of their solid films, the thiophene derivatives form amorphous films. The BMA-nT compounds show luminescence from the blue (n=1) to the orange (n=4), and additionally they posses hole-transport properties making them attractive materials for organic light-emitting diodes (OLEDs). The UPS results show that the position of the highest occupied molecular orbital (HOMO) of the end-substituted oligothiophenes at the metal-organic interface is dependent on the number of thiophene rings present, i.e. the effective conjugation length of the molecule. We will discuss this property and its implications in the context of carrier injection in an OLED.

9:00am **OF+EL+SS-ThM3 Electronic Properties of @pi@-Conjugated Organic Molecular Semiconductor Interfaces**, ***A. Kahn,*** Princeton University **INVITED**

Metal/organic interfaces are central to a number of organic-based devices. Their electronic structure and chemistry control charge injection. Modeling these interfaces requires an accurate knowledge of the injection barriers, i.e. the position of the transport levels with respect to the metal Fermi level, and of the role of interface chemical reactions. This talk reviews our latest results obtained via direct and inverse photoemission and scanning tunneling spectroscopy on metal interfaces with five organic materials (PTCDA, CuPc, Alq@sub 3@, @alpha@-NPD, @alpha@-6T) of interest for light emitting device and TFT applications. We present the first accurate picture of the transport levels in these materials, levels which are generally unknown because of the strongly correlated nature of molecular solids. The transport gap is found to be significantly larger, i.e. by the exciton binding energy, than the optical gap usually used to describe interface and bulk molecular level diagrams. The exciton binding energy ranges from 0.4eV to 1.4 eV in the materials investigated. Furthermore, we present a detailed and systematic investigation of molecular level alignment at interfaces of organic thin films deposited on a series of metals with different work function. These demonstrate that one of three mechanisms is involved in the formation of the dipole barriers generally observed at such interfaces: (1) lowering of the metal work function by the molecules; (2) electron transfer from the metal to the organics; (3) chemical bonding. Knowledge of the transport gap, interface level alignment mechanisms and interface chemistry leads to a more accurate description of these organic interfaces. Work supported by the MRSEC program of the National Science Foundation (DMR-9809483).

9:40am **OF+EL+SS-ThM5 Effect of Alkyl Substituents on the Adsorption of Thienylenevinylene Oligomers on the Si(100) Surface**, ***B. Grandidier***, *J.P. Nys, D. Stievenard, C. Krzeminski, C. Delerue,* IEMN/ISEN, France; *P. Blanchard, J. Roncali,* IMMO Universite d'Angers, France

Conjugated thiophene-based oligomers are subject to intense research activity due among others to their potential use as molecular wires in future molecular electronic devices. As microelectronics technology is based on the use of silicon substrates, there is an increasing need to connect these organic molecules to the existing silicon technology. Due to the low intrinsic solubility of the rigid conjugated chains, the synthesis of the longuest chains required the substitution of alkyl chains to the thiophene ring in order to increase the solubility. Whereas such a substitution has limited effect on the electronic structure of the oligomers, it exerts a strong effect on the interactions of the molecules with their physical and chemical environment. The adsorption of unsubstituted and substituted thienylenevinylene oligomers on the Si(100) surface has been investigated using scanning tunneling microscopy. The mode of substitution of the thiophene ring exerts a strong influence on the adsorption configurations and the images of the oligomer based on 3,4-dihexyl thiophene are highly voltage dependent. We discuss the influence of the alkyl chains on the adsorption process and on the appearance of the molecules in the STM images.

10:00am **OF+EL+SS-ThM6 Growth of Films of Thiophene Oligomers by Seeded Supersonic Beams to Improve Control on their Quality and Properties**, ***S. Iannotta***, *T. Toccoli, A. Boschetti,* CeFSA - Research Center CNR-ITC for the Physics of Aggregates, Italy; *P. Milani,* INFM - Universit@aa a@ di Milano, Italy; *S. Ronchin,* INFM - Universit@aa a@ di Trento, Italy; *A. Podest@aa a@,* INFM - Universit@aa a@ Bicocca, Italy

The growing interest in pi-conjugated organic molecular materials and polymers, driven by wide potential technological impact in electronics and photonics, still faces severe limitations. Applications would be much more favored by improving control on morphology and structure in the solid state. Standard growth methods are based on the self-assembling of the molecules resulting more or less affected by the interaction with the substrate. Very often the resulting films show an inadequate ordering. These problems become severe as the thickness increases over a few monolayers. Fully considering the major role played by the initial state of the molecules at early stages of growth, we approached the problem combining a supersonic free jets that permit to control kinetic energy, momentum and flux with a UHV deposition apparatus. We perform the deposition and simultaneously control the initial state of the seeded organic molecules by varying the parameters of the supersonic expansion (dilution, temperature of the source, form and diameter of nozzle, etc) [P. Milani and S. Iannotta, Synthesis of Nanophase Materials by Cluster Beam Deposition, Springer, Berlin (1999)]. We have prepared a series of films of alpha quaterthiophene that are then characterized by optical measurement, TM-AFM and X-ray diffraction. We report an overall strong evidence of an unprecedented control on morphology, structure and optical response that correlate well to the beam's parameters. PL spectra at low temperature show the vibronic molecular structure very well resolved depending on the initial state of the oligomer in the beam. Films, several hundreds nm thick, show a high degree of ordering with surface morphologies characterized by layered structures of molecular height. X-ray diffraction confirms the high degree of ordering induced by the growth from highly supersonic beams. Correlation between morphology, degree of ordering and the optical response of these films will be discussed.

10:20am **OF+EL+SS-ThM7 Scanning Tunneling Microscopy/Spectroscopy Investigation of the Organic Molecules PTCDA and HBC on Au(100)**, ***T. Fritz***, *M. Toerker, H. Proehl, F. Sellam, K. Leo,* TU Dresden, Institut fuer Angewandte Photophysik, Germany

Highly ordered organic thin films on gold single crystals have been investigated by Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS) at room temperature. The organic dye molecule perylene-tetracarboxylic-dianhydride (PTCDA) has been deposited as submonolayer coverage on Au(100). I-V-spectroscopy at fixed tip-sample-separations has been performed alternately on the PTCDA islands and on uncovered areas of the Au(100) surface. The corresponding normalized derivatives of these I-V-curves have then been compared to inverse photoelectron spectroscopy data known from literature, indicating resonant tunneling via the lowest unoccupied molecular orbital. As a second molecule peri-hexabenzocorone (HBC), also deposited on Au(100), has been investigated. The Au(100) surface has been fully covered by a few monolayers thick, highly ordered HBC film. The normalized derivatives of I-V-curves measured on these films show a pronounced local maximum at a negative voltage of about -1.4 V. By comparison with ultraviolet photoelectron spectroscopy (UPS) measurements of HBC on Au(111) we can show that this peak in the tunneling spectroscopy plot is due to resonant tunneling via the highest occupied molecular orbital of HBC.

10:40am **OF+EL+SS-ThM8 STM, AFM, & Electrochemical Investigations of Squaraine Thin Films***, **M.E. Stawasz**, N. Takeda, B.A. Parkinson,* Colorado State University

Squaraines are a class of organic photoconductors which have found industrial use in photoreceptors of laser printers and xerographic devices, as well as in ablative optical recording material. They have also been investigated for their nonlinear optical characteristics as well as their ability to sensitize large-bandgap semiconductors in photoelectrochemical solar cells. Central to its various uses and characteristics is the squaraine molecules' ability to form organized aggregates, both in solution and in the solid state. Few studies have been done, however, to relate the molecular structure of squaraines to the structure of the aggregates that spontaneously form in thin films. We report STM and AFM data which unambiguously determines thin film/monolayer aggregate structure for a series of hydroxylated and non-hydroxylated dialkylamino-phenyl squaraines with varying alkyl tail lengths deposited on HOPG. Results show that alkyl tail length significantly affects squaraine aggregate structure while the presence or absence of hydroxyl groups does not. Electrochemical investigations of the redox behavior of squaraine thin films using HOPG as the working electrode were also performed. Remarkable redox behavior was observed suggesting a structural change in the squaraine aggregate state upon oxidation. In addition, the effect of electrolyte anion and film thickness on the redox behavior of squaraines was observed, thus providing additional insight into the charge transfer abilities of the squaraine film in the direction normal to the substrate surface.

11:00am **OF+EL+SS-ThM9 Work Function Modification and Surface Chemistry of Indium Tin Oxide with Organosilane Self Assembled Monolayers***, J.A. Chaney,* Naval Research Laboratory*; F. Farzad,* Geo-Centers, Inc. and Naval Research Laboratory*; C.S. Dulcey, R. Shashidar, **P.E. Pehrsson**,* Naval Research Laboratory

Attachment of organosilane SAM's with monomers having different dipole magnitude and direction may permit control of the work function (@PHI@) of indium tin oxide (ITO) substrates used in OLED's. However, reliable measurement of @DELTA@@PHI@ requires reproducible control of the environmental conditions. In this work, ITO substrates were treated with SAM's having different head and attachment groups and then inserted into an ultra high vacuum (UHV) chamber. The SAM/ITO work function was measured using an in-vacuo Kelvin probe calibrated with a graphite standard. Surface chemistry was probed by high resolution electron energy loss spectroscopy (HREELS), and electronic structure was investigated by energy loss spectroscopy (ELS). The SAM-modified surfaces usually had lower work functions (@PHI@ = ~4.8-5.3 eV), than bare, oxygen-plasma treated ITO (@PHI@ = ~5.3 eV). The SAM monomers had either one or three Si-OCH@sub 2@CH@sub 3@ units for attachment to the ITO surface. Trifunctional SAM's gave higher @PHI@ values than monofunctional SAM's. The HREELS of monofunctional SAM/ITO showed structure which may be attributable to bending modes. These modes were more intense than on the trifunctional counterpart, possibly due to tighter binding of the latter with ITO. Most SAM modified surfaces showed significant deviation in @PHI@ with time and temperature (up to 200°C), suggesting that adsorption of ambient gasses, even in UHV, affects the SAM/ITO system. However, the work function of some SAM's with hydrophobic head groups was apparently unaffected by adsorption. Differences in the band edge transitions of clean ITO vs. SAM/ITO indicate electronic interactions between the SAM and substrate.

11:20am **OF+EL+SS-ThM10 Effect of Fluoride Layer Insertion on the Electronic Structures of Al/Organic Interfaces@footnote 1@***, **Y. Park**,* Korea Research Institute of Standards and Science, Korea*; D. Kim,* Hallym University, Korea*; S. Cho, O. Kwon, G. Lee,* Korea Research Institute of Standards and Science, Korea*; E. Cho,* Chonnam National University, Korea

We have investigated the electronic structures of interfaces between Al and tris-(8-hydroxyquinoline)aluminum (Alq@sub 3@), which is a prototypical organic electroluminescent (EL) material. It has been well known that the insertion of alkali metal fluoride, such as LiF, greatly enhances the EL performance and the origin of such behaviors have been controversial. We used photoelectron spectroscopy techniques including X-ray and UV photoelectron spectroscopy (XPS and UPS) as well as resonant photoemission (RPES) to probe the electronic structure change caused by the insertion of thin layer of various alkaline and alkaline earth metal fluorides between Al and Alq@sub 3@. As previously known, the presence of LiF layer enhanced gap-state formation, but even without the LiF layer, Al deposition significantly alters the electronic structures of Alq@sub 3@. While the insertion of CsF layer showed clear enhancement of the gap states, it was much less obvious for CaF@sub 2@ layer. For both materials, the RPES showed very weak resonant enhancement when excited with photons with the energy near Cs and Ca core level absorption edge. We report similar measurements for various other fluoride materials and discuss their implications. @FootnoteText@ @footnote 1@ This work was supported in part by MOST of Korea through National Research Laboratory Program and Atomic-scale Surface Science Research Center.

11:40am **OF+EL+SS-ThM11 Interface of Aluminum and Poly(vinylidene fluoride with Trifluoroethylene) Copolymer***, **B. Xu**, C.N. Borca, S. Ducharme, A.V. Sorokin, P.A. Dowben,* University of Nebraska, Lincoln*; V.M. Fridkin, S.P. Palto, N. Petukhova, S.G. Yudin,* Institute of Crystallography, Russia

The interface between aluminum and crystalline copolymer thin films of vinylidene fluoride (70%) with trifluoroethylene (30%) [PVDF-TrFE] has been studied. The ratio of carbon 1s and aluminum 2p core level photoemission peak intensities changes little with increasing emission angle, even after deposition of 5 Å aluminum on the surface of PVDF-TrFE. This indicates that the distribution of aluminum atoms in the copolymer film is quite uniform in the near surface region and that the interface is not abrupt. The contributions to the C 1s core level shift ~1eV to lower binding energy, while the relative ratio of the intensity of C 1s peaks changes, provides further evidence for changes in screening with aluminum doping within the polymer film. The XRD data also shows the crystalline structure of the copolymer film can be deformed with aluminum doping, if the polymer film is annealed.

Semiconductors
Room 306 - Session SC+EL+SS-ThM

Hydrogen On and In Semiconductors

Moderator: J.T. Yates, Jr., University of Pittsburgh

8:20am **SC+EL+SS-ThM1 Step Structures and Energies on Vicinal Si(001) Monohydride Surfaces: Dependence on H Chemical Potential***, **A. Laracuente**, L.J. Whitman,* Naval Research Laboratory

It is well known that foreign adsorbates can alter the equilibrium step structure on surfaces and often have a dramatic effect on film growth. Given that most semiconductor devices are fabricated in hydrogen-rich environments on silicon substrates, a comprehensive understanding of how hydrogen affects Si step energies is essential to the development of accurate models of semiconductor growth and processing. We have determined the equilibrium step structures and step formation energies for the whole range of monohydride-terminated (001)-terrace-plus-step surfaces. Compared with the clean surfaces, hydrogen termination alters the atomic-scale step edge structure and, in many cases, causes large-scale changes in the surface morphology. The structural modifications result directly from a change in the relative energies of the possible single- and double-layer step configurations. On nominal Si(001), the S@sub B@ steps are mostly non-rebonded and rougher after H passivation. A kink distribution analysis reveals that H reduces the nearest neighbor interaction across the S@sub B@ steps by an order of magnitude. Whereas the nearest neighbor interaction strongly depends on H@sub 2@ pressure, i.e. the H chemical potential, the step formation energies do not. On D@sub B@-stepped surfaces, such as Si(1 1 11), a statistical analysis of the steps shows that H lowers the formation energy of non-rebonded D@sub B@ and S@sub B@ steps, making them close in energy to the rebonded D@sub B@ steps. Post annealing a monohydride Si(1 1 11) surface without H significantly changes the n-D@sub B@/r-D@sub B@ ratio, indicating that the D@sub B@ step formation energies strongly depend on H chemical potential.

8:40am **SC+EL+SS-ThM2 Si(100) Surface Roughening and H Atom Absorption: Surface and Bulk Characterizations.**, ***S.K. Jo**, J.H. Kang,* Kyung Won University, S. Korea*; X. Yan, J.M. White, J.G. Ekerdt,* University of Texas at Austin*; J. Lee,* Seoul National University, S. Korea*; J.Y. Maeng, S.H. Kim,* Korea Advanced Institute of Science and Technology

Absorption of thermal-energy gaseous hydrogen atoms by Si(100), exceeding by far the dopant and other impurity concentrations, occurs within a narrow substrate temperature (T@sub s@) window centered at ~ 460 K. The absorbed hydrogen persists in the crystalline bulk as highly mobile species before migrating out and desorbing as molecular hydrogen at T@sub s@ as high as 900 K, well above the recombinative desorption temperatures of surface-adsorbed H. Developing and sustaining atomic-scale surface roughness, by H-induced silicon etching, is a prerequisite for H absorption and determines the T@sub s@ window. In support of these conclusions are our TPD, Raman, SIMS, TEM, and STM data for this fundamental and interesting phenomenon of thermal H atom absorption by Si(100).

9:00am **SC+EL+SS-ThM3 Dissociation Pathways of Molecular Hydrogen on Silicon Surfaces@footnote 1@***, **U. Höfer**,* Philipps Universität Marburg, Germany **INVITED**

The dissociative adsorption of H@sub 2@ on Si(001) has emerged as a prototype for activated chemical reactions on semiconductor surfaces. One of the most distinctive features of this basic reaction is the low sticking probability for dissociative adsorption (< 10@super -11@) and the fact that thermally induced distortions of the Si lattice enhance the reactivity by many orders of magnitude. In order to reveal the atomic-scale motion responsible for "phonon assisted sticking" we have performed a series of experiments employing optical second-harmonic generation (SHG), supersonic molecular beam dosing, and scanning tunnelling microscopy (STM). It will be demonstrated that, similar to thermally activated dynamical distortions, the reactivity can be enhanced by static distortions of the surface by precoverage with atomic hydrogen or by steps. The barriers to adsorption at these well-defined sites were determined. They revealed systematic trends that could be reproduced by density functional calculations and traced back to the interplay between electronic structure and local distortions of the Si surface. We find that hydrogen adsorption proceeds via inter-dimer reaction pathways in all cases. Whenever the energy splitting between the reactive dangling-bond states of adjacent dimers may be reduced by low-energy displacements of Si atoms, the adsorption barrier is found to be low. @FootnoteText@ @footnote 1@ Work performed in collaboration with W. Brenig, A. Biedermann, M. Dürr, T. F. Heinz, M. Hilf, Z. Hu, P. Kratzer, E. Pehlke, M. B. Raschke and M. Scheffler.

9:40am **SC+EL+SS-ThM5 Hydrogen Bonding on Compound Semiconductor Surfaces***, **R.F. Hicks**, Q. Fu,* University of California, Los Angeles*; L. Li,* University of Wisconsin, Milwaukee*; C.H. Li,* University of California, Los Angeles

Hydrogen adsorption on gallium arsenide and indium phosphide (001) surfaces has been studied by scanning-tunneling microscopy and internal-reflection infrared spectroscopy combined with ab initio molecular cluster calculations. The calculations are based on a series of clusters that accurately simulate the group III and V dimer termination of the surface. Good agreement has been achieved between the vibrational frequencies predicted by the theory and those observed in the experiments. On the anion-rich surfaces, hydrogen adsorbs on arsenic (or phosphorous) dimers to form isolated and coupled monohydrogen bonds and dihydrogen bonds. Conversely, on the cation-rich surface, hydrogen adsorbs on gallium (or indium) dimers to form terminal and bridged metal hydrides. The latter species occur in isolated or coupled structures involving two or three metal atoms. The implications of these results for the surface science of compound semiconductors will be discussed at the meeting.

10:00am **SC+EL+SS-ThM6 Scanning Tunneling Microscopy of Low Temperature Adsorption H2 on GaAs(001)***, **H. Xu**,* National University of Singapore, Singapore*; Y. Lee, J. Lee, A. Lee,* National University of Singapore

The variable temperature scanning tunneling microscope (VT-STM) has been used to study in-situ the transition of 2x6 reconstruction of GaAs (001) at low temperature. High resolution STM images show that the metastable As dimers rows of 2x6 reconstruction in GaAs (001) becomes unstable under the attack of the dissociated adsorption H@sub2@. As dimers were broken firstly due to the formation of double atom lines structure by the attacking of hydrogen on As dimers atoms. Furthermore, the opened As atoms rows on the top of this surface were twisted gradually up to coalesce together with a width of 3 As dimers. Unexpectedly, these compressed As atoms suddenly extend along the original As dimers rows direction(-110) gives rise to form a metastable trimer As rows.

10:20am **SC+EL+SS-ThM7 Theoretical Approaches for Predicting SiGe Heteroepitaxy***, **C. Mui**, S.F. Bent, C.B. Musgrave,* Stanford University

The demand for silicon-germanium devices has been growing in recent years due to potential applications in areas such as infrared photodetection, wireless communications and quantum nanostructures. The need for improved SiGe processing has motivated efforts to better understand the detailed reaction mechanisms of SiGe heteroepitaxy, including the adsorption of gas phase precursors and the removal of hydrogen from SiGe surfaces. We have used Becke3LYP density functional theory to study the effect of Ge alloying on the energetics and kinetics of H2 desorption from SiGe surfaces. We have investigated H2 desorption from the Si-Si homodimer, the Si-Ge heterodimer and the Ge-Ge homodimer sites. We found that in the transition state the two desorbing hydrogen atoms are localized above one surface atom, such that the structure resembles a dihydride species. The transition states on all three types of dimers have similar geometries, independent of the identity of the surface dimer atoms. Furthermore, the activation barriers depend only on the identity of the dimer atom not bonded to the desorbing hydrogens. For example, the activation barrier for H2 desorption from the Si site of a Si-Ge heterodimer is lower than that from a Si-Si homodimer by 10.6 kcal/mol. However, the barrier for desorption from the Ge-Ge homodimer is the same as that from the Si site of a Si-Ge heterodimer. We also found that the activation barrier for H2 desorption is only affected by surface Ge, and not Ge in the bulk. Calculations on a three dimer cluster showed that the activation barriers are dependent on cluster size, indicating that charge transfer and surface strain play a role in the desorption process. Finally, we will present results concerning additional surface reactions including the adsorption of germane on SiGe surface dimers.

10:40am **SC+EL+SS-ThM8 Real-time Monitoring of H@sub 2@ Adsorption on C(001) at High Temperature by Ultraviolet Photoelectron Spectroscopy***, **Y. Takakuwa**, M. Asano,* Tohoku University, Japan

The hydrogen-terminated diamond surface has attracted much attention not only as a high efficiency electron emitter because of its electron affinity being negative (NEA) but also as a p-type conductive surface for field-effect-transistor devices. On the other hand, H@sub 2@ desorption on the hydrogen-terminated diamond surface occurs appreciably at higher temperature than 900@super o@C. This suggests that during the synthesis of diamond thin films by chemical vapor deposition using hydrocarbon gases such as methane the diamond-growing surface could be terminated by hydrogen and therefore NEA, even though the growth temperature is as high as 800-1000@super o@C. In this study, the electron affinity, secondary electron emission and pinning position of the Fermi level during exposing a diamond C(001) surface to H@sub 2@ at 700@super o@C and 1x10@super -5@ Torr were investigated by a real-time monitoring method of ultraviolet photoelectron spectroscopy. It was observed that (1) molecular hydrogen not activated by a hot tungsten filament absorbs dissociatively on the C(001) surface, wile it takes about 120 min to cover wholly the surface with hydrogen; (2) the electron affinity decreases from +0.4 eV for the clean surface to a negative value when the hydrogen coverage is about 90%; (3) the Fermi level is positioned at 0.61 eV above the valence band maximum just when the diamond surface changes to NEA; (4) the secondary electron yield increase with the hydrogen exposure time even after the complete termination of the surface with hydrogen. On the basis of the observed results, the time evolution of the surface electronic state during the hydrogen adsorption on the C(001) surface is discussed.

11:00am **SC+EL+SS-ThM9 Infrared Studies of Hydrogen on Diamond (100)***,* ***J.N. Russell, Jr.**,* Naval Research Laboratory*; J. Hovis, R.J. Hamers,* University of Wisconsin*; G.T. Wang, S.F. Bent,* Stanford University*; M.P. D'Evelyn,* General Electric CRD*; J.E. Butler,* Naval Research Laboratory

Hydrogen atoms play a critical role in the chemical vapor deposition of diamond thin films. Currently, hydrogen plasmas are used to produce reproducible, clean, smooth, diamond (100) single-crystal surfaces. The use of diamond films for microelectronic or surface acoustic wave devices requires a fundamental understanding of the diamond surface termination and its interaction with adsorbed species. The hydrogen terminated diamond (100) surface is comprised of two 2x1 domains of monohydride surface dimers. Using s- and p-polarized multiple internal reflection infrared spectroscopy, the symmetric and asymmetric stretches of the HCCH surface dimer are easily resolved and are compared to ab initio calculations of the frequencies. The thermal dependence of the CH stretches is monitored as a function of the anneal temperature. When the hydrogen terminated surface is covered with a condensed layer of physisorbed molecules, the surface CH vibrational frequency is significantly influenced. We discuss the implications of these observations.

11:20am **SC+EL+SS-ThM10 Fundamental Connection Between the ESD of H/D at Silicon Surfaces and at Oxide/Silicon Interfaces*, K. Cheng*,** *J. Lee, Z. Chen, J.-P. Leburton, E. Rosenbaum, K. Hess, J.W. Lyding,* University of Illinois, Urbana-Champaign

Parallels can be drawn between electron stimulated desorption (ESD) of hydrogen at silicon surfaces in UHV and the ESD of hydrogen at the oxide/silicon interface in CMOS transistors. In particular, the multiple carrier vibrational heating mechanism for ESD, and the giant hydrogen/deuterium isotope effect play important roles in interface degradation. In this paper we will present results demonstrating the primary role of channel hot carriers in the degradation of the oxide/silicon interface of transistors. Experiments performed on p-channel MOSFET's show essentially no isotope effect for the creation of interface traps when carriers are injected into the oxide. However, a large isotope effect, consistent with vibrational heating, is observed when carriers flow along the oxide/silicon interface. One key difference between a H-passivated silicon surface and a H-passivated oxide/silicon interface is that there is a distribution of Si-H bond strengths at the interface due to variations in the amorphous oxide matrix. Experimental results will be presented which directly measure this distribution as well as show its ramifications in terms of rapid interface trap creation. The significance of this study comes from the fact that it is still a widely held view that the dominant transistor degradation mechanisms arise from carrier injection into the oxide, and therefore will be scaled away as industry trends progress. However, by performing new experiments and using basic surface science as a setting for their interpretation, we are able to show that there are fundamental problems with this view. Our results are supported by the fact that even state-of-the-art 0.18mm, 1.5 V CMOS chips show hundreds times lifetime improvement when hydrogen is substituted by deuterium.

11:40am **SC+EL+SS-ThM11 Depth-Resolved Determination of the Hydrogen Concentration at Buried SiO@sub 2@/Si(100) Interfaces by Resonant Nuclear Reaction Analysis*, M. Wilde*,** *M. Matsumoto, K. Fukutani,* University of Tokyo, Japan*; Z. Liu, Y. Kawashima,* NEC Corp., Japan

Hydrogen at the SiO@sub 2@/Si interface has been discussed to affect the electronic performance of MOS diodes by influencing the density of states at the interface. Drastic improvements of the reverse current resistance were reported after H@sub 2@-annealing of such devices.@footnote 1@ In this study the hydrogen concentration at the SiO@sub 2@/Si interface is measured directly by a Nuclear Reaction Analysis (NRA, based on the @sup 1@H(@sup 15@N, @alpha@@gamma@)@sup 12@C reaction), and the influence of H@sub 2@-annealing is investigated. Oxidized Si(100) samples with SiO@sub 2@ films of (19.0 - 41.5 nm) thickness were studied. In the as-oxidized condition, H near the SiO@sub 2@/Si interface is identified at a concentration lower than 4x10@sup 19@ cm@sup -3@. In the NRA depth profiles of all samples the center of the near-interface H-distribution appears at a depth (5±1) nm shallower than the interface location determined by ellipsometry. While no H is found in the silicon substrate, hydrogen is accumulated in a several nm wide layer within the oxide film adjacent to the interface. This result supports the idea of a transition region between the mere interface and the SiO@sub 2@ material, where stoichiometry and strain-induced defects may act as local bonding sites for hydrogen. In-situ annealing of the oxidized wafers in ambient H@sub 2@ gas causes a substantial increase of the H-concentration near the SiO@sub 2@/Si(100) interface, whereas the width of the H-distribution and its position within the oxide film remain unchanged. The H-distribution is thermally stable below the annealing temperature of 400@deg@C. On heating to higher temperatures in vacuum depletion of H from the interface layer occurs to a concentration level below the as-oxidized condition. Hydrogen can be replenished at the interface by repeating the H@sub 2@-annealing procedure. @FootnoteText@ @footnote 1@ S. Fujieda, H. Nobusawa, M. Hamada, T. Tanigawa, J. Appl. Phys. 84 (1998) 2732.

Surface Science
Room 208 - Session SS1+MC-ThM
Oxide Applications and Oxidation

Moderator: E.I. Altman, Yale University

8:20am **SS1+MC-ThM1 Synthesis and Characterization of Self-assembled Cu@sub2@O Quantum Dots on SrTiO@sub3@(001) Surface*, Y. Liang*,** *D.E. McCready, A.S. Lea, S.A. Chambers, S. Gan,* Pacific Northwest National Laboratory

Self-assembled quantum dots have received much attention recently because their atom-like electronic and optical behavior can be tailored. One common problem with many quantum dots has been the poor chemical and thermal stability as most of them are made of conventional semiconductors. An alternative to this problem is to use oxide based quantum dots due to their superior stability. We have successfully synthesized self-assembled Cu@sub2@O quantum dots on SrTiO@sub3@ substrates using a molecular beam epitaxial method. The structure and chemical states of Cu@sub2@O quantum dots have been confirmed by x-ray diffraction and x-ray photoelectron spectroscopy (XPS). Reflection high energy electron diffraction (RHEED), atomic force mic roscopy (AFM), and high-resolution scanning Auger microscopy (SAM) show that formation of Cu@sub2@O quantum dots occurs after deposition of a few monolayers of Cu@sub2@O due to the large compressive lattice mismatches between Cu@sub2@O and SrTiO@sub3@. SAM reveals that the interdiffusion between Cu@sub2@O quantum dots and SrTiO@sub3@ is significantly less than many other quantum-dot systems. XPS further shows that the interfacial electronic structure of Cu@sub2@O/SrTiO@sub3@ exhibits the so-called the type-II heterojunction, i.e., the valance and conduction bands of Cu@sub2@O are both higher than that of SrTiO@sub3@. Consequently the photo-excited electrons and holes are spatially separated with holes being confined to Cu@sub2@O quantum dots and electrons confined to SrTiO@sub3@, a property important for photocatalysis and solar cell applications. We are currently using AFM-based surface potential measurements to elucidate the spatial charge separation behavior of this system upon photo-excitation at different wavelengths. @FootnoteText@ # Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

8:40am **SS1+MC-ThM2 Correlation of Electronic Structure with Photoluminescence Properties in Oxidized Silicon Nanoclusters*, J.A. Carlisle*,** *I. Germanenko, Y. Pithawalla, M.S. El-Shall,* Virginia Commonwealth University

The relationship between morphology, band-gap size, and photoluminescence data in surface-oxidized silicon nanoclusters is established using photon-yield measurements at the Advanced Light Source. After removal from the growth chamber, photoluminescence (PL) results indicate that as the clusters oxidize, the main PL peak moves from 1.83 eV to 1.94 eV in energy. The central focus of this work is to establish the origin of the PL peak, whether it arises due to quantum size effects or due to the formation of suboxides as the clusters oxidize. The changes in the morphology and bonding structure of the clusters were established using soft-x-ray fluorescence spectroscopy (SXF) and photon-yield near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, which probe the element-specific density of occupied (SXF) and unoccupied (NEXAFS) electronic structure. Our finding is that the as-synthesized nanoclusters consist of a pure, crystalline Si core within a nearly pure SiO2 shell. Very few suboxides are present, and the oxidation process does not lead to an increase in the amount of suboxides present within the particles. As the nanoclusters oxidize, the radius of the crystalline core decreases in size, which gives rise to the change in the position of the PL signal.

9:00am **SS1+MC-ThM3 The Behavior of Ultrathin Al@sub 2@O@sub 3@ Films in Very High Electric Fields: STM-induced Pitting and Dielectric Breakdown**, *N.P. Magtoto, C. Niu,* ***J.A. Kelber,*** University of North Texas

The behavior of ultrathin oxides under high electric fields is of critical importance to areas as diverse as microelectronics (gate oxides, magnetoresistance devices) and corrosion. We report the use of high electric fields applied via the STM to induce pits and dielectric breakdown in ultrathin @gamma@'-Al@sub 2@O@sub 3@ films (7 Å thick) grown on Ni@sub 3@Al(111) substrates in UHV. Voltage pulses (bias voltages of 1-6 V, either polarity) are applied to a specific location on the oxide surface with the feedback current loop operative to prevent tip/sample physical interaction. Subsequent imaging at 0.1 V bias voltage and 1 nA feedback current reveal the effects of high field on surface composition and topography. Results show that dielectric breakdown occurs at a field of 12.3±0.7 MV/cm. Breakdown is marked by the creation of an area ~20 nm high and 100 nm wide and the loss of the insulating nature of the oxide as deduced from I/V spectroscopy. Once the threshold breakdown voltage is reached, the STM tip retracts precipitously (~20-25nm) from the sample surface due to the onset of the leakage current. At fields ~ 60 % of breakdown, small pits in the oxide that are 0.4-0.8 nm deep can be created. Repeated application of this field within the pit will cause dielectric breakdown, even though the same field will not induce breakdown in regions away from the pit. The results provide direct evidence of the ability of localized defects to decrease the barrier to dielectric breakdown in an ordered oxide film.

9:20am **SS1+MC-ThM4 Oxidation of Sn/Pt (111) Surface Alloys under UHV Conditions- Formation of Ultrathin SnOx Films on Pt(111)***, M. Batzill, D. Beck, **B.E. Koel,*** University of Southern California

Platinum-tin systems are important as hydrocarbon reforming catalysts when supported on alumina. The tin may however exist in oxidic form and thus SnOx may be responsible for the altered catalytic properties of the Sn-Pt system compared to pure Pt, rather than alloying of Sn and Pt. In order to study ultrathin SnOx overlayers on Platinum we have oxidized both ordered Sn/Pt(111) surface alloys (the p(2x2) and the (sqr3 x sqr3)R30 alloy structure) using NO2 as an oxidant. The structure, chemical state and thermal stability of the oxide films have been examined by LEED, STM, XPS, AES and TPD. Oxidation of p(2x2) alloy results in a discontinuous mono-layer thick SnOx film that decomposes at 760 K. Oxidation of the (sqr3 x sqr3)R30 in contrast forms a thermally more stable continuous overlayer that shows two ordered surface phases depending on the annealing temperature. These structures have been analyzed using LEED and STM. The chemical activity of these surfaces was probed by small hydrocarbon molecules and CO.

9:40am **SS1+MC-ThM5 Monte Carlo Simulation of Initial Al(111) Oxidation***, **D.E. Oner,** R. Chakarova, I. Zori@aa c@, B. Kasemo,* Chalmers University of Technology, Sweden

In this work a Monte Carlo simulation technique is applied, exploring the influence of several models for O@sub 2@ dissociation on the initial Al(111) oxidation. The primary experimental data motivating this are the STM studies by Brune et al. (J. Chem. Phys. 99 (1993) 2128). The simulations are performed to gain more insight into the kinetics of the oxidation process. The Monte Carlo simulation is based on the lattice-gas approach using the Metropolis algorithm. The simulations assume alternatively "normal" dissociation (deposition of O atoms at adjacent surface sites), hot dimer dissociation (widely separated O atoms due to hot dissociation fragments) or abstraction (one of the separating O atoms performs a ballistic motion away from the surface). Further elements of the model are surface mobility, attractive forces between adsorbed O-atoms (i.e. adsorbate-adsorbate interaction), and in-diffusion of O atoms into the 2nd and deeper layers to form 2D and 3D oxide. Input data are, when available, taken from experiments or first-principles calculations. The results of this computational work are compared to the experimental results by Brune et al. The calculated surface configurations of chemisorbed O-atoms at 300 K in the low coverage regime, based on the hot dimer dissociation model, are in good agreement with the observed experimental STM data. The simulations of thermal annealing of chemisorbed oxygen islands are in fair agreement with the observed island kinetics by Trost et al. (J. Chem. Phys. 108 (1998) 1740). In the latter case, the O-O interaction strength is a crucial parameter. The present simulation model provides a useful platform for further simulations of Al oxidation. @FootnoteText@ Keywords: Monte Carlo simulation, surface oxidation, oxide nucleation and growth, hot chemisorption, metal oxidation, kinetics, aluminium.

10:00am **SS1+MC-ThM6 Thin Epitaxial Oxide Films and Interfaces for Advanced Microlectronics and Magnetics***, **S.A. Chambers,*** Pacific Northwest National Laboratory **INVITED**

Metal oxides constitute an extremely diverse class of materials, with virtually all types of electronic and magnetic behavior represented. These materials thus possess many properties that make them unique and potentially important for future technologies. No other class of materials exhibits such a wide range of behavior: band gaps spanning the visible and UV; electronic properties ranging from superconducting to metallic to semiconducting to insulating; magnetic properties ranging from ferromagnetic to antiferroma gnetic; and dielectric properties ranging from low-k to ferroelectric and piezoelectric. In addition, metal oxides exhibit a wide range of crystal structures, including spinel, perovskite, and corundum. As a result, a variety of heteroepitaxial structures can be designed and synthesized. In this talk, I present recent results on three heteroepitaxial oxide systems that illustrate the fascinating interface physics and potential technological advantages of these materials: (1) SrTiO@sub 3@(001)/Si(001), (2) CoFe@sub 2@O@sub 4@(001)/MgO(001) and, (3) MgO(001)/Ag(001) and Pt(111)/@alpha@-Cr@sub 2@O@sub 3@(0001)/Pt(111)/@alpha@-Al@sub 2@O@sub 3@(0001). System 1 is of considerable interest as a high-k gate oxide in next-generation MOSFETs.@footnote 1@ System 2 is a model that permits us to investigate thin films of what appears to be a very promising high-magnetic-anisotropy, insulating ferrimagnet.@footnote 2@ System 3 allows us to examine the effects of polarizable metals on the optical, electronic and magnetic properties of ultrathin oxides that are within electronic screening lengths of the metal.@footnote 3@ Structural, electronic and magnetic properties of these systems, all grown by molecular beam epitaxy, will be presented. @FootnoteText@ @footnote 1@ R.A. KcKee et al., Phys. Rev. Lett. 72, 2741 (1994). @footnote 2@ Y. Suzuki et al., Appl. Phys. Lett. 68, 714 (1996). @footnote 3@ S. Altieri et al., Phys. Rev. B59, R2517 (1999).

10:40am **SS1+MC-ThM8 The Oxidation of Pd(100)***, **G. Zheng**, E.I. Altman,* Yale University

Motivated by interest in Pd as a catalyst for oxidation reactions and the catalytic combustion of CH@sub 4@, the interaction of Pd(100) with O@sub 2@ was studied using LEED, STM, and TPD. Initial exposure of Pd(100) to O@sub 2@ at room temperature resulted in a (2x2) structure that saturated at an oxygen coverage of 0.25 ML (1 ML = 1 O/Surface Pd) following 30 L exposure. Further exposure to O@sub 2@ at room temperature resulted in a mixture of (2x2) and p(5x5) LEED patterns, which persisted until the oxygen coverage reached a saturation value of 0.68 ML. Increasing the exposure temperature to 475 K resulted in the p(5x5) structure in the oxygen coverage range of 0.60-0.80 ML, which transformed into a (@sr@5x@sr@5)R27° pattern beyond 0.80 ML. TPD experiments revealed four oxygen desorption features from Pd(100) following exposure to O@sub 2@, including peaks at 800 K, 700 K and 650 K, as well as a low temperature oxygen shoulder at 600 K. The highest temperature peak corresponds to the (2x2) chemisorption structure, and the other two peaks fall into the regime where p(5x5) and (@sr@5x@sr@5)R27° patterns appear. The three peaks saturated in sequence, and the low temperature shoulder showed up before saturation of the 650 K peak. These results indicate at least four distinct oxygen states on Pd(100). Upon annealing, the (@sr@5x@sr@5)R27° LEED pattern transformed into the (2x2) pattern without stepping through the p(5x5), and the p(5x5) structure converted into the (2x2) pattern. The temperature dependence of oxygen up-take was also studied. Oxygen was found to have the highest sticking coefficient on Pd(100) at 550 K. STM studies revealed the atomic structures of various oxygen phases on Pd(100), as well as their relative reactivity towards reduction by in-situ monitoring of the surface during exposure to CO and propylene.

11:00am **SS1+MC-ThM9 Surface Characterization of Oxidative Corrosion of U-Nb Alloys***, **D. Kelly,*** Los Alamos National Laboratory*; W.L. Manner,* Union Carbide Corporation*; J.A. Lillard, R.J. Hanrahan, Jr., M.T. Paffett,* Los Alamos National Laboratory

We have studied the relative rates of oxidative corrosion of U-Nb alloys containing 2 to 8 wt. % Nb, using X-ray photoelectron spectroscopy (XPS) and depth profiling by sputtered neutrals mass spectroscopy (SNMS), The alloys have been characterized after exposure to dry and humidified air (up to 50% relative humidity) at temperatures from 25 to 125 @super o@C, and exposure to electrochemical solutions. XPS studies of U-6 wt. % Nb following oxidation at 300 K with oxygen indicate formation of a thin overlayer of stoichiometric UO@sub 2@ intermixed with Nb@sub 2@O@sub 5@. This same stoichiometry is exhibited upon oxygen treatment at 500 K, however, niobium is much less oxidized, forming a mixture of NbO and Nb. SNMS depth profiling indicates that oxides formed using oxygen are thicker than those obtained using water. The formation of a critical density of Nb@sub 2@O@sub 5@ is suggested to enhance corrosion resistance by preventing diffusion of oxygen and/or hydroxyl species into the oxide/metal interface region. Tube furnace oxidation of the U-Nb alloys produces oxide layers comprised of UO@sub 2@ and Nb@sub 2@O@sub 5@ under all experimental conditions used. The thickness of the oxides increased with treatment time and temperature, but decreased with increasing Nb alloy content. For example, a 48 hour treatment at 75 @super o@C and 50% relative humidity results in oxide thickness on U-2%Nb that are three times that on U-8%Nb. Electrochemical oxidation of U-Nb alloys facilely generated UO@sub 3@ and Nb@sub 2@O@sub 5@ oxide layers with thicknesses qualitatively similar to thermal oxidation results. U-Nb alloys electrochemically oxidized at low pH exhibit oxide layers with near-surface regions (50 ???) enhanced in Nb content, as compared to the bulk material. Surface UO@sub 3@ was not readily reduced upon exposure to molecular D@sub 2@; however, D atoms facilely reduced UO@sub 3@ to UO@sub 2@.

11:20am **SS1+MC-ThM10 AFM Non-contact Imaging of Titaniumdioxid at Variable Temperatures**, *A. Bettac,* ***P. Güthner,*** *S. Molitor, A. Feltz, T. Berghaus,* Omicron Vakuumphysik GmbH, Germany; *A.W. Grant, S. Fain,* University of Washington

True atomic resolution in AFM non-contact mode has been achieved on several samples. Here we present first images on a TiO@sub 2@ (110) single crystal at sample temperatures from as low as 50 K up to 400° C. A new instrument design allows to perform true atomic resolution AFM images in a temperature range from 25 K to 1000 K. The sample was prepared by several cycles of ion sputtering and annealing in UHV. After this treatment it is conducting enough to perform STM measurements for controlling the quality of surface preparation. Non-contact AFM images on the TiO@sub 2@ (110) crystal show atomic resolution across mono-atomic steps. The surface is mostly showing a 1x1 reconstruction. At the step edges, lines with 1x2 reconstruction are starting. These lines may be associated with the formation of Ti@sub 2@O@sub 3@ strings along the surface. The density of areas with 1x2 reconstruction is increased with the annealing temperature which can be explained by the desorbtion of oxygen during the annealing process. Atomic resolution images on the TiO@sub 2@ (110) crystal were achieved at low temperatures down to 50 K sample temperature and at high temperatures up to 400° C.

11:40am **SS1+MC-ThM11 Plasma Oxidation as a Tool to Design Oxide Films at Low Temperatures**, ***R. Schennach,*** Lamar University; *D.G. Naugle,* Texas A&M University; *H. McWhinney,* Prairie View A&M University; *D.L. Cocke,* Lamar University

Interfacial oxidation is an established approach to produce surface thin films for catalysts, corrosion, ware protective coatings and electronic structures. The three main oxidation methods: thermal, anodic and plasma, still lack adequate fundamental physical-chemical models that can allow film design, particularly on alloys. Plasma oxidation of a CuZr alloy is studied using XPS (X-ray Photoelectron Spectroscopy). The dependence of the resulting oxide film on alloy composition and sample temperature during plasma oxidation is investigated. In contrast to thermal and electrochemical oxidation which lead to the formation of a zirconium oxide film, plasma oxidation leads to the formation of a copper oxide or metallic copper over layer depending on temperature and copper concentration in the bulk. It is shown that plasma oxidation can be used to design oxide films at room temperature, which require high temperatures using thermal oxidation.

Surface Science
Room 209 - Session SS2+VT-ThM
Adsorption and Desorption Phenomena II

Moderator: J.C. Hemminger, University of California, Irvine

8:20am **SS2+VT-ThM1 Alkali Metal and H@sub 2@O Co-adsorption and Reaction on Graphite(0001)**, ***M.A. Gleeson,*** *D.V. Chakarov, B. Kasemo,* Chalmers University of Technology and Göteborg University, Sweden

A comparative study of alkali metal (Na, K, Cs) adsorption, co-adsorption and reaction with H@sub 2@O on the basal plane of graphite has been performed. Water molecules are stabilised by interaction with alkali atoms, and undergo coverage and temperature dependent reactions. The surface solvation number is similar for all three alkali metals at low coverages (3 to 4 H@sub 2@O molecules per alkali atom). The critical alkali coverage for reactive co-adsorption at 98 K ranges between 0.1 to 0.25 ML. Reaction between H@sub 2@O and the alkali metals leads to the formation of hydroxide, hydride and oxide species on the surface. Additional peaks appear in the water desorption spectra due to alkali-stabilised H@sub 2@O and hydroxide decomposition. Decomposition of alkali oxides at high temperature can result in oxidation of the graphite and subsequent CO@sub 2@ evolution. Similarities and differences between the alkali metals are discussed.

8:40am **SS2+VT-ThM2 Adsorption of Hydrogen on Clean and Alkali-modified Low-index and Stepped Copper Surfaces**, *L. Thomsen,* Odense University/University of Southern Denmark; ***J. Onsgaard,*** Odense University/University of Southern Denmark, Denmark; *P.J. Godowski,* University of Wroclaw, Poland; *S.V. Hoffmann,* University of Aarhus, Denmark; *L. Bech, P. Moller,* Odense University/University of Southern Denmark

The interest for adsorption of low molecular gases like H and CO@sub 2@ on alkali-modified copper surfaces stems from the promoting role of the alkali metals in heterogeneous catalysis. Due to the substantial lowering of the work function with the addition of the alkali metal, pronounced changes in the adsorption and reaction properties of the copper surfaces are observed. The adsorption of atomic hydrogen on clean and potassium-modified Cu(110), Cu(100) surfaces and the stepped Cu(115), Cu(117) and Cu(112) surfaces has been studied. Typically, two hydrogen-induced states in the valence band have been found on the clean crystal and assigned to one state receding in the subsurface and another state at the surface of the crystal. Two states due to hydrogen are also observed on the potassium-modified surfaces and assigned to a potassium-hydrogen bond and a copper-hydrogen bond. Coadsorption of H and CO@sub 2@ on the K/Cu surface results in formation of formate with high efficiency on the most corrugated surfaces.

9:00am **SS2+VT-ThM3 Angle Resolved Photoemission Study on Adsorption and Desorption of Cobaltocene on Cu(111)**, ***J. Choi,*** Louisiana State University; *P.A. Dowben,* University of Nebraska, Lincoln

The molecular adsorption and desorption of cobaltocene, Co(C5H5)2, on Cu(111) have been studied by angle resolved photoemission spectroscopy (ARPES). We have measured the molecular orientation and bonding of adsorbed cobaltocene on Cu(111). Photoemission results indicate that the initially adsorbed surface species closely resembles that of molecular cobaltocene. The shift in photoemission binding energies relative to gas phase is largely independent of the molecular orbital. The molecule is adsorbed with cyclopentadienyl (C5H5) ring ligands parallel to the surface at 150K, and the molecular axis normal to the surface at the low coverage (below 10 Langmuir). The molecularly adsorbed cobaltocene loses the normal preferential orientation, at the higher coverages. Furthermore, molecular orientation is strongly affected by annealing temperature, indicating that there are more than one molecular adsorption states. With increasing of temperature, molecularly adsorbed cobaltocene on Cu(111) is desorbed.

9:20am **SS2+VT-ThM4 Angle Effects on the Nucleation of Polymeric Thin Films from Molecular Cluster Deposition: Molecular Dynamics Simulations**, ***Y. Hu,*** *S.B. Sinnott,* The University of Kentucky

Cluster beam deposition of organic material is thought to result in thin-film formation through rapid chemical reactions that occur at the impact site between the cluster and the surface. These reactions occur on the order of a few picoseconds and so are ideal for study with atomistic simulations. In this work, classical molecular dynamics simulations are used to investigate the effect of incident angle on the nucleation and growth of polymeric thin films through organic molecular cluster deposition. The classical reactive empirical bond order method is used in the simulations.@footnote 1@ The specific system under study consists of clusters of ethylene being deposited on a diamond and amorphous carbon substrate at room temperature at various incident angles. The results show how the incident angle affects the nucleation of a thin film from the deposition. In addition, the dependence of this angle effect on substrate rigidity is investigated. This work is supported by the National Science Foundation (CHE-9708049). @FootnoteText@ @footnote 1@ S.B. Sinnott, L. Qi, O.A. Shenderova, D.W. Brenner, in Chapter 1 of Volume IV of ADVANCES IN CLASSICAL TRAJECTORY METHODS, Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces, Ed. W. Hase (JAI Press, Inc., Stamford, CT, 1999), pp. 1-26.

9:40am **SS2+VT-ThM5 Geometrical Structure and Orientation of Metal Tetraphenylporphyrins on Au (111)**, *K.W. Hipps,* ***L. Scudiero,*** *D.E. Barlow,* Washington State University

Geometrical structure and orientation of metal tetraphenylporphyrins on Au (111). Metal (II) tetraphenylporphyrin (MTPP) complexes adsorbed on polycrystalline Au and Au (111) are studied by Fourier transform reflectance-absorption infrared (FT-RAIR), X-ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscope (STM). XPS and FT-RAIR data indicate that the chemical composition of those complexes is preserved when they are vapor deposited on Au. FT-RAIR data also suggests that the first few adsorbed layers are oriented with the porphyrin ring parallel to the Au surface. STM images are presented for several transition metal ions. At low coverage, STM images show monolayer islands randomly distributed on Au (111) and high-resolution images display a square unit cell.

10:00am **SS2+VT-ThM6 Experimental and Theoretical STM Imaging of Xylene Isomers on Pd(111)@footnote 1@***, D. Futaba, J.P. Landry,* ***A. Loui****, S. Chiang,* University of California, Davis

We have performed both theoretical and experimental studies of the three isomers of xylene, C@sub 6@H @sub 4@(CH@sub 3@)@sub 2@, adsorbed on Pd(111). Simulated scanning tunneling microscope (STM) images, calculated using a relatively simple computational method based on extended Hückel molecular orbital theory (EHT), showed no observable differences in surface features between occupied and unoccupied states images, nor between adsorption on the various high symmetry binding sites. The calculated binding energies suggest that xylene molecules prefer to bind in particular orientations on hollow and bridge sites. The computed images for xylene on Pd displayed almost identical surface features and symmetries as those calculated on Rh(111).@footnote 2@ Using STM and low-energy electron diffraction (LEED), we imaged the characteristic surface structures and investigated the molecular ordering for the three isomers on Pd(111). Experimental STM images showed each of the isomers exhibiting the characteristic geometries predicted by EHT. Both meta(m-)xylene and ortho(o-)xylene are characterized by an overall triangular shape, with m-xylene nearly equilateral. Para(p-)xylene shows a distinct diamond shape. M-xylene molecules adsorbed to upper step edges, usually with one side of the molecule aligned with the step edge and parallel to the close-packed directions of the Pd lattice. Only the p-xylene isomer showed long range order, forming a hexagonal structure with the long axes of the molecules parallel to each other. Translation and rotation of p-xylene molecules between consecutive scans were observed for the saturated Pd surface, causing disorder in previously ordered regions. @FootnoteText@ @footnote 1@ Supported by NSF CHE-95-20366 and UCOP CLC. @footnote 2@ D. N. Futaba and S. Chiang, Surf. Sci., 448, L175 (2000).

10:20am **SS2+VT-ThM7 Reactions of cis-, trans-, and 1,1-dichloroethene on Pd(111) Studied by TDS, LITD, and STM***, D.E. Hunka, D.M. Jaramillo,* University of California, Davis*; D.C. Herman,* University of North Carolina, Chapel Hill*; K.D. Lormand, D. Futaba, S. Chiang,* ***D.P. Land****,* University of California, Davis

Chloroethylenes are the among the most abundant groundwater and soil contaminants. Catalytic degradation on transition metal surfaces offers a promising method for the alleviation of this ubiquitous problem. Large differences in the reaction rates of the various compounds have been observed. However, little is known about the reaction mechanisms or the origin of these rate differences. In aqueous solutions, for example, cis-dichloroethylene (cis-DCE) reacts an order of magnitude more slowly on Fe than do trans- or 1,1-DCE. The reactivities do not follow any monotonic trends in dipole, solubility, or bond strength. Addition of Pd to Fe catalysts has been shown to increase the rate of reaction for some of these species by orders of magnitude. We have undertaken to study the reactivity of the three isomers of DCE on Pd(111). As in aqueous solution, the cis isomer reacts very differently from the other two isomers. Decomposition on Pd(111) occurs below room temperature and H@sub 2@ is evolved with C and Cl remaining on the surface to very high temperatures. In contrast, both trans- and 1,1-DCE rearrange to yield chlorinated intermediates that decompose in two steps above room temperature liberating HCl. Some subtle differences exist in the reaction mechanisms, but both are drastically different from the cis isomer. Laser-induced thermal desorption and conventional thermal desorption with FT mass spectrometry, infrared spectroscopy, scannin tunneling microscopy and other surface techniques are used to elucidate the surface reaction mechanisms and energetics.

10:40am **SS2+VT-ThM8 Wet Oxidation of CO on Pt(111)***,* ***J. Bergeld****, D.V. Chakarov, B. Kasemo,* Chalmers University of Technology and Göteborg University, Sweden

Presence of small amounts of OH is found to initiate the CO oxidation on Pt(111) surface. We have studied water coadsorption with CO on atomic oxygen precovered platinum surface with temperature programmed desorption (TPD) and found distinct relationship between the low temperature, @beta@@sub 3@ peak intensity and the presence and amount of coadsorbed OH. High initial CO coverage is another prerequisite for the low temperature start of the reaction. We are proposing and discussing several feasible mechanisms of the phenomenon, giving preference to autocatalytic reaction between CO and OH at the boundaries of ordered CO and oxygen/hydroxyl islands.

11:00am **SS2+VT-ThM9 The Behavior of Zirconium Surfaces in the Presence of Oxygen, Nitrogen, and Hydrogen Containing Adsorbates***,* ***Y.C. Kang****, D.A. Clauss, R.D. Ramsier,* University of Akron

Zirconium and its alloys exhibit a unique combination of physical properties that have led to their widespread use as structural materials in fission reactors as well as in a variety of chemical engineering applications involving harsh environments. Common to these applications is the presence of oxygen, nitrogen, and hydrogen containing moieties. Mechanistic studies of the chemistry of such species on zirconium surfaces are necessary to answer fundamental questions which cannot be addressed by phenomenological models of environmentally assisted degradation in these systems. As part of an effort to address these questions, low energy electron diffraction (LEED) and temperature programmed desorption (TPD) techniques have been applied to the adsorption of water, nitric oxide, and ammonia on Zr(0001) surfaces. Water adsorption at 180 K at exposures above 0.75 L results in water desorption in a broad TPD feature near 550 K. Data from LEED indicate that this adsorption does not result in ordered layers until 700 K annealing, and that the formation of ordered structures depends on exposure and annealing conditions. Low exposures of nitric oxide and ammonia at 160 K results in essentially no thermal desorption features, but high (greater than 20 L) ammonia exposures results in the production of water during TPD experiments and the formation of complex residual LEED patterns. These TPD and LEED data indicate a competition between the kinetics of recombination and desorption with those of diffusion involving the near-surface regions.

11:20am **SS2+VT-ThM10 Chlorosilane Adsorption on Clean Si Surfaces: STM and FT-IR Studies***,* ***M. Nishizawa****, T. Yasuda, S. Yamasaki,* Joint Research Center for Atom Technology (JRCAT), Japan*; M. Shinohara, Y. Kimura, M. Niwano,* Research Institute of Electrical Communication (RIEC), Japan

Understanding the interaction of silane and chlorosilane molecules, (SiH@sub n@Cl@sub 4-n@), with Si surfaces is the base for atomic-scale control of Si growth. A Si(111) surface exhibits the DAS structure which has 7 kinds of dangling bonds with different electron occupancy, while a Si(100) surface reconstructs to the asymmetric-dimer structure. We are interested in the interaction of chlorosilane with these qualitatively different surfaces. This paper discusses structures of SiH@sub 2@Cl@sub 2@-chemisorbed Si(111)-(7x7) and Si(100)-(2x1) surfaces. We have employed STM to identify reaction sites, and FT-IR to probe their local structure. In the STM topographs for adsorption on the Si(111)-(7x7) surface, reacted adatom sites appear darker than the unreacted ones. At a low coverage, we find that SiH@sub 2@Cl@sub 2@ molecules preferentially react with corner adatoms in the unfaulted half of the (7x7) unit cell to produce surface species - SiH@sub 2@Cl and -Cl. Komura et al. proposed a structural model in which the - SiH@sub 2@Cl group is adsorbed on the corner-hole atom.@footnote 1@ Our STM results agree with this model. On the other hand, FT-IR spectra measured for this surface showed two sharp peaks at 2108 cm@super -1@ and 2123 cm@super -1@. These peaks are tentatively assigned to the symmetric and asymmetric Si-H stretching vibrations of the surface - SiH@sub 2@Cl group. However, the observed peak positions of the Si-H stretching vibrations are much lower than those predicted from the semi-empirical formula by Locovsky.@footnote 2@ The reason for this discrepancy is under consideration. Results for the Si(100) surface will be reported at the presentation. This study, partly supported by NEDO, was performed at JRCAT under the joint research agreement between NAIR and ATP. @FootnoteText@ @footnote 1@ T. Komura et al., Appl Surf. Sci. 130 (1998) 23. @footnote 2@ G. Lucovsky, Solid State Commun. 29 (1979) 571.

11:40am **SS2+VT-ThM11 A Far-IRAS Study of Water Adsorption on V@sub2@O@sub3@(0001)***,* ***M.J. Pilling****,* University of Wisconsin, Milwaukee*; D.S. Toledano,* Yale University*; C.J. Hirschmugl,* University of Wisconsin, Milwaukee*; V.E. Henrich,* Yale University

The high brightness of a synchrotron radiation source has been utilized to investigate adsorption occurring on a single crystal transition metal oxide surface with far infrared reflection absorption spectroscopy (IRAS). The adsorption of H@sub2@O, H@sub2@@super18@O and oxygen on V@sub2@O@sub3@(0001) was investigated between 154K and 224K. Infrared absorption bands at 992 cm@super-1@ and 1040cm@super-1@ are observed in the spectra above and below the desorption temperature of multilayer water, indicating the presence of a chemisorbed surface species.

Surface Science
Room 210 - Session SS3-ThM
Surface and Interface Structure II

Moderator: A.P. Baddorf, Oak Ridge National Laboratory

8:20am **SS3-ThM1 Polar Oxide Surfaces***, **M. Gajdardziska-Josifovska,*** University of Wisconsin, Milwaukee **INVITED**

The stability of polar oxide surfaces has long been a problematic question in surface science. A bulk terminated polar surface has an infinite surface energy because alternating layers of oppositely charged ions produce a large dipole moment perpendicular to the surface. Such a singularity presents many interesting questions ranging from the fundamental "Can polar oxide surfaces exist?" via the mechanistic "How can they get stabilized?" to the applied "Would they have unique and useful surface and interface properties?". Both theory and experiment have provided several contrary answers to the first two questions, and the last is largely unexplored. In the seventies, the problem was considered closed with consensus between theory and experiment that polar oxide surfaces can not exist but must facet into neutral planes to gain finite surface energy. In the nineties the problem was reopened with experimental discoveries of reconstructed polar oxide surfaces and with theoretical predictions of clean reconstructed surfaces based on the idea of smallest neutral building blocks. At present, there is disagreement between the few proposed and solved polar oxide surface structures, and the reconstruction mechanism is under construction. An additional controversy surrounds the 1x1 structure of polar oxide surfaces. Classical electrostatic approaches predict that such structures can exist only by adsorption of charged species, OH being the currently favored termination, but quantum mechanical approaches predict two dimensional surface metalization of the clean 1x1 surface. I will review the present state of knowledge, with illustrations from our multi-technique experimental studies of the polar MgO and NiO (111) surfaces and their neutral (100) and (110) counterparts. Our data favors the reconstruction mechanism at high temperatures, and the OH adsorption mechanism at lower temperatures.

9:00am **SS3-ThM3 Helium Atom Scattering Study of the Surface Structure and Dynamics of in situ Cleaved MgO(001) Single Crystals@footnote 1@***, **J.G. Skofronick,*** Florida State University*; G. Benedek,* Dipartimento di Fisica dell'Universita'*; G. Brusdeylins, D. Schmicker, S. Schmidt, V. Senz, J.P. Toennies, F. Traeger, R. Vollmer,* Max-Planck-Institute fuer Stroemungsforschung, Germany

A high resolution helium atom scattering study on the surface structure and dynamics of in situ cleaved MgO(001) single crystals, under ultra high vacuum conditions, in both high symmetry directions, has been performed. The Rayleigh modes were observed over most of the reduced surface Brillouin zone; these results agree with previous measurements and theory. Two new modes at and near the zone boundary for the and the high symmetry directions are observed at 40 meV and 36 meV, respectively. A weak half order reconstruction is observed in diffraction scans in the direction. A suggested mechanism for the latter is given. Refined bound state resonance information, giving the energy levels of the laterally averaged He+MgO(001) surface potential are included. @FootnoteText@ @footnote 1@ Supported in part (JGS) by DOE Grant No. DE-FG02-97ER45635.

9:20am **SS3-ThM4 Molecular Beam Epitaxy-Scanning Tunneling Microscopy of Wurtzite GaN Thin Films***, **Q.Z. Xue,** Q.K. Xue, S. Kuwano, K.F. Kelly, S. Nakayama, I.S.T. Tsong, T. Sakurai,* Tohoku University, Japan*; T. Ohno,* National Research Institute of Metals, Japan

Gallium nitride has been known for their enormous potential applications for optoelectronics devices operating in the spectral range from blue to ultraviolet. As the present application depends critically on controlled heteroepitaxy of GaN thin films, complete knowledge of its growth behavior and fundamental physical properties is highly desired to optimize its film growth and device applications. GaN can crystallize into both hexagonal and cubic forms, depending on the substrates and the growth conditions. And the hexagonal GaN has a further freedom in its film polarity, which has direct influence on its surface structure and growth process. In the present work, a systematic investigation of the growth and the surface reconstructions of the wurtzite GaN have been in-situ performed using molecular beam epitaxy (MBE) combined with scanning tunneling microscopy (STM) system. A two-step method is developed to prepare the 6H-SiC substrate, and the Ga-polar GaN(0001) and N-polar thin films are grown by plasma-assisted-MBE on the Si-polar and C-polar 6H-SiC respectively. Through the post-growth Ga-deposition, distinctly different series of surface reconstructions have been obtained on the films for each polarity, that is, on GaN(0001) surface, 1x1, 2x2, 4x4, @sr@7x@sr@7, 5x5, 5@sr@3x2@sr@13, 10x10 and 1x1-Ga fluid are formed, while on GaN(000-1) surface, 2x4, 6x6, 2@sr@7x2@sr@7 are observed. All these phases are Ga-rich, and no ordered N-rich phase has been observed. Based on the atomically-resolved STM images and first principles total energy calculations, we will show that the structures of these phases can be understood under Ga-adatom scheme. Since many of them are not satisfied with electron counting which is popular for the conventional semiconductors, we will document that stability of these phases can be interpreted by Peierls or Mott-Hubbard metal-insulator transitions due to the many-body effects.

9:40am **SS3-ThM5 One-Dimensional Noble Metal Growth on Si(5 5 12)***, **A.A. Baski,** K.M. Jones, K.M. Saoud,* Virginia Commonwealth University **INVITED**

Metal-semiconductor systems that exhibit 1-D growth have lately been of interest, particularly those that form nanometer-scale metal rows on a semiconductor. The recently discovered surface of Si(5 5 12) forms a single-domain reconstruction composed of row-like structures.@footnote 1@ providing a unique template for the growth of 1-D nanostructures. Our recent scanning tunneling microscopy (STM) studies show that noble metals such as Ag and Au deposited onto Si(5 5 12) and annealed indeed form a wide variety of well-ordered overlayer rows.@footnote 2@ At coverages below 0.25 monolayers (ML), both metals grow as monatomic rows with an inter-row spacing of ~5 nm. These metal rows preferentially nucleate along the more reactive Si tetramer rows of the surface reconstruction, leading to their growth in a periodic array. Scanning tunneling spectroscopy (STS) data show that Ag wires have a finite density of states at zero volts, indicating metallic behavior. At higher coverages and annealing temperatures, the underlying Si reconstruction is removed and the growth behavior of Ag and Au diverges. Up to ~0.5 ML, Ag forms sawtooth rows which evolve with coverage to an extremely well-ordered array of stepped double rows. Surprisingly, this phase has a significant band gap (1.25 V) compared to the clean Si surface (0.5 V). At comparable coverages and annealing temperatures, Au growth is usually less ordered; however, significantly elevated temperatures (>500C) lead to the creation of well-ordered facet planes [e.g. (7 7 15) and (225)]. For all coverages and annealing temperatures studied here, deposits of Au and Ag form row-like morphologies on the Si(5 5 12) surface, indicating the utility of this high-index surface as a template for the growth of 1-D nanostructures. @FootnoteText@ @footnote 1@ A. A. Baski, S. C. Erwin, and L. J. Whitman, Science 269, 1556 (1995). @footnote 2@ H.H. Song, K.M. Jones, and A.A. Baski, J. Vac. Sci. Technol. A 17(4), 1696 (1999).

10:20am **SS3-ThM7 Stability and Nuclear Formation of Si(111)-7x7 Structure as Determined from Charge Redistribution in Surface Layers***, **K. Miyake,** T. Kaikoh, Y.J. Li,* University of Tsukuba, Japan*; R. Morita, M. Yamashita,* Hokkaido University, Japan*; H. Shigekawa,* University of Tsukuba, Japan

Reconstruction of the Si(111) surface has been extensively studied by various experiments as well as theoretical considerations. And 7x7 structure has been concluded to be the most stable phase on the Si(111) surface in equilibrium condition. In fact, the 7x7 phase is completed on the well annealed surface, and phase transition between high-temperature "1x1" and 7x7 phases was directly observed around the critical temperature by using scanning tunneling microscopy (STM). The dimer-adatomstacking-fault (DAS) structure proposed by Takayanagi et al., @footnote 1@ which is compatible with the experimental and theoretical results, is widely accepted as the model for the Si(111)-7x7 reconstructed surface structure. And atomic arrangement of the DAS structure in the static form is now well established. However, since the DAS structure involves few surface layers and is very complicated, dynamics of the surface, mechanism for the formation and stabilizing processes of the structure, has not yet been completely clarified, and is still attracting considerable attention. By considering the charge transfer from adatoms to rest atoms, we can analyze the structure of the dimer and stacking-fault (DS) layers in the Si(111) dimer-adatomstacking-fault (DAS) structure in a subunit level. In comparison with the modified model of Vanderbilt, corner holes with the completed DS structure in the second layer, completed corner hole, was confirmed to play a key role not only in the mechanism to stabilize the DAS structure, but also in the formation process of it; formation of the completed corner hole works as a rate limiting process for the growth of the DAS structure.@footnote 2@ This mechanism was shown to be quite consistent with the experimental results which had been obtained by STM on the quenched and HBO@SUB 2@ molecules irradiated

Si(111) surface.@footnote 3@ Phase transition from Si(111)-7x7 to the B-induced @sr@3x@sr@3 structure, and the structure near the step edge was analyzed in detail. @FootnoteText@ @footnote 1@K. Takayanagi et al, J. Vac. Sci. Technol., A 3 (1985) 1502. @footnote 2@K. Miyake et al., Surf. Sci., 429 (1999) 260-273. @footnote 3@K. Miyake et al., Jpn. J. Appl. Phys., 38 (1999) 3841.

10:40am **SS3-ThM8 First Principles Study of Cross-sectional Surface Structure of III-V Heterostructures***, **S.-G. Kim,*** Vanderbilt University*; S.C. Erwin, B.Z. Nosho, L.J. Whitman,* Naval Research Laboratory

Heterostructures of III-V semiconductors form the basis for a variety of devices. The performance of these multilayer structures is extremely sensitive to the thickness of the layers and the nature of the interfaces between them. As the layers are made thinner, a microscopic understanding of interface structure and chemistry will become increasingly important for optimizing device performance. The challenge is how best to achieve a complete microscopic characterization. We demonstrate the power of combining density-functional theory with experimental data from cross-sectional scanning tunneling microscopy (XSTM). We use first-principles computational methods to interpret XSTM images that we have obtained from the (110) cleavage surface of 6.1-Å III-V heterostructures. We begin by determining theoretically the fully relaxed geometry of cleaved InAs/GaSb superlattices, using the local-density approximation (LDA) to density-functional theory. To understand the relative importance of electronic vs. structural effects in the STM topography, we generate simulated XSTM images over the cross-sectional surface and compare with our measured XSTM images. We also focus on the role played by the specific interface bond type (In-Sb vs. Ga-As bonds) and show, for example, that XSTM can indeed be used reliably to identify the interface bond type. Finally, we study in detail the thermodynamics of defect formation due to diffusion across the interface; these theoretical predictions compare very favorably with our XSTM studies, and form the basis for further studies of the impact of interfacial disorder on device performance.

11:00am **SS3-ThM9 Reflectance Difference Spectroscopy of Mixed Arsenic-Rich Phases of Gallium Arsenide (001)***, **D.C. Law,** M.J. Begarney,* University of California, Los Angeles*; L. Li,* University of Wisconsin, Milwaukee*; C.H. Li, Q. Fu, R.F. Hicks,* University of California, Los Angeles

The relationship between the reflectance difference spectra and the atomic structure of arsenic-rich reconstructions of GaAs (001) has been investigated. Scanning tunneling micrographs reveal that a complex roughening process occurs as the surface structure changes with decreasing arsenic coverage from 1.75 to 0.75 monolayers (ML). With the loss of 0.1 ML of As, small pits, one bilayer in depth and having the same c(4x4) reconstruction as the top layer, form in the terraces. At the same time, gallium atoms are liberated to the surface, disrupting the c(4x4) ordering. With further arsenic loss, (2x4) domains nucleate and grow on top of the c(4x4). This underlying layer gradually decomposes into a metastable (2xn) phase, and finally into the (2x4). In the reflectance difference spectra, negative peaks at 2.25 and 2.8 eV correlate with the c(4x4)-like arsenic dimers. However, the intensity of the latter feature strongly depends on the presence of adsorbates, such as alkyl groups and gallium adatoms. A positive peak at 3.25 eV appears to be related to the (2xn) structure. Finally, the intensity of the positive peak at 2.9 eV is shown to be proportional to the density of (2x4)-type dimers.

11:20am **SS3-ThM10 Dynamics of the Flip-Flop Motion of Single Buckled Dimers of Si(100)***, **H. Kenji,*** University of Tsukuba, Japan*; M. Ryuji, Y. Mikio,* University of Hokkaido, Japan*; H. Shigekawa,* University of Tsukuba, Japan

We report the direct observation of the flip-flop motion of single buckled dimers of Si(100) in real space by hovering the tunneling tip of scanning tunneling microscope over a pre-selected atom of the flip-flopping dimers and measuring the tunneling current. By this method, the complete time trace of the flip-flop motion of single dimers can be obtained, and from it, any desired properties of the dynamics can be deduced. Each dynamical flip-flop event (up to 200,000) was clearly resolved, and the time trace of the tunneling current shows that the flip-flop motion is a switching between two stable configurations. A statistical analysis of the autocorrelation function elucidates that the flip-flop motion is a stochastic process described by a two level system. The influence of the local environment on the dynamics of the flop-flop motion can be mapped out by executing the measurements on neighboring dimers. We found that the details of the dynamics of the flip-flop motion differ from dimer to dimer and from domain to domain. The activation energy of the flip-flop motion differs significantly (measured 32 meV, estimated 110~ meV) for dimers in different domains. http://dora.ims.tsukuba.ac.jp

11:40am **SS3-ThM11 Molecular Dynamics Simulations of Energetic Silicon Cluster Deposition on Graphite (0001)***, **R. Neuendorf**, R.E. Palmer,* The University of Birmingham, UK*; R. Smith,* Loughborough University, UK

Microcanonical Molecular Dynamics (MD) Simulations using classical interaction potentials@footnote 1@ have been employed to study the deposition of small Silicon clusters (3 to 55 atoms / cluster) onto a graphite (0001) surface. The clusters have been deposited with kinetic energies from 1 eV up to 100 eV per atom. We find that the deposition behaviour can be divided into four different regimes: i) wetting of the substrate for small clusters at low deposition energies leading to the creation of monolayer high isalnds ii) soft landing of larger clusters at low deposition energies iii) implantation of the clusters into the substrate at high deposition energies, leading to "hole drilling" as also found in the case of metal cluster deposition.@footnote 2@ iv) a regime of more complicated behaviour at intermediate deposition energies. @FootnoteText@@footnote 1@S. J. Carroll, S. G. Hall, R. E. Palmer and R. Smith, Phys. Rev. Lett. 81(17), 3715 (1998) @footnote 2@S. J. Carroll, P. D. Nellist, R. E. Palmer, S. Hobday and R. Smith, Phys. Rev. Lett. 84(12), 2654 (2000).

Semiconductors
Room 306 - Session SC+SS+EL-ThA
III-Nitride Growth and Nucleation
Moderator: V.M. Bermudez, Naval Research Laboratory

2:00pm **SC+SS+EL-ThA1 Kinetics of GaN Growth and Decomposition*, D.D. Koleske*,** *A.E. Wickenden, R.L. Henry, M.E. Twigg, J.C. Culbertson,* Naval Research Laboratory **INVITED**

While many devices have been demonstrated in the group III nitrides, details of the chemical reaction mechanisms for producing high quality GaN using metallorganic vapor phase epitaxy (MOVPE) continues to be an active area of research. In this presentation, I will highlight the results from several kinetic studies of GaN growth. This will include investigations of GaN decomposition in a commercial MOVPE reactor at temperatures and pressures typically used for growth. The GaN decomposition rates were measured in H@sub 2@, N@sub 2@, mixed H@sub 2@ and N@sub 2@, and mixed H@sub 2@ and NH@sub 3@. From these studies an enhancement in the GaN decomposition rate is observed in pure H@sub 2@ and mixed H@sub 2@ and NH@sub 3@ flows as the reactor pressure is increased above 100 torr. @footnote 1@ The mechanism for enhanced GaN decomposition will be presented. Measurements of GaN growth (with trimethylgallium) and decomposition (without trimethylgallium) rates under otherwise identical conditions indicate the extent of decomposition and incorporation during growth. GaN decomposition also accounts for a decrease in the GaN nucleation at higher pressures during the initial high temperature growth. This decrease in the nucleation density leads to increased grain size and higher quality GaN films.@footnote 2@ Kinetic issues relating to incorporation of defects will also be presented. These issues include a growth model for stoichiometric GaN growth,@footnote 3@ and the kinetics of surface carbon removal. All work sponsored by the Office of Naval Research. @FootnoteText@ @footnote 1@ D.D. Koleske, et al., Appl. Phys. Lett. 73, 2018 (1998); ibid. 75, 1646 (1999). @footnote 2@ A.E. Wickenden, et al., J. Electron. Mat. 29, 21 (2000). @footnote 3@ D.D. Koleske, et al., J. Appl. Phys. 84, 1998 (1998).

2:40pm **SC+SS+EL-ThA3 Carbonization of Si (111) by Gas Source Molecular Beam Epitaxy using Triethyl Gallium and Subsequent GaN Growth*, E. Kim,*** *A. Tempez, A. Bensaoula,* University of Houston

Next to sapphire, SiC is the most commonly utilized substrate for GaN heteroepitaxy. In addition to a better lattice match it has the advantage of being available in either conducting or insulating form. The most desirable substrate from both processing and cost point of view is Si since it will allow direct integration of GaN-based devices with conventional Si technology. To that end many approaches have been attempted to overcome the lattice mismatch and nucleation issues for GaN deposition on Si. We have already reported on RF-MBE and chemical beam epitaxy (CBE) of GaN on Si(111) using AlN buffer layers and demonstrated LEDs from our materials. To further improve on our previous results we explored the use of SiC as a buffer layer for the growth of GaN on Si. In this paper we demonstrate deposition of GaN on a SiC buffer layer formed by in situ carbonization of Si using a metalorganic precursor (triethylgallium: TEG) as the carbon source. The carbonization of the Si (111) surface is identified using in-situ time of flight low energy ion scattering, ex-situ XPS and XRD. The thickness, the crystalline quality and the surface morphology of the carbonized layer are found to be very temperature dependent. A 6H-SiC polycrystalline thin film is formed above 780°C. Layers formed at 800°C are thicker and rougher than those formed at 780°C. In either case, Ga is not incorporated into the SiC layer. The SiC layer is shown to efficiently block the formation of SiO@subx@N@suby@ surface species which hinders the GaN nucleation and makes GaN/Si heteroepitaxy non-reproducible. GaN layers deposited in the same reactor by CBE using TEG and ammonia were analyzed as a function of the SiC layer thickness and annealing temperature. Data from these layers as well as from RF-MBE GaN deposited on these SiC buffer layers will also be presented. This project was funded by a NASA cooperative grant #NCC8-127 to the Space Vacuum Epitaxy Center.

3:00pm **SC+SS+EL-ThA4 Epitaxial III-V Nitride Growth on SiC(0001) by Means of A@super 3@@Sigma@@sub u@@super +@ Metastable Molecular Nitrogen*, D.C. Jordan,*** *D.J. Smith, I.S.T. Tsong, R.B. Doak,* Arizona State University

High quality epitaxial III-N semiconductor films, ranging in thickness from 300 to 900 Å, have been grown using A@super 3@@Sigma@@sub u@@super +@ metastable nitrogen molecules. The work employed a corona discharge supersonic free-jet (CD-SFJ) to generate a molecular beam containing exclusively the A@super 3@@Sigma@@sub u@@super +@ activation state in an otherwise ground state N@sub 2@ beam. AlN films were grown on 6H-SiC(0001) and Si(001) substrates. GaN films were grown on the same substrates and on buffer layers of AlN deposited in situ on 6H-SiC(0001). The N-atom incorporation efficiency (defined as the number of N-atoms attaching to a III-N surface per incident metastable A@super 3@@Sigma@@sub u@@super +@ molecule) approached 100% in most instances and was found to be independent of substrate temperature from 600 to 900 Â°C, implying direct molecular chemisorption as the underlying reaction mechanism. These measurements support theoretical predictions that A@super 3@@Sigma@@sub u@@super +@ is an ideal precursor for III-N growth.

3:20pm **SC+SS+EL-ThA5 Crystal Growth Kinetics and Transport in GaN Epitaxial Lateral Overgrowth*, M.E. Coltrin,*** *C.C. Willan, M.E. Bartram,* Sandia National Laboratories **INVITED**

Epitaxial Lateral Overgrowth (ELO) is a useful technique to improve material quality and reduce defects in GaN. In ELO, a mask pattern of dielectric material, usually either silicon nitride or silicon dioxide, is deposited on top of a GaN buffer layer. Further growth of GaN occurs selectively on exposed areas of the underlying buffer layer, and not on the dielectric material. Typically, ELO conditions are optimized for a maximum lateral - to - vertical growth rate ratio. Growth kinetics of GaN crystal faces and transport effects will be discussed in this paper. Dimensions of the exposed and masked areas in line and dot patterns, pattern orientation with respect to the underlying substrate, and growth time were systematically varied. Growth rate information was obtained from scanning electron microscope (SEM) measurements. The coupling between transport and kinetic effects was examined by means of 2-D and 3-D numerical simulations. In general, transport of material from the masked to the unmasked regions is quite efficient. However, ELO deposition growth efficiency is shown to decrease dramatically when the ratio of exposed to masked areas becomes very small. ELO experiments incorporating deep trenches will be described, which are designed to distinguish between lateral transport of material via gas-phase vs. surface diffusion. Gas-phase transport of material appears to dominate. We have found a quantitative way to translate results from different pattern dimensions into a pseudo time basis by scaling growth features by a length scale W, the size of the exposed deposition window.

4:00pm **SC+SS+EL-ThA7 Thick GaN on Si Substrate by Hydride Vapor Phase Epitaxy using Epitaxial Lateral Overgrowth Technique*, J.W. Lee,*** *J.B. Yoo,* Sungkyunkwan University, Korea

The thick GaN growth is a very essential issue for the fabrication of GaN substrate. Epitaxial lateral overgrowth (ELOG) is one of the promising techniques for the high quality GaN epilayer as a fabrication of optical and electronic devices. In this study, two-step growth of GaN was optimized to grow high-quality GaN. First, we attempt ELOG technique for growth of GaN on a Si(111) substrate by MOCVD. Then the thick GaN film was overgrown on ELOG GaN by HVPE. Because of their large lattice mismatch between GaN and Si, the use of an intermediate layer or buffer layer is essential. For the growth of GaN on Si substrate the AlN layer was used to buffer layer. The AlN buffer layer was deposited by RF sputtering. The LT-GaN by was induced another buffer layer on Si substrate. The ELOG GaN on Si substrate was grown by MOCVD. The TMGa and ammonia were used as source gases. The growth temperature of ELOG GaN was changed range in 500°C to 1100°C. The thick GaN was grown by conventional HVPE. The chlorinated gallium and ammonia were used as source gas for Ga and N, respectively. The growth temperature of thick GaN was varied from 800°C to 1100°C. The SiO@sub 2@ was grown by PECVD for the use of ELOG mask on buffer layers. The stripe pattern was developed along and crystal axis of GaN. The various stripe windows with a different spacing between stripes were developed on the SiO@sub 2@ mask by conventional photolithography and wet chemical etching. The effect of growth parameters such as AlN, LT-GaN, growth temperature, stripe patterned direction were investigated. Surface roughness and morphologies of ELOG GaN film were analyzed by atomic force microscopy (AFM) and scanning electron microscope (SEM). The effect of ELOG on thick GaN-film was characterized by double crystal x-ray diffractometer (DCXRD), low temperature photoluminescence (PL) and transmission electron microscope (TEM).

4:20pm **SC+SS+EL-ThA8 Growth and Electronic Structure of ScN, a New Refractory III-V Semiconductor***, **D. Gall**, I. Petrov, J.E. Greene,* University of Illinois, Urbana

ScN layers, 40 to 345 nm thick, were grown on MgO(001) substrates at 750 °C by ultra-high-vacuum reactive unbalanced magnetron sputter deposition in pure N@sub 2@ discharges at 5 mTorr. All films were stoichiometric with N/Sc ratios of 1.00±0.02. Microstructural and surface morphological evolution were found to depend strongly on the energy E@sub i@ of N@sub 2@@super +@ ions incident at the film surface during deposition. Nucleation and the initial growth of ScN layers deposited with E@sub i@ = 13 eV are dominated by the formation of 111 and 002-oriented islands which exhibit local epitaxy. However, preferred orientation rapidly evolves toward a purely 111 texture by a film thickness of ~50 nm as 002 grains grow out of existence in a kinetically-limited competitive growth mode. In distinct contrast, ScN layers deposited with E@sub i@ = 20 eV are single crystals which grow in a cube-on-cube epitaxial relationship with MgO(001). ScN optical properties were determined by transmission, reflection, and spectroscopic ellipsometry while in-situ x-ray and UV valence-band photoelectron spectroscopy were used to determine the density of states (DOS) below the Fermi level. The measured DOS exhibits peaks at 3.8 and 5.2 eV stemming from the N 2p bands and at 15.3 eV due to the N 2s bands. The imaginary part of the measured dielectric function @epsilon@@sub 2@ consists of two primary features due to direct X- and @GAMMA@-point transitions at photon energies of 2.7 and 3.8 eV, respectively. The ScN band structure was calculated using an ab initio Kohn-Sham approach which treats the exchange interactions exactly within density-functional theory. Combining experimental and computational results, we show that ScN is a semiconductor with an indirect @GAMMA@-X bandgap of 1.3±0.3 eV and a direct X-point gap of 2.4±0.3 eV.

4:40pm **SC+SS+EL-ThA9 Structure and Optical Properties of ScN(001) Grown by Molecular Beam Epitaxy***, **H. Al-Brithen**, A.R. Smith, W.M. Jadwisienczak, H.J. Lozykowski,* Ohio University

Scandium nitride is grown by molecular beam epitaxy on MgO(001) substrates. Reflection high energy electron diffraction and x-ray diffraction both confirm the (001)-orientation of the ScN layer. The measured lattice constant is in close agreement with the expected lattice constant a = 4.501 Å, and there is no sign of strain aside from that due to differential thermal contraction between film and substrate during cooling. As measured by atomic force microscopy and scanning tunneling microscopy (STM), these films are found to be smooth, with terraces separated by steps of height a/2. As the Sc flux is varied, the growth morphology also varies - from that of plateaus and pyramids (for lower Sc flux) to that of spiral mounds (for higher Sc flux). We associate the transition with a particular ratio of Sc flux to N flux. Films grown with a lower Sc/N flux ratio have a distinct reddish appearance, and a turn-on feature at 570 nm in the cathodoluminescence (CL) spectrum is measured, consistent with a band gap energy of about 2.2 eV. Films grown with higher Sc/N flux ratio are dark in appearance, and no turn-on feature at 570 nm is observed in the CL spectrum. STM images atomically resolve the rock-salt surface lattice for films grown with lower Sc/N flux ratios; however, for films of higher Sc/N flux ratio, small protrusions are observed on the terraces, which are most likely excess Sc atoms. The effect of the Sc/N flux ratio on the stoichiometry of the films will also be discussed.

5:00pm **SC+SS+EL-ThA10 ScN Thin Films and Thin Film Devices***, **X. Bai**, M.E. Kordesch,* Ohio University

ScN films have been grown by plasma assisted physical vapor deposition (PAPVD) and reactive sputtering on quartz, sapphire, silicon and MgO. Growth temperature ranges from 300K to 1100K, thickness ranges from 50nm to 800nm. For PAPVD films, the XRD results show that ScN grows with (111) texture on quartz, both ScN (111) and (200) textures are observed on sapphire (0001), and (200) textured growth on Si (100). ScN films grown at 300 K are amorphous. Sputtered films show both (111) and (200) texture under various conditions. ScN grows epitaxially on MgO (100). Measurement of the lattice constant ranges from 0.442 nm on quartz to 0.458 nm on silicon. Temperature dependent condcutivity measurements show that ScN is a semiconductor. Intrinsic, p type and n type ScN can be synthesized, with carrier concentrations between 10@super12@ cm@super-3@ to 10@super22@cm@super-3@. The index of refraction is determined from IR measurements to be 2.46 ± 5%. The best optical bandgap result from our measurements is 2.26 eV. There are theoretical predictions of an indirect gap at about 1 eV, outside of our measurement range. ScN films have been used to fabricate p-n junctions, junctions with p and n type Si, and lattice mismatched isotype n-n junction with GaN. Functional ohmic contacts to ScN have been fabricated using Ti, Pd and Ni.

Surface Science
Room 208 - Session SS1+MC-ThA

Oxidation and Molecule-Oxide Interactions

Moderator: S.A. Joyce, Pacific Northwest National Laboratory

2:00pm **SS1+MC-ThA1 Real Time TEM Observations of the Oxidation of Silicon***, **F.M. Ross**,* IBM Research Division **INVITED**

By making real-time observations of the progressive changes occurring at the silicon/oxide interface during oxidation, it is possible to examine the mechanism of the reaction and accurately measure the oxidation kinetics. In this presentation we will describe experiments carried out in a UHV transmission electron microscope which has been modified to allow images to be obtained before, during and after oxidation. By careful choice of imaging conditions we can follow the motion of the silicon/oxide interface in real time during oxidation, and in particular we can observe the configuration of interface steps. Our experiments show that passive oxidation, in which SiO@sub 2@ is formed, occurs in a layer-by-layer fashion with no flow of interface steps. Active oxidation is also a terrace reaction, although the SiO which is formed evaporates preferentially from surface steps. We will briefly discuss how the observation and analysis of step and terrace contrast is a powerful tool for examining the mechanism of other silicon surface reactions, such as epitaxial growth or silicide formation, as well as oxidation.

2:40pm **SS1+MC-ThA3 Comparison of Electrochemical Corrosion Properties and Oxidation Kinetics of Ozone- and Oxygen-formed Aluminum Oxide Films***, **A. Kuznetsova**, I. Popova, V. Zhukov, G. Zhou, J.C. Yang, J.T. Yates, Jr,* University of Pittsburgh

Ozone, O@sub 3@, has been employed to produce an aluminum oxide layer (thickness about 20 Å), on Al(111)and also on polycrystalline Al surfaces. It has been found, by electrochemical impedance spectroscopy, that the impedance of such films is about 10 times higher than films grown to similar thickness with O@sub 2@.Transmission electron microscopy studies have shown that the average pore size of Al@sub 2@O@sub 3@ films grown with O@sub 3@ (20 Å) is smaller than in films grown with O@sub 2@ (100 Å). In addition, electron diffraction studies of amorphous film have shown that the density of oxide film grown with O@sub 3@ is 10% greater than for oxide films grown with O@sub 2@. Thus the enhanced corrosion passivation properties of O@sub 3@-grown aluminum oxide films may be caused by the reduction of defect site density when O@sub 3@ is used.

3:00pm **SS1+MC-ThA4 Temperature Dependent Adsorption of Oxygen on TiO@sub 2@ (110): A Photoemission Study***, **H. Geisler**,* Xavier University of Louisiana*; E.L.D. Hebenstreit, W. Hebenstreit, M. Li, U. Diebold,* Tulane University*; S.N. Thornburg, C.A. Ventrice, Jr.,* University of New Orleans*; D.A. Hite, P.T. Sprunger,* CAMD/ Louisiana State University

The Titanium dioxide (110) surface is one of the most thoroughly studied metal oxide systems. One of the primary reasons for this interest is the fact that TiO@sub 2@ is easily reduced by annealing in vacuum. During the annealing process, oxygen vacancies and titanium interstitial are created, which can increase the conductivity of the substrate sufficiently to allow characterization with electron and ion spectroscopies. In order to heal the surface region, the reduced crystals are exposed to oxygen at various temperatures and pressures. To determine the effect of oxygen adsorption on the electronic structure of reduced TiO@sub 2@ crystals, angular resolved photoelectron spectroscopy (UPS) measurements have been performed in conjunction with scanning tunneling microscopy (STM) measurements. STM indicates that the adsorption of oxygen on TiO@sub 2@ (110) at temperatures above 400 °C or below 200 °C results in an unreconstructed surface. However, adsorption between 200 °C and 400 °C results in a rosette-like structure that represents an incomplete restructured TiO@sub 2@ (110) surface with coordinatively unsaturated surface atoms.@footnote 1@ UPS measurements of the vacuum-annealed, reduced TiO@sub 2@ surface show emission from a defect state centered at approximately 1 eV below the Fermi level. The onset of emission from the TiO@sub 2@ valence band occurs ~3 eV below the Fermi level. After dosing oxygen at room temperature the defect state disappears with only slight modifications to the valence band structure. On the other hand, UPS spectra from the rosette- structured surface show an enhancement of the emission from the defect state and strong modifications of the TiO@sub 2@ valence band emissions. @FootnoteText@@footnote 1@ M. Li, W. Hebenstreit, L. Gross, et al., Surf. Sci. 437, 173-190 (1999)

3:20pm **SS1+MC-ThA5 Water Reactions at Plutonium Oxide: Surface Chemistry***, **J.D. Farr**, R.K. Schulze, M.P. Neu, L.A. Morales,* Los Alamos National Laboratory

We have examined the surface chemistry of water at both monolithic and high surface area plutonium oxide using Auger and X-ray photelectron spectroscopy (AES and XPS). This work investigates the chemical reactions at the Pu oxide surfaces, primarily to help address issues that are critical for plutonium stabilization and 50-year storage. Interactions between PuO@sub 2@ particles and the adsorbed water vapor play a dominant role in potential catalytic gas generation reactions. Understanding the chemistry at this interface, particularly with respect to reactions with water and water vapor is crucial for predicting the storage behavior of Pu oxide powders. XPS indicates that water adsorbs initially at active sites to form surface hydroxyls groups. Upon saturation of these sites and at substantially higher exposures, particularly with high surface area oxides, the water adsorbs in molecular form as part of the surface layer. Heating the oxide to 200°C in vacuum results in removal of the adsorbed water and partial removal (conversion) of the hydroxyl. Above 400°C the oxide surface continues to undergo a transformation and the removal of hydroxyl is largely complete at 600°C. The tenacious nature of these surface groups suggests that most of the active sites at the surface are irreversibly saturated at room temperature and up to a temperature in excess of 200°C, with some of them irreversibly saturated up to 600°C, or greater. The surface reaction will be discussed in the context of reaction energetics for the active sites at the PuO@sub 2@ surface.

3:40pm **SS1+MC-ThA6 Studies of Water Plasma Treatments on Silicon Oxide Films***, **N.A. Alcantar**,* University of California, Santa Barbara*; T.L. Kuhl,* University of California, Davis*; A. Stacy, J. Au, E.S. Aydil, J.N. Israelachvili,* University of California, Santa Barbara

Chemically active oxide surfaces can react with polymers to enhance their surface properties. Surfaces covered with polyethylene glycol have been shown to reject biological attack and protein adhesion. We activate silicon dioxide (i.e., silica) films by exposing them to water vapor plasma. These activated films are then reacted with polyethylene glycol (PEG, OH-(CH@sub 2@-CH@sub 2@-O)@sub n@-H) to make them biocompatible. We have characterized silica films prepared by plasma enhanced chemical vapor deposition (PECVD) before and after water plasma activation. We found that water plasma treatments chemically and physically modify the silica surface. For instance, water plasma fully saturates the silica surface with hydroxyl groups, significantly reduces their surface roughness without affecting the thickness of the deposited films and increases their cohesion force. This surface modification was monitored by in situ real time attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Other characterization techniques such as ellipsometry, atomic force microscopy (AFM), surface forces apparatus (SFA) and contact angle measurements were utilized to fully establish the effects of this surface modification. The optimal water plasma parameters for creating smooth, chemically reactive silicon oxide films were also obtained.

4:00pm **SS1+MC-ThA7 The Nature of Oxygen at Rocksalt and Spinel Oxide Surfaces***, **M.A. Langell**, J.G Kim, S. Chapman, H.Y. Xu,* University of Nebraska

The chemical environment of oxygen in mixed metal oxides with compositions M@subx@M'@sub(x-1)@O and M@subx@M'@sub(3x-1)@O@sub4@, (M, M' = Li, Mn, Fe, Ni, Co) has been studied by Auger electron spectroscopy, x-ray photoelectron spectroscopy and high resolution electron energy loss spectroscopy. While there is a single type of lattice oxygen in the bulk structure of simple rocksalt and spinel oxides, the nature of oxygen at the surface of the mixed-metal oxide materials is considerably more complex. Photoemission from core oxygen states in these materials often shows multiple peaks and satellite structure which have been attributed to a range of intrinsic and extrinsic oxygen states. Mixed-metal oxides form an ideal set of systems to investigate the nature of the lattice oxygen through their ability to tailor cation oxidation state and site occupancy within the crystal structure and thus affect the chemical environment of the lattice oxygen. All of these 3d transition metal oxides show a single, intense O1s core photoemission peak at approximately 529.6 eV. However, a second peak is often observed at about 1-1.5 eV higher binding energy, depending upon the types and distribution of the cations, and the history of the substrate surfaces. Surface hydroxylation, cation clustering and final state effects in the photoemission mechanism can all contribute to the O1s photoemission process and will be discussed in view of the data obtained for the mixed-metal oxides.

4:20pm **SS1+MC-ThA8 Direct Observation of Native Hydrogen Adatoms on Rutile TiO@sub 2@(110) Surface***, **T. Fujino**, K. Inudzuka, T. Okuno, M. Katayama, K. Oura,* Osaka University, Japan

Titanium dioxide (TiO@sub 2@) surface has received considerable attention because TiO@sub 2@ is the material of photocatalyst such as the photodecomposition of water. Over the past few years a considerable number of studies have been made on the analysis of rutile TiO@sub 2@(110) surface composition and structure. Most of these studies were conducted using microscopic techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM). However, the information of hydrogen atoms adsorbed on TiO@sub 2@(110) surface seems to be lacking because it is difficult to detect the surface hydrogen using STM or AFM. In the present study, we have investigated the structure and composition of the rutile TiO@sub 2@(110) using coaxial impact collision ion scattering spectroscopy (CAICISS), time-of-flight elastic recoil detection analysis (TOF-ERDA) and low energy electron diffraction (LEED). CAICISS and TOF-ERDA have been proved to be useful techniques for in situ observation of surface structure and composition, in particular, for the determination of the amount of surface hydrogen atoms. When the sample was introduced into ultra high vacuum (UHV) chamber without any treatments, a large quantity of hydrogen and oxygen atoms adsorb on the surface. These atoms can be attributed to water molecules. After annealing the sample at 800°C in UHV, the clean surface of TiO@sub 2@(110) with the LEED pattern of a sharp 1x1 spots was obtained. It was found from the CAICISS measurement that this surface formed bulk terminated structure, known as bridging oxygen rows model. However, it was also found from the TOF-ERDA measurement that the hydrogen atoms still resided on the surface. These hydrogen atoms are not components of water molecules but directly chemisorb on the TiO@sub 2@(110)1x1 surface. Thus, native hydrogen adatoms on the TiO@sub 2@ surface was directly observed and evidenced. Detailed results will be discussed in the presentation.

4:40pm **SS1+MC-ThA9 Work Function Changes and Surface Chemistry of Oxygen and Hydrogen on Indium Tin Oxide***, **J.A. Chaney**, P.E. Pehrsson,* Naval Research Laboratory

Indium tin oxide (ITO) is used as a transparent, semiconducting substrate for many device applications. However, there is an inadequate understanding of ITO surface properties, its interaction with gaseous species, and the physical/electronic changes imposed by its surface chemistry. The surface physics and chemistry of oxygen plasma treated ITO were investigated under ultra high vacuum conditions. The work function (@PHI@) of ITO was determined by a vibrating Kelvin probe calibrated with a graphite standard. Sample composition, electronic structure and chemistry were examined by Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), and high resolution electron energy loss spectroscopy (HREELS). Commercial ITO films were heated in-vacuo to remove physisorbed species and then exposed in-situ to oxygen or deuterium activated with a hot metal filament. Oxidation increased the work function from 5.2 to 5.6 eV, but @PHI@ then decayed to <5.2 eV, possibly due to oxygen diffusion into the bulk along defects and grain boundaries. The AES oxygen level was stable after oxidation, and the ELS spectrum consistently showed a strong feature at 0.7 eV for oxidized samples. Deuteration visibly metallized the film and sharply reduced the surface oxygen level. The ELS feature simultaneously disappeared, and the work function decreased to 4.6 eV. The HREELS of clean ITO revealed substantial C-H contamination, which persisted after heating to ~300°C. Even substantial oxygen treatment did not remove the hydrogen signal, suggesting that C-H permeates the ITO film.

5:00pm **SS1+MC-ThA10 Adsorption of Atomic Hydrogen on Both Polar Surfaces of ZnO***, Th. Becker, M. Kunat, Ch. Boas, **U. Burghaus**, C. Wöll,* Ruhr-University Bochum, Germany

The interaction of atomic hydrogen with Zn-ZnO and O-ZnO surfaces has been investigated by LEED, He atom scattering, He atom reflectivity measurements (as a function of H exposure and surface temperature, T@sub s@), and XPS. Furthermore, measurements of adsorption probabilities of CO on the two polar surfaces of ZnO are presented (see [1] for CO/O-ZnO) as well as the effect of pre-exposed atomic hydrogen on the adsorption dynamics of CO. He atom diffraction measurements indicate the formation of a well ordered H overlayer structure. The strong attenuation of the specular He atom reflectivity by hydrogen exposure indicates, however, a second competing reaction pathway; since extensive exposure to atomic hydrogen leads to a high degree of disorder on the surface. Values for the heat of adsorption for H were estimated from He-atom reflectivity curves, measured as a function of T@sub s@. The shape of the coverage dependent adsorption probability curves, S(@theta@@sub

CO@), of CO are for both surfaces consistent with a precursor mediated adsorption; adsorbate assisted adsorption dominates the adsorption. The He atom reflectivity measurements point to the influence of an intrinsic precursor state. A comparison of He atom reflectivity with S(@theta@@sub CO@) curves, respectively, showed that CO initially populates defect sites. The coadsorption of H and CO can be explained by a site blocking mechanism; leading to an estimate of @theta@@sub H@. [1] Th. Becker, Ch. Boas, U. Burghaus, Ch. Wöll, Phys. Rev. B 61(7) (2000) 4538.

Surface Science
Room 209 - Session SS2+NS-ThA
Tribology and Adhesion

Moderator: J. Krim, North Carolina State University

2:00pm **SS2+NS-ThA1 Friction at High Speeds@footnote 1@*, J.E. Hammerberg*,** *T.C. Germann, B.L. Holian, P.S. Lomdahl,* Los Alamos National Laboratory **INVITED**

The mechanisms of dissipation at dry sliding metal-metal interfaces are complex, nonlinear, and involve a range of length and time scales. Depending upon the magnitude of the relative sliding velocity and the material pressure, phenomena described by phonons, dislocation generation and dynamics, microstructure formation, and mechanical mixing of materials are important. We discuss the variety of these phenomena as seen in extensive very large-scale molecular dynamics simulations for copper and Lennard-Jones systems in two and three dimensions. These simulations suggest universal behavior at large sliding speeds and we discuss some of the theoretical descriptions of these phenomena and recent high speed experimental results. @FootnoteText@ @footnote 1@Work performed under auspices of U.S. DOE at LANL under contract W-7405-Eng-36.

2:40pm **SS2+NS-ThA3 Energy Dissipation Thresholds During Interfacial Shear*, N.D. Shinn,*** *R.W. Cernosek, S.J. Martin,* Sandia National Laboratories

By measuring the power spectra of clean and surface-modified quartz crystal microbalance resonators in contact with nanometer thick fluid layers, we can detect and quantify energetic thresholds for interfacial slip and other dissipation mechanisms at interfaces under dynamic shear. Understanding fundamental dissipation mechanisms is a necessary prerequisite to mitigating friction via interfacial lubricants or surface coatings. Using an amplified network analyzer, we vary the QCM peak-to-peak potentials, and hence the shear acceleration, over a wide range (0.002-30V) and detect any resultant changes in resonant frequency or resonance damping. This approach allows us to access shear forces otherwise unavailable using traditional QCM oscillator circuits [1] or standard network analyzer systems and therefore to probe stronger interfacial adhesive forces. Initial experiments for water adsorption on polycrystalline Au(111) electrode surfaces with and without a hydrophobic (methyl-terminated) alkanethiol self-assembled monolayer reveal no new dissipation thresholds. This suggests that interfacial slip is not occurring because the nanometer-scale surface roughness is sufficient to entrain the water layer or the energetic barrier for lateral motion remains insurmountable. Experiments are in progress to distinguish interfacial slip thresholds from mechanical entrapment effects by preparing atomically flat microcrystalline domains, contrasting polar and non-polar fluids, and modifying the electrode surfaces with other functionalized monolayers. Research supported by DOE-BES 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. @FootnoteText@ @footnote 1@J. Krim and A. Widom, Phys. Rev. B38, 12184 (1988).

3:00pm **SS2+NS-ThA4 Chemical and Mechanical Contributions to the Friction In Self-Assembled Monolayers on Au Surfaces*, H.I. Kim,*** *J.E. Houston,* Sandia National Laboratories

By studying various combinations of chemically distinct end groups on alkanethiol molecules self-assembled on Au probe/substrate surfaces, and by varying the odd-even length of the chains, we are able to delineate the contributions of chemical and mechani cal effects to interfacial friction. Because it is stable and quantitative throughout the entire range of the interfacial interactions (including the attractive load regime), we use the interfacial force microscope (IFM) to measure the friction force as a function of applied load. For even-length molecular chains, the friction forces progressively increase in the order CH3-CH3, CH3-COOH, COOH-COOH, while the interfacial adhesive force remains virtually identical. In contrast, for odd chain lengths, fricti on and adhesion are low for both CH3-CH3 and CH3-COOH combinations, but much higher for COOH-COOH. By systematically correlating the interfacial adhesion and friction, we conclude that energy dissipation giving rise to sliding friction has distinct chemic al and mechanical components. The making and breaking of hydrogen bonds, due to either intra- or inter-film interactions, gives rise to the "chemical" dissipation while simply disturbing the structure of the film under interfacial sliding invokes the "mechanical" component. This work was supported by the US Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

3:20pm **SS2+NS-ThA5 Atomic and Molecular Level Insight into Discreet Frictional Events*, S.S. Perry,*** *T.R. Lee, S.H. Lee, K.I. Kim, R. Colorado, P. Cao, Y.S. Shon, M. Graupe,* University of Houston **INVITED**

Technological advances in a number of industries has driven the need to understand interfacial friction on an atomic and molecular level. This level of understanding requires the careful design of model interfaces and experimental approaches sensitive to atomic and molecular scale events. This has been achieved in our studies by combining two recently developed techniques that operate at the subnanometer scale: control of the interfacial composition through molecular self-assembly or chemical modification under controlled UHV conditions and tribological measurements performed with the atomic force microscope. With this approach, we are able to control or measure the specific chemical composition and structure of interfaces and to correlate changes in composition and structure to the frictional properties of a single asperity contact. Examples will be drawn from both molecularly-thin organic film systems and composite coating systems to illustrate the origins of interfacial friction in terms of the composition and structure of the interface.

4:00pm **SS2+NS-ThA7 Molecular Tribology of Highly Ordered Monolayers*,*** *D. Gourdon,* University of California, Santa Barbara*; C. Duschl,* Swiss Federal Institute of Technology*;* ***N.A. Burnham,*** Worcester Polytechnic Institute

In order to investigate friction at a fundamental level, atomic force microscopy (AFM) in the wearless regime was performed on a model system - a highly ordered thiolipid monolayer on mica. In the monolayer, condensed domains with long-range orientational order were present. These domains revealed strong friction anisotropies as well as non-negligible asymmetries in the quasistatic friction loops. The directionality of these two effects appeared to correlate well with the tilt direction of the molecules (more specifically of their terminal alkyl chains) in the monolayer. The friction was measured as a function of applied load. The measurements versus load revealed two or three different frictional regimes (depending on the load range), that correlated well with a systematic stepwise behavior of the height of the domain as measured simultaneously. These discrete effects were attributed to molecular gauche defects created under the stress applied by the tip. Other studies include the friction as a function of sliding velocity, chemical preparation of the tip, alternative molecules, and nature of the substrate. Our work suggests that friction on this system is primarily a mechanical phenomenon.

4:20pm **SS2+NS-ThA8 The Effect of C60 on Interfacial Friction and Wetting of Toluene*, T.S. Coffey,*** *M. Abdelmaksoud, J. Krim,* North Carolina State University

Experimental investigations of friction, lubrication, and adhesion at nanometer length scales have traditionally been performed using atomic force microscopy (AFM), surface forces apparatus (SFA), or quartz crystal microbalance (QCM) techniques. While collectively these techniques yielded useful information, their results have never been cross-referenced. In order to achieve a cross referencing, we investigated the sliding friction of C60 using AFM, QCM, and macroscopic contact angle measurements. (Recent studies@footnote 1@ suggest that a larger contact angle implies a more slippery interface.) C60 has been previously studied by S.E. Campbell et al. with SFA,@footnote 2@ whereby it was reported that C60 at a toluene/mica interface resulted in a full-slip boundary condition, and C60 was recommended as a possible lubricant. Our contact angle measurements reveal that the contact angle of C60/toluene solutions on mica is greater than the contact angle of toluene alone and therefore support Campbell's result. Using QCM, we have also studied the system toluene/Ag(111) with and without C60 deposited on the silver. These studies indicate that toluene on the C60/silver surface is less slippery than the toluene on the silver alone, and that the contact angle for toluene on C60/silver surface is less than the contact angle for the toluene on the silver. This indicates that C60 is not a good lubricant for a silver surface. We believe that this seeming contradiction with Campbell's result is due to the manner in which the C60 is bound to the mica surface vs. the silver surface. We complete our cross referencing of C60/toluene solutions on these substrates by employing AFM. @footnote 3@ @FootnoteText@ @footnote 1@ J.L. Barrat and L. Bocquet, Physical Review Letters, vol. 82, p. 4671 (1999). @footnote 2@ S.E. Campbell, G. Luengo, V.I. Srdanov, F. Wudl, and J.I. Israelachvili, Nature, vol. 382, p. 520 (1996). @footnote 3@ This work is supported by NSF, AFOSR, and a GAANN fellowship.

4:40pm **SS2+NS-ThA9 Mechanical Behaviour of Confined Films: An In-situ Study of Silane Monolayers by Second Harmonic Generation (SHG)***, **M.T. Strobel**, J. Blümmel, W. Eck, M. Buck, M. Grunze,* University of Heidelberg, Germany

Understanding the tribological properties of ultrathin organic films is of vital interest for their application in micro electro-mechanical systems (MEMS). To elucidate structural aspects of layers confined between two solids SHG was applied to trace force-induced changes of the polar and azimuthal orientation of molecular entities. As a model system monolayers of a silane bearing an SHG-active moiety were adsorbed on a glass-substrate. Mechanical loading and shearing of the film was achieved by a lens pressing against or rolling over the substrate. Mapping the contact area reveals pronounced, site dependent changes of both the tilt angle and the azimuthal alignment of the SHG active moiety upon loading. Whereas the azimuthal alignment persists after unloading and can be controlled by the rolling direction of the lens, the tilt angle is largely reversible for a loading unloading cycle. A quantitative evaluation of the data shows that the degree of the aligment is significantly larger than expected from simple models of contact mechanics.

5:00pm **SS2+NS-ThA10 New Aspects of Friction Force Microscopy in Ultra-high Vacuum***, **R. Bennewitz**, E. Gnecco, T. Gyalog, O. Pfeiffer, Ch. Loppacher, M. Guggisberg, E. Meyer,* University of Basel, Switzerland

Recent experimental results of Friction Force Microscopy in ultra-high vacuum on well defined surfaces give new insight into the atomic processes of friction. On Cu(111), atomic stick-slip behaviour was found for the first time on a metal surface. Lateral stiffness of the contact and its I(V)-characteristic indicate that a copper neck between tip and sample is dragged over the surface.@footnote 1@ The velocity dependence of atomic stick-slip processes was studied on Cu(111) and on NaCl(100) revealing a logarithmic increase of the friction with increasing scan velocity.@footnote 2@ This dependence can be explained by introducing the effects of thermal activation into the Tomlinson model for atomic friction. A new experimental approach to study dissipation processes on atomic scale is the measurement of the damping of vertical and horizontal tip oscillations in the non-contact mode, where power losses of the order of 100 meV per tip osccilation can be detected. @FootnoteText@ @footnote 1@ R. Bennewitz et al., Phys. Rev. B60 (1999) R11301 @footnote 2@ E. Gnecco et al., Phys. Rev. Lett. 84 (2000) 1172.

Surface Science
Room 209 - Session SS+MC-FrM
Characterization of Oxides and Thin Films

Moderator: J.A. Kelber, University of North Texas

8:20am **SS+MC-FrM1 Characterisation and Microreactor Studies of Nanofabricated Model Pt/Ceria Catalysts*, C. Werdinius,*** Chalmers University of Technology, Sweden*; O. Hjortsberg,* Volvo Technological Development Corporation, Sweden*; L. Österlund, B. Kasemo,* Chalmers University of Technology, Sweden

In modern automotive catalysts, ceria is an important component for transient storage and release, respectively, of oxygen during lean and rich conditions. In order to study the detailed kinetics of the oxygen storage, well-characterised samples are required. Model catalysts (1 cm@super 2@ sample area) of platinum particles on ceria were nano-fabricated by a novel method called "colloidal lithography".@footnote 1@ Its principal feature is the ability of fast parallel fabrication of almost mono-sized, evenly distributed nano-particles. The manufacturing consists of the following steps; (i) deposit a ceria film on a silicon wafer, (ii) deposit a Pt film of desired thickness, (iii) deposit an array of colloidal particles of desired size and spatial separation, (iv) remove all Pt not shadowed by the particles, using Ar-ion beam etching, (v) remove the particles. The final step leaves an array of Pt particles with size and separation reflecting the colloidal particle size and separation. Samples with different Pt-particle densities and particle sizes (40 and 110 nm) were made, and characterised by several surface analytical techniques, including SEM and XPS. Preliminary results of pulsed CO oxidation experiments in a specially designed microreactor are presented, along with vacuum CO TPD measurements. @FootnoteText@ @footnote 1@ P. Hanarp, D. Sutherland, J. Gold, and B. Kasemo, Nanostructured Materials 12, 429-432 (1999).

8:40am **SS+MC-FrM2 Characterization of Hf and Zr Oxides, Silicides and Silicates, Formed on the (0001) Surfaces of HfB@sub 2@ and ZrB@sub 2@, by AES, XPS, LEED and STM*, R. Singh,*** University of Illinois at Chicago*; Y. Paderno,* Academy of Sciences of Ukraine*; T. Tanaka,* National Institute for Research in Inorganic Materials, Japan*; M. Trenary,* University of Illinois at Chicago

Transition metal (TM) diborides have comparable and often higher degrees of hardness, chemical inertness and thermal stability than their nitride and carbide counterparts. Therefore, TM-diborides are attractive for the same type of applications as nitrides and carbides such as for hard coatings and diffusion barriers. In order to explore their usefulness as diffusion barriers and gate dielectrics, a series of experiments with silicon were performed. Silicon was deposited by the UHV-CVD of silane gas on clean and oxygen covered HfB@sub 2@ and ZrB@sub 2@(0001) surfaces. On the clean surfaces, HfSi@sub 2@ and ZrSi@sub 2@ were formed. A p(2x2)R30° LEED pattern was observed. The structure of Si on the surfaces was also investigated with STM. On the oxygen covered surfaces, silicates were formed. Oxidation of the crystals leads to the formation of HfO@sub 2@ and ZrO@sub2@, which both exhibited a (3x3) LEED pattern at a high exposure (5 L) and a p(2x2)R30 pattern at a low exposure (0.5 L). Information gained from exposure of oxygen to ZrB@sub 2@ was crucial in interpreting the O 1s region in HfB@sub2@, which partially overlaps with the Hf 4s peak.

9:00am **SS+MC-FrM3 Controlled Coordination and Oxidation State of Copper and Manganese Cations in Complex Nickel-Copper-Cobalt-Manganese Oxide Thin Films*, D.A. KuKuruznyak,*** *M.-H. Lee, K.A. Omland, M.C. Gregg, F.S. Ohuchi,* University of Washington

Ionic configuration and cation distribution of the nickel-copper manganite spinels have profound effects on their electrical conduction. As these materials are being widely used for thermistor applications, it is important to find a way of controlling the oxidation states of transition metal cations in these mixed oxides. We have therefore undertaken our research developing a unique method fabricating thermistor composition by chemical solution deposition where cations with unusual coordination and unusual oxidation state can be obtained. Organometallic films deposited on silicon and glass substrates by spin-coating of a liquid precursor solution were decomposed in air at 550°C followed by furnace-annealing at temperatures ranging from 600° to 800°C to obtain single-phase cubic spinel of chemical composition Ni@sub 0.48@Co@sub 0.24@Cu@sub 0.6@Mn@sub 1.68@O@sub 4-x@. XPS, FTIR, and Mossbauer spectroscopy have been used to study oxidation states of transition metal ions. Octahedrally coordinated Cu@super +1@ observed from the specimens (prepared below 700°C) showed unusually large negative binding energy shifts in Cu(2p) peak relative to metallic Cu, of which origin was attributed to the difference in the Madelung potentials. Annealing at higher temperatures causes oxidation of copper to Cu@super 2+@ and reduction of manganese cations from Mn@super 4+@ to Mn@super 3+@. The annealing temperature can precisely control oxidation state distribution of copper and manganese cations.

9:20am **SS+MC-FrM4 Behavior of Lightly Doped-electrons on the Electronic Structure of SrTiO@sub 3@: An Angle-resolved Photoemission Study*, Y. Aiura,*** *H. Bando, I. Hase,* Electrotechnical Laboratory, Japan*; T. Yasue,* Tsukuba University, Japan*; T. Saitoh, D.A. Dessau,* University of Colorado

Behavior of lightly doped-electrons on the electronic structure of SrTiO@sub 3@ has been studied using angle-resolved photoemission spectroscopy (ARPES). Two states in the band gap region of SrTiO@sub 3@ (in-gap states) are observed; a state with a sharp Fermi cut-off (metallic state) and a broad state centered at ~1.5eV below the Fermi level (~1.5eV state). In order to study the origin of the metallic state, we have calculated the energy-band of non-doped (stoichiometric) SrTiO@sub 3@ and lightly electron-doped SrTiO@sub 3@ based on the full-potential linearized augmented plane wave (FLAPW) method. From comparison between the calculated results and the experimental ones from ARPES, it was shown that the metallic state can be quite well explained by the rigid-band behavior based on one-electron band theory. For the ~1.5eV state, on the other hand, ARPES spectra showed that there is no visible empirical energy dispersion and that its spectral intensity is very sensitive to the surface condition. These experimental results means that the ~1.5eV state is not caused by the bulk electronic structure, but the surface one due to the surface defects.

9:40am **SS+MC-FrM5 Reactions of Acetaldehyde over UO@sub2@(111) Single Crystal Surfaces: Evidence of Benzene Formation*, S.V. Chong,*** *H. Idriss,* The University of Auckland, New Zealand

The reactions of aldehydes on metal oxide surfaces have exposed some of the most exquisite chemistry compared to their alcohol and carboxylic acid counterparts. Due to the intermediate oxidation state of the carbonyl carbon on an aldehyde, reactions such as the Cannizzaro reaction (forming alcohol and carboxylate) and Tishchenko reaction (forming ester) have been observed on various metal oxide surfaces. Furthermore, condensation reactions have also been observed on aldehydes possessing alpha-H atom(s) over stoichiometric metal oxide surfaces, while surface defect sites are able to reductively couple two aldehyde adsorbates to yield alkene. Herein, we present the reactions of acetaldehyde over the stoichiometric, electron irradiated, and H@sub2@ reduced surfaces of UO@sub2@(111) single crystal. TPD results over the three surfaces show evidence of benzene formation, and it appears that electron irradiation slightly increases the conversion to benzene, while H@sub2@ reduction doubles it. Thus, the amount of benzene yield might be a novel way to quantify the extent of surface defects. No C@sub4@ hydrocarbon (crotonaldehyde nor butadiene) traces were observed, indicating that the formation of benzene through aldol condensation pathways might be ruled out.

10:00am **SS+MC-FrM6 Synchrotron-based XPS Study of 1-Decanethiol Chemisorbed on Au(111)*, Y.W. Yang,*** Synchrotron Radiation Research Center, Taiwan*; L.J. Fan,* National Tsing Hua University, Taiwan*; L.J. Lai,* Synchrotron Radiation Research Center, Taiwan

Self-assembled monolayers have been the subject of intense research due to their potential applications in areas of lubrications, corrosion inhibitions, gas sensors, etc. We combined TDS and synchrotron-based, high resolution core level spectroscopy to study the chemisorption of 1-decanethiol monolayer on Au(111) surface with the molecular films prepared from both gas-phase dosing and solution immersion. On heating to temperatures higher than 400 K, decanethiolate starts to decompose, forming 1-decene via @beta@-hydrogen elimination, and leaves atomic sulfur on the surface. For thin films produced by both methods, S2p core level exhibits a single, well-characterized spin-orbit doublet with S2p@sub 2/3@ at 162.1 eV, indicating identical chemical interaction between sulfur and gold atoms in the films. However, C 1s core level starts from 284.0 eV at low coverage, develops a high-binding shoulder at intermediate coverage and eventually becomes a single peak at 285.0 eV for the high coverage prepared from solution phase. Angle-resolved XPS measurements of substrate core level signal provide a direct measure of the film thickness. The increases of C 1s binding energy is found to be associated with the incomplete final-state relaxation of the carbon atoms due to the thickness increase of the film as the carbon chains tilt toward the surface normal. Moreover, the implication of observing only a well-defined doublet of S 2p signal will be discussed in relation to the sulfur dimer model.

10:20am **SS+MC-FrM7 STM Studies of Pyrrole-sdsorbed Si(111)-7*7 Surfaces*, Z.L. Yuan,*** National University of Singapore, Singapore

The Si(111)-7*7 surfaces is particularly appropriate in Si surface chemistry, because it contains dangling bonds on several different sites within the surface unit cell, and also STM has been used to provide direct and local information on an atomic scale.@footnote 1@ In the present work, the topographic and spectroscopic analysis of pyrrole adsorption on Si(111)-7*7 surfaces at room temperature under different pyrrole exposures is investigated by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). No significant changes in the surface reconstruction are observed, some adatoms become dark, however this is not due to the vacancies of Si adatoms, because these adatom are visible under the higher sample bias, the disappearance of adatoms is the result of changes in electronic structure upon reaction with pyrrole. the preservation of the 7*7 reconstruction suggests that the reaction with pyrrole has primarily saturated existing dangling bonds on Si(111)-7*7 surfaces. The adsorption is site selective, the faulted center adatoms are most favored for adsorption among the adatoms. The rest atoms also react with pyrrole from STS observation. Based on our STM/STS and HREELS data, a possible adsorption mechanism of pyrrole chemsorption on Si(111)-7*7 surfaces is also discussed. @FootnoteText@ @footnote 1@R. Wolkow and Ph Avouris, Phys. Rev. Lett. 1988, 60:1049; Phys. Rev. B,1989, 39:5091; J. Yoshinobu et al, Phys. Rev. B 1992, 46:9520; Jpn. J. Appl. Phys. 1993, 32:1171; M. N. Piancastelli et al, Phy. Rev. B 1993, 48:17892,R. A. Wolkow, Annau. Rev. Phys. Chem. 1999, 50:413.

10:40am **SS+MC-FrM8 Characterization of Bound Ultrathin Perfluoropolyether-Functionalized Polysiloxane Films on Silicon Oxide Surfaces*, F. Parsapour,*** Colorado State University*; D.G. Castner,* University of Washington*; D.W. Grainger,* Colorado State University

Current technological demands for magnetic recording media lubrication include a reduction in the head-disk gap, elimination of stiction, and fabrication of a low adhesion protective surface which can withstand thermal and mechanical stresses associated with hard disk drive operation. Perfluoropolyethers (PFPE) are the most commonly used lubricants in the magnetic recording media. These polymers are typically applied thin films to the hard drive overcoat to which they are generally physisorbed. As a result, they are subject to thermal degradation and "spin-off", ultimately resulting in tribological failure modes. Direct attachment of PFPE films is potentially interesting as a foundation for improved friction and wear performance. We have previously reported fabrication of ultrathin films of polysiloxanes functionalized with perfluoropolyether side chains chemisorbed to surfaces and exhibiting structural anisotropy due to separation of various polymer-grafted components normal to the interface. We now report analogous polymer monolayers but with the important chemical and functional distinction of surface bonding to silicon oxide through alkylsilane anchoring groups. These copolymers were synthesized in a single step through the respective PFPE functional and alkylsilane anchor group coupling reactions. Monolayer films were formed on silicon oxide surfaces through the dip-coating method, resulting in hydrophobic immobilized films ~3 nm thick. XPS measurements support a stratified three-layer film chemistry within the monolayer, and an outer interface enriched with the PFPE moiety. AFM experiments show a high degree of coverage of the oxide surface by the copolymer film, and a relatively uniform surface. LFM measurements exhibit low frictional forces in the areas covered by the monolayer film. Force-displacement curves obtained in a fluid environment reveal a low adhesion surface compared to films prepared from copolymers without the PFPE functional group.

11:00am **SS+MC-FrM9 Aerial Oxidation of Self-assembled Monolayers studied by SIMS, AFM and Contact Angle Measurement*, N.J. Brewer,*** *G.J. Leggett,* University of Manchester Institute of Science and Technology, UK

For many applications, the long term stability of self-assembled monolayers (SAMs) is a critical issue. We have undertaken a systematic study of SAM oxidation using secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM) and contact angle measurements. Samples were left in an ambient environment for specific periods of time and then surface analytical techniques were used to observe any changes in the SAMs. SAMs were formed from long and short chain methyl, carboxylic acid and hydroxyl terminated alkanethiols. By using SIMS, we were able to monitor the rate of oxidation. We found that DDT, a long chain methyl terminated SAM, oxidised in seven hours, but the long chain carboxylic terminated SAM was unoxidised after seven hours. This shows that long chain carboxylic acid terminated SAMs exhibit increased stability in air. AFM was used to record the friction coefficients of the SAMs over a period of hours. The change in the coefficient of friction was slow and it was little changed after times when SIMS showed complete conversion of thiolates to sulfonates had occurred. This suggests that although the sulfur-gold bond is broken, the interchain forces still hold the structure together. The collapse of the system is gradual and this is reflected in the slow change in the friction coefficients. Advancing water contact angle measurements exhibited a sharp change in contact angle for carboxylic acid and hydroxyl terminated SAMs due to adsorption of contaminants, but a small change for the methyl terminated SAMs. It is concluded that SAMs may oxidise reasonably rapidly on exposure to air, but that the degradation of their structures and properties is much slower.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index

Author Index

Author Index

Author Index