Nanometer-scale Science and Technology Division Room 321/322/323 - Session NS+SS-MoM

Tribology, Adhesion and Interfacial Forces Moderator: J.E. Houston, Sandia National Laboratories

8:20am NS+SS-MoM1 Nanotribological Interactions: Hard and Soft Interfacial Junctions, *U. Landman*, Georgia Institute of Technology INVITED Certain aspects of the dependence of materials properties on their size will be addressed, particularly at the nanometer length scale where new behaviour emerges when the physical dimensions of the system approach, or are reduced below, a characteristic length relevant for the phenomenon or physical process being probed. We focus on computer simulation studies of formation mechanisms, structural, mechanical, electronic, transport, dynamic and rheological properties of nanoscale hard (solid nanowires) and soft (confined liquid) interfacial junctions. These issues are central to research in nanotribology, that is explorations of the atomic and molecular scale origins and methods of control of friction and lubrication, and are relevant to modern miniaturization technologies. Work supported by DOE and AFOSR.

9:00am NS+SS-MoM3 Measuring Nanocontact Adhesion and Deformation, J.B. Pethica, University of Oxford, United Kingdom INVITED Nanoscale probe techniques such as nanoindentation and AFM have given new insight into contact mechanics, and hence into adhesion and tribology problems. Almost all local mechanical, and several electrical parameters of the component surface materials can be measured. The key is a reliable determination of the test probe displacement (lateral as well as normal) as a function of applied forces. Accurate determination of storage and loss moduli in thin polymer films, along with their frequency and temperature variation, will be described as one example of these capabilities, and of the associated stringent experimental requirements. During the approach to contact, sensitive force-distance spectroscopy, close to atomic scale spatial resolution, allows mapping of the interaction potential between the surfaces. Some of the outstanding problems will also be discussed. These include the effect of adsorbates, especially on the onset of irreversible or dissipative deformation, and the determination of contact area in systems which are anything other than clean and homogeneous.

9:40am NS+SS-MoM5 Adhesive Interactions and Damage Mechanisms in Scanning Probe Microscopy: A Study by Interfacial Force Microscopy, *J.F.*

Graham, O.L. Warren, P.R. Norton, University of Western Ontario, Canada It is often observed that contact mode scanning probe imaging with hard tips at loads of 10's of nN will damage soft surfaces, such as those of polymers. We have studied the origin of damage mechanisms on cellulose acetate (CA) calibration grids with the interfacial force microscope (IFM) using parabolic tungsten probes of 100 to 200 nm radius and forces of ~ 75 nN. The parabolic geometry of our W tips possesses a smooth profile at the apex with no sharp or discontinuous edges that can cause exceedingly high and damaging local stresses. The CA grid (elastic modulus ~ 2 GPa) can be imaged many times with a clean tungsten tip (modulus ~370 GPa) without visible damage, provided the maximum static force does not exceed that for plastic deformation of the CA. This force is readily and quantitatively determined by the IFM. After determination of a force (f) versus distance (d) curve (from which the nanomechanical properties are derived) during which the plastic limit of the CA was exceeded, contact mode imaging at the same force which had previously caused no damage, produced rapid, irreversible damage to the CA surface. It was also observed that there was a distinctive adhesion event (in the sense that it was not related to capillary forces) in the withdrawal curves of those f-d curves which preceeded damage. Further, occasionally we observed a sub-micron polymer particle on the surface after operation of the IFM in the tapping mode after an indentation experiment. This specific adhesive interaction (as well as the capillary forces) was eliminated by carrying out the measurements under hexadecane. The origin of the damage mechansim therefore appears to be: 1. the adhesive transfer of polymer to the tip; 2. the formation of adhesive contacts between this polymer "coated" tip and the CA surface; 3. repetitive formation and breaking through shear forces of polymerpolymer contacts at the interface.

10:00am NS+SS-MoM6 Friction and Adhesion in the Attractive Regime, A.R. Burns, J.E. Houston, R.W. Carpick, Sandia National Laboratories

Recent molecular level measurements and simulations have shown a strong connection between adhesive bonding forces and energy dissipation

in sliding friction. In order to observe this directly, we have constructed a scanning force microscope with de-coupled lateral and normal force sensors to simultaneously observe the onset of both friction and chemical bond formation. Furthermore, by using a mechanically-stable interfacial force sensor,@footnote 1@ we are able to map the entire attractive interaction between the probe tip and the sample surface. Measurements made on self-assembling alkanethiol films with chemically different head groups show that friction can be directly attributed to bond formation and rupture well before repulsive contact. Thus we are able to separate chemical friction from more traditional mechanical sources of energy dissipation.@footnote 2@ @FootnoteText@ @footnote 1@ S. A. Joyce and J. E. Houston, Rev. Sci. Instrum. 62, 710 (1991). @footnote 2@ 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.

10:20am NS+SS-MoM7 Tribology and Mechanical Properties of Langmuir-Blodgett Monolayers, K.J. Wahl, W.R. Barger, S. Asif, Naval Research Laboratory

Mechanical properties of contacts with nanometer-scale dimensions are important in understanding the behavior of microscale sliding contacts. Monolayer films provide a model system to study fundamentals of relationships between adhesion, friction and mechanics. In this study, we deposited monolayers of distearoyl phosphatidyl ethanolamine (DSPE) and dioleoyl phosphatidyl ethanolamine (DOPE) (both mixed and single component) on freshly cleaved mica by the Langmuir-Blodgett technique. We use atomic force microscopy to examine morphology, adhesion and shear (sliding) behavior as well as modulation techniques to investigate mechanical properties of the monolayers as a function of deposition pressure. Measurements of film elastic/viscoelastic mechanical response via force modulation techniques are compared and contrasted with the surface compressional modulus determined during film deposition as well as to mechanical properties via nanoindentation.

10:40am NS+SS-MOM8 Deformation and Friction of Organic Monolayers, J.D. Kiely, J.E. Houston, Sandia National Laboratories

The use of organic monolayers as lubricating films has received considerable attention recently, especially with regard to their potential use in micromachine applications. We have used the interfacial force microscope (IFM) to characterize, on the nanometer scale, tribological properties of alkanethiol self-assembled monolayers on Au and monolayers of octadecyltrichlorosilane and perfluorodecyltrichlorosilane on Si. The IFM is similar to the atomic force microscope (AFM) but is distinguished by it use of a quantitative, mechanically stable, zero-compliance force sensor which allows us to measure both normal and frictional forces in a controlled fashion (i.e., without 'snap-to-contact'). We quantitatively relate monolayer deformation (chracterized by using the IFM in a nanoindentation mode) to friction, and find that, in the absence of appreciable adhesion/adhesion hysteresis, friction is very well correlated with deformation hysteresis. Additionally, we have identified the effects of wear, monolayer preparation procedure, and the environment (e.g., UV exposure and humidity) on tribological properties. This work was supported by the U.S. Department of Energy under Contract DEAC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. Department of Energy.

11:00am NS+SS-MoM9 Structure-Dependent Viscoelasticity During Alkane Thiol Monolayer Growth, N.D. Shinn, T.M. Mayer, T.A. Michalske, Sandia National Laboratories

Organic monolayers adsorbed on contacting surfaces (e.g., as micromachine lubricants) modify both the chemistry and the mechanical properties of the interface. Whereas the chemistry can be predicted from the terminal functionality of the individual molecules, the viscoelastic properties reflect inadequately understood molecular ensemble dynamics. For example, the isomorphic self-assembled monolayers of methylterminated alkane thiol homologues [HS(CH@sub 2@)@sub n-1@CH@sub 3@ denoted as C@sub n@] have complex shear moduli that vary by orders of magnitude. We are using Acoustic Wave Damping (AWD) techniques and spectroscopic ellipsometry to elucidate the structure-dependent viscoelasticity of alkane thiols on polycrystalline Au(111) quartz crystal microbalance substrates. Multi-frequency analysis yields the complex shear modulus of equilibrium structures and a high-sensitivity oscillator circuit @footnote 1@ permits simultaneous measurement of the adsorption kinetics and energy dissipation during monolayer growth from the gas phase. Monolayer elasticity increases with alkane chain length. Co-

adsorbed physisorbed molecules, chemisorbed two-dimensional fluid phases, and the nucleation and growth of condensed-phase islands each contribute to dissipation in the growing monolayers. Short chain (n < 10) thiol monolayers grow via Langmuir kinetics into a two-dimensional gas phase followed by slow condensation into ordered domains. However, the C@sub 12@ thiol exhibits surprising precursor-mediated kinetics and a highly viscous initial phase. Thiol dimerization is considered as a mechanistic explanation for the observed differences. 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@@footnote1@ K. Wessendorf, Sandia Nat. Labs. (patent pending).

11:20am NS+SS-MoM10 Lubrication Brought to Light: Optical Signatures of Nanomechanical Effects in Organic Thin Films, *R.W. Carpick*, *D.Y. Sasaki, S. Singh, A.R. Burns*, Sandia National Laboratories

The properties of organic lubricant films composed of hydrocarbon chain molecules is currently of great interest, as the detailed molecular response of these films to mechanical stress remains to be understood. Molecular films of polydiacetylenes are composed of ordered hydrocarbon chains attached to a chromophoric polymer backbone. These materials exhibit strong fluorescence emission and optical absorption which can be altered by mechanical stress (mechanochromism), providing the opporutunity to exploit the optical response as a signature of specific molecular behavior. Furthermore, structurally distinct chromatic phases ("blue" and "red" phases) of the film can be produced by a combination of Langmuir-Blodgett deposition and photopolymerization. We have studied the response of these films to mechanical stress at the nanometer level using a novel scanning force microscope. The instrument combines near-field optical detection with a displacement-controlled (non-compliant) normal force sensor and a decoupled lateral force sensor. Nanomechanical properties, including local elastic modulus, adhesion, and friction are compared for different chromatic phases of the film. We examine the modes of film deformation at the molecular level by monitoring the fluorescence emission while varying the mechanical stress applied to a nanometer-sized contact area. * 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.

11:40am NS+SS-MoM11 In-situ Investigation of the Influence of a Mechanical Load on the Orientation of Organic Monolayers with Second Harmonic Generation, *M. Gurka*, *F. Eisert*, *M. Buck*, *M. Grunze*, University of Heidelberg, Germany

Understanding mechanical properties of ultrathin organic films is of fundamental importance due to their vital role in numerous technological applications such as hard disc drive lubrication or as moulde release agents in the injection moulding process. The relationship between macroscopically applied forces and processes taking place on the molecular scale can be studied in situ by photon-based techniques. Second harmonic generation (SHG) is a nonlinear optical technique which allows to investigate the effect of normal and shear forces on the order and orientation of confined monolayers. We have set up a model experiment consisting of an SHG-active silane film self-assembled onto a glas prism. A pressure in the range of 30 - 50 MPa is applied to the monolayer by pressing a quartz lens against the prism. Changes of the film structure are monitored by in situ polarization dependent SHG experiments. The SHG signal reflects the response of the SHG-active endgroup of the monolayer to the mechanical load and allows to determine the average tilt angle of the monolayer and also the in-plane symmetry of the molecular layer. During loading we observe only a minor change in the mean tilt angle of the endgroup whereas shear forces cause the molecules to align.

Surface Science Division Room 308 - Session SS1-MoM

Issues in Surface Electronic Structure

Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am SS1-MoM1 The Physical Origin of Surface Relaxation@footnote 1@, T. Zhang, University of Tennessee, Knoxville; J.-H. Cho, Oak Ridge National Laboratory; E.W. Plummer, University of Tennessee, Knoxville; Z. Zhang, Oak Ridge National Laboratory

The subtantial difference in the valence charge distributions between sp and df metals can be so large that for hcp (0001) surfaces, the first interlayer spacing of berillium will expand while that of zirconium will contract. This difference in relaxation can be traced to a difference in the direction of the traditional Smoluchowsky charge smoothing at the two surfaces. The failure of the Finnis-Heine (FH) picture in explaining material dependence of surface relaxation lies in its neglect of this critical difference in valence charge distributions. This work is supported by Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract number DE-AC05-96OR22464 @FootnoteText@ @footnote 1@ Tianjiao Zhang, Jun-Hyung Cho, E.Ward Plummer, Zhenyu Zhang, submitted to Physical Review Letters @footnote 2@ R. Smoluchowsky, Physical Review,60,661(1941) @footnote 3@ M W Finnis and Volker Heine, J. Phys. F: Metal Phys., 4, L37(1974)

8:40am SS1-MoM2 Unoccupied States vs Coverage in Alkali Metals on Mo(110) by Auger Decay, NEXAFS, and Bandmapping, *E. Rotenberg*, *C.M. Lee,* Lawrence Berkeley National Laboratory; *S.D. Kevan,* University of Oregon

In recent years, the nature of the chemical bonding between alkali metals (AMs) and metal substrates has been intensely debated. For many alkalis on metals, the workfunction rapidly falls with coverage, reaching a minimum at about 1/2 monolayer before recovering somewhat up to saturation. The key issue is whether this work function change directly reflects a strong change in the charge distribution around the AM, as proposed by Langmuir and Gurney (LG) over 60 years ago, or whether the charge distribution somewhere else (in the substrate or in the space between adsorbate and substrate) dominates the workfunction change. Using localized, core-hole processes at the AM (near edge xray absorption fine-structure spectroscopy (NEXAFS) and Auger decay) we can now infer the alkali s-level occupation as a function of coverage, and correlate this with other measurements such as bandmapping and workfunction measurements. Measurements were performed for Li or K on Mo(110). At low coverages (below about ~0.1 ML) we find no occupied states at the AM atoms. At somewhat higher coverages, we observe a reoccupation of the AM valence orbital. This reoccupation, however, appears largely complete before the workfunction minimum occurs. Therefore, we conclude that there is a significant change in AM valence occupation with coverage, roughly following the LG model (donation of charge from AM to the substrate at low coverage, followed by backdonation at higher coverages). However, the workfunction change cannot be explained only by our measurements of the AM valence occupation, but instead has additional contributions from redistribution within the substrate.

9:00am SS1-MoM3 Auger Photoelectron Coincidence Spectroscopy of Ag and the Ag/Cu(100) Surface Alloy, *D.A. Arena*, *R.A. Bartynski*, Rutgers, The State University of New Jersey; *Q. Qian*, New Jersey Institute of Technology; *S.L. Hulbert*, Brookhaven National Laboratory

The question of atomic versus band-like contributions to the core-valencevalence (CVV) Auger line shape in Ag remains a controversy. Theoretical predictions are ambiguous as the correlation energy, U, is comparable to the 4d valence band width, W. Using Auger-photoelectron coincidence spectroscopy (APECS), we measured the line shape of the Ag M@sub 4,5@VV and N@sub 2,3@VV Auger transitions from single crystal Ag. In addition to a dominant atomic-like component, both spectra show a significant contribution from band-like decays. However, the N@sub 2,3@VV spectrum cannot be accounted for within the Cini-Sawatzky theory, suggesting that dynamical effects of the very rapid 4p core hole decay influences the lineshape. Furthermore, the N@sub 2,3@VV transition exhibits a much larger low energy tail that may be of the same origin. We have also measured the Ag CVV Auger spectra for 0.1ML Ag/Cu(100) to investigate the electronic structure of this prototypical surface alloy. In contrast to theoretical predictions, the Auger lineshape suggests that the Ag d-band shifts towards the Fermi level.

9:20am SS1-MoM4 Photoelectron Spectroscopy Studies of Adhesion, Alloying and Segregation in the Platinum - Tungsten Bimetallic System, J.J. Kolodziej, T.E. Madey, Rutgers University; J.W. Keister, J.E. Rowe, North Carolina State University

High resolution soft X-ray photoelectron spectroscopy (SXPS) using synchrotron radiation, and Auger electron spectroscopy, are used to study Pt films on W (211). It is found that the films grow in layer-by-layer mode at 300 K. As a function of Pt film thickness four different Pt 4f@sub7/2@ photoemission peaks are observed, corresponding to a single monolayer of Pt/W, a Pt interface layer, Pt surface atoms and Pt bulk atoms. A single monolayer of Pt is stable up to the onset of desorption. In contrast, when multilayer Pt films are annealed above 600 K, substrate W atoms diffuse in the Pt overlayer to form an alloy. Evidence for a dilute alloy, in which the W

4f@sub7/2@ signal from the W impurity in a Pt host is found to have a binding energy 1 eV higher than bulk W, is observed up to 900K. The evolution of the bimetallic Pt - W sample as a function of Pt coverage and annealing temperature is diagnosed by analysis of intensities and angular dependencies of the W 4f@sub7/2@ and Pt 4f@sub7/2@ features. In all cases a single monolayer of Pt "skin" covers the alloy film. The data provide detailed information on energetics of adhesion, segregation and alloying in an early d - late d transition metal system.

9:40am SS1-MoM5 Electronic Structure of Sn/Ge(111) along the @sr@3 x @sr@3 to 3x3 Phase Transition, J. Avila, LURE and CSIC, France; A. Mascaraque, Universidad Autonoma Madrid, Spain; G. LeLay, CRMC2-CNRS, France; E.G. Michel, Universidad Autonoma Madrid, Spain; M.C. Asensio, LURE and CSIC, France

The @sr@3 x @sr@3-Sn/Ge(111) structure undergoes a phase transition to a 3x3 phase at low temperature,@footnote 1@@footnote 2@ which has been interpreted as a charge-density-wave@footnote 1@ where electron localization gives rise to strong correlation effects.@footnote 2@ We report an angle-resolved photoemission investigation on the band structure and the Fermi vector of this interface along the phase transition. The electronic bands at room temperature exhibit a prominent surface state originated from Sn p@sub z@ orbitals, dispersing 0.3 eV with minima at K points. The Fermi vector obtained from these data is close to 0.3 Å@super -@@super 1@, much smaller that the calculated value.@footnote 1@ The surface state band splits at low temperature in two dispersing bands with strong 3x3 periodicity, at variance with previous data.@footnote 2@ The observation of these two bands correlates with the appearance of two components in the shallow Sn core levels. These data together with several other evidences support that the phase transition is of the order-disorder type. The mechanism driving the phase transition will be discussed in view of different theoretical models. @FootnoteText@ @footnote 1@J.M. Carpinelli et al, Phys.Rev.Lett. 79, 2859 (1997). @footnote 2@A. Goldoni and S. Modesti, Phys.Rev. Lett. 79, 3266 (1997).

10:00am SS1-MoM6 Surface Electronic Structure of Wurtzite GaN(0001)1x1 Studied with Angle-Resolved Photoemission, Y.-C. Chao, C.B. Stagarescu, J. Downes, K.E. Smith, Boston University; D. Hanser, M. Bremser, North Carolina State University; R.F. Davis, North Carolina State University, US

The surface electronic structure of the n-type, Si-doped, wurtzite GaN(0001)1x1 surface has been studied in detail with angle-resolved photoemission. The GaN film was grown on a AIN buffer layer on a 6H-SiC(0001) Si-face, on-axis substrate using a low-pressure metalorganic vapor phase epitaxy technique. A very sharp 1x1 LEED pattern was observed from the surface after the cleaning by repeated cycles of sputtering with nitrogen ions and annealing in ultra-high vacuum. The photoemission spectra reveal a previous unidentified highly dispersive surface-state band. The dispersion of this surface state has been determined along the [@GAMMA@KM] azimuthal direction of the 1x1 surface Brillouin zone. At @GAMMA@ point, the surface state is located at ~2 eV below the valence band maximum. For small emssion angles, this surface state rapidly disperses towards the VBM by ~1 eV. As the emssion angle is increased, the state starts to disperse downward and moves into the projected bulk band gap close to the K point. The identification of this state as originating from a surface band is confirmed by exposure of the surface to activated hydrogen. The intensity of emission from the surface state decreases dramatically following H exposure. This work was supported in part by the National Science Foundation under grant umber DMR-95-04948.

10:20am **SS1-MoM7 Fermi Surface and Metallization of the Ag/Si(111)7x7 Interface**, *J. Avila*, LURE, Centre Universitaire Paris Sud and ICMM, France; *M. DeSeta*, III Universita di Roma, Italy; *M.C. Asensio*, LURE, Centre Universitaire Paris Sud and ICMM, France

The determination of the metallization onset of metal/semiconductor interfaces is an important goal for diverse applications as well as for its fundamental interest. In this field, the early stage of nucleation and growth plays an essential role in determining the final morphology and electronic structure of the interfaces. In this work, we address this particular issue for the epitaxial growth of silver overlayers on Si(111)7x7 surfaces studied by LEED, Photoelectron Diffraction and High Energy Resolution Angular Resolved Photoemission. The films were prepared by Ag deposition at room temperature and the silicon substrates were chemically treated previously to be introduced to the ultra high vacuum system. The evolution of the valence band as a function of the silver coverage, at particular high

symmetry points of the reciprocal space, has put clearly in evidence the onset of the metallization of this interface. The presence of Si features even at 4 silver monolayers is consistent with the existence of Ag islands since the first layers. The Fermi Surface of the Ag/Si(111)7x7 interface, measured in situ, shows the coexistence of two domains of Ag(111) rotated 60° each others. In addition, the valence bands recorded along the @GAMMA@K, @GAMMA@M and @GAMMA@M' azimuths are in excellent agreement with band theoretical calculations.

10:40am SS1-MoM8 Analysis of High-Index Si(001) Surfaces by Reflectance-Difference Spectroscopy, *L. Mantese*, University of Texas, Austin; *Q. Xue*, Tohoku University, Japan; *D.E. Aspnes*, North Carolina State University

High-index Si surfaces are of interest as potential substrates for electronic device applications. The growth properties of these surfaces are expected to be superior to those of the commonly used (001) and (111) orientations. It is believed that higher concentrations of surface steps may lead to higher nucleation densities. In addition, these surfaces provide new opportunities for meeting the requirements demanded by increasingly complex structures. Here, we consider the surface-induced optical anisotropies (SIOA) of three high-index Si surfaces: (113), (114) and (115) representing offcut angles of 25.2, 19.5, and 15.8 degrees from (001) toward [110], respectively. The SIOA of these surfaces were measured first in their airoxidized conditions, second as-cleaned by heating, and third following Ge deposition. In some instances previous results on lower index Si(001) surfaces offcut 6 and 10 degrees toward [110] are available for comparison. The air-oxidized surfaces show sharp derivative-type structures near the critical point energies of bulk Si, consistent the lower index Si(001) surfaces. We have previously interpreted these structures in terms of photon-induced localization of the excited electronic states, which results from final-state correlation effects ordinarily discarded in conventional descriptions of optical absorption in solids. Spectra of clean reconstructed surfaces show a broad feature near 3 eV and a small step-related structure near the (E@sub 0@',E@sub 1@) transition of bulk Si. Atomic H exposure decreases the amplitude of the broad 3 eV feature suggesting it to be a dangling-bond-related state. In contrast, H exposure of Ge-deposited Si surfaces sharpens and enhances features below 3 eV while structures near the critical point energies of bulk Si remain. The optical response of Si(114) is consistent with its STM analysis, which indicates that this is the highestindex surface to demonstrate a terrace-plus-step morphology.

11:00am SS1-MoM9 HRPES Study of Acetylene Adsorption and Reaction with Si(100)-2x1 Surface, S.H. Xu, Y. Yang, H. Cruguel, Montana State University; E. Rotenberg, Lawrence Berkeley National Laboratory; G.J. Lapeyre, Montana State University; J.T. Yates Jr., University of Pittsburgh The adsorption and reaction of acetylene with Si(100)-2x1 surface has been studied using high resolution photoemission measurement the Si 2p. C 1s and valence band(VB)spectra as a function of acetylene coverage and post annealings at several temperatures. After the clean Si(100) surface is exposed to 0.5 ML acetylene, the surface state in valence bands is totally gone. Meanwhile, there is only one interface component in the Si 2p core line. These results indicate that the asymmetry of Si dimers is gone after acetylene adsorption, which is in excellent agreement with the tetra-@sigma@ model proposed by our previous photoelectron holographic results.@super [1]@ Significant changes in the electronic structure(Si 2p, C 1s and VB) are found after subsequent annealing of a saturation overlayer. Annealing at lower temperatures can induce a bit of acetylene desorption but most of the molecules decompose to C@sub 2@H@sub x@ (x=1, 0) and H species. After annealing at above 650 °C, there develops a surface state in valence bands and a Si 2p surface core-level component indicating some restoration of a Si(100)-2x1 structure. The C 1s line shows a single component indicating that a SiC compound forms on the Si surface. Both of the reacted components of the Si 2p and C 1s lines show that the SiC species form cluster-like feature. At the same time, the surface core-level components indicate that the clean surface Si dimers reappear on the silicon surface. This work is supported by NSF. The ALS of LBNL is supported by the DOE. [1]. G. J. Lapeyre et al., to be published.

11:20am SS1-MoM10 The Electronic Structure of Nanosized Mg Clusters on MgO Surfaces: Characterization with MIES, J. Günster, J. Stultz, S. Krischok, Texas A&M University; P. Stracke, V. Kempter, Technische Universitat Clausthal, Germany; D.W. Goodman, Texas A&M University

MgO films (2nm thick) were grown on Mo and W substrates with "in situ" investigation by MIES and UPS(HeI). Apart from the valence band emission no additional spectral features could be detected with electron spectroscopies. The oxide surface was exposed to Mg atoms (substrate

temperature between 100 K and RT). An additional peak, not seen in UPS, located within the bandgap developed in MIES, located about 2.3eV above the top of the valence band with ca. 1.5eV FWHM at the lowest exposures. Both the energetic position and the peak width depended (weakly) on the exposure time. This additional emission could be detected in MIES until its intensity fell below a level of 10 ppm of that from the valence band. We attribute this additional emission to the formation of small, non-metallic Mg clusters. For small exposures these are 2D clusters.@footnote 1@ It is remarkable that the energetic position of the cluster emission closely matches that expected for the ionization of surface Fs+ / Fscenters.@footnote 2@ Indeed, the existence of Mg-induced F-type centers an MgO has recently been detected by both ESR@footnote 3@ EELS.@footnote 4@ Therefore, we suggest that in the initial phase of Mg exposure F-type point defects are produced when the Mg adsorbs close to extended defects, such as steps, corners etc. These point defects may play an important role as nucleation sites for the cluster formation. @FootnoteText@ @footnote 1@C.T. Campbell: Surf. Sci. Rep. 27 (1997) 1 @footnote 2@L.N. Kantorovich, J.M. Holender, M.J. Gillan: Surf. Sci. 343 (1995) 221 @footnote 3@E. Giamello, A. Ferrero, S. Coluccia, A. Zecchina: J. Phys. Chem. 95 (1991) 9385 @footnote 4@K.-M. Schr@um o@der, D. Peterka, H. Pfn@um u@r: DPG Fr@um o@hjahrstagung Regensburg, and to be published in Surf. Sci.

11:40am SS1-MoM11 Scattered and Recoiled Ion Fractions From Cd- and S-Terminated CdS(0001) Surfaces, L. Houssiau, M. Liu, J.W. Rabalais, University of Houston; J. Wolfgang, P. Nordlander, Rice University

Scattered and recoiled ion fractions from CdS(0001) and CdS(000-1) surfaces have been determined by means of time-of-flight scattering and recoiling (TOF-SARS) spectrometry. An acceleration tube placed between the sample and the CEM detector enabled separation of the ions and neutrals. By applying a positive (negative) high voltage on the tube, the negative (positive) ions are accelerated, giving rise to neutral and ion peaks in the TOF spectra. On the Cd-terminated surface, 4 keV Ne@super +@ ions scattered at an incident angle @alpha@ = 11° through a scattering angle @theta@ = 50° exhibit a pronounced angular dependence, i.e. the lowest ion fractions (Ne@super +@/Ne@super 0@) are observed along the close packed atomic rows and . On the S-terminated surface however, the same experiment exhibits the opposite angular dependence, i.e. the highest ion fractions (Ne@super +@/Ne@super 0@) being now observed along the close packed rows. 4 keV Kr@super +@ ions were also used to study the S recoiled ion fractions. On the Cd-terminated surface, the lowest S@super -@ ion fractions are found along both the and rows. On the Sterminated surface, the lowest S@super -@ ion fractions are found along the rows, but the highest ion fractions are found along the rows. The final charge state of the ejected atoms is determined by electron tunneling between the surface and the atom as it leaves the surface. This process has been modeled using ab initio calculations of the potentials in the CdS surfaces. In conclusion, it is found that the ion fractions and their angular dependence are extremely sensitive to the nature of the surface terminating layer. This is important in determining the microscopic reactive sites on surfaces.

Surface Science Division Room 309 - Session SS2-MoM

Molecular Adsorbates on Metals

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

8:20am SS2-MoM1 An X-ray Absorption Study of Saturated Hydrocarbons Physisorbed on Metal Surfaces, K. Weiss, C. Wöll, Ruhr-Universität Bochum, Germany

Monolayers of linear and cyclic saturated hydrocarbons (n-hexane, cyclohexane, n-octane, n-hexatriacontane) physisorbed on several metal surfaces (Cu(111), Au(111), Ru(0001) and Pt(111)) have been investigated by K-edge X-ray absorption spectroscopy (XAS). Whereas the corresponding multilayer data qualitatively resembles the core excitation spectrum observed for the free molecules, a strong quenching of the Rydberg R-resonance at 287.7 eV is observed for molecules in direct contact with the substrate. The intereaction with the metal surface is found to result in the formation of a new, sharp resonance which is assigned to a novel surface-induced Rydberg state. In addition the broad feature observed in the saturated hydrocarbon monolayer XAS-spectra at 285.1 eV is identified as a transition into metal-molecule hybrid orbitals, indicating a significant chemical interaction between saturated hydrocarbon and the metal surface. This C-H-activation is shown to correlate with the well-

known soft C-H--stretch modes seen in IR-spectroscopy for many saturated hydrocarbon/metal surface combinations.@footnote 1@ @FootnoteText@ @footnote 1@G. Witte, K. Weiss, P. Jakob, J. Braun, K.L. Kostov, and Ch. Wöll, Phys. Rev. Lett. 80, 121, (1998)

8:40am SS2-MoM2 An Atom Specific Probe of the Surface Chemical Bond Using X-ray Emission Spectroscopy, J. Hasselstrom, A. Fohlisch, O. Karis, A. Nilsson, Uppsala University, Sweden; M. Nyberg, L.G.M. Pettersson, Stockholm University, Sweden; J. Stohr, IBM Almaden Research Division

When a molecule is adsorbed on a metal surface by chemical bonding new electronic states are formed. The direct observation and identification of these states is still an experimental challenge. In this contribution we will show how X-ray Emission Spectroscopy (XES), in spite of its inherent bulk sensitivity, can be used to investigate adsorbed molecules. We have applied XES to CO and NH@sub 3@ adsorbed on single crystal Cu surfaces. These molecules have lone pair orbitals in its @sigma@-systems and adsorb with these towards the substrate. Due to the localization of the core excited intermediate state, XE spectroscopy allows an atom specific probe of the valence electrons, i.e. the molecular contributions can be separated from those of the substrate. In combination with ab initio calculation, new details of the chemical bond formed at the surface can be revealed. It is, for CO adsorbed on Cu(100), found that the surface chemical bond formation can be related to the @pi@-system interacting with the metal d band. The overall interaction of the @sigma@-system, i.e. the 5@sigma@ lone pair, is found to be repulsive. In contrast, the @sigma@system, involving the 3a@sub 1@ lone pair, of ammonia is found to comprise the main covalent contribution to the adsorption energy of the NH@sub 3@/Cu(110) system; the degenerated 1e orbitals, often referred to as the N-H @pi@-system preserve much of its molecular character. Our results indicate that the different bonding mechanisms can be related to the energy position of the lone pair valence orbitals as compared to the metal bands, and furthermore to the corresponding symmetries of the lowest unoccupied molecular orbitals.

9:00am SS2-MoM3 The Role of Steps and Kinks in Catalytic Activity, L. Ford, P. Blowers, R. Masel, University of Illinois, Urbana

In the literature, there is the idea that steps and kinks are active sites for chemical reactions, but the experimental data is far from convincing. In this paper we see if there is a correlation between step and kink density and reactivity for a number of simple decomposition and hydrogenation reactions on platinum. We have examined the decomposition of ethylene, methanol, methylamine, ethanol, propanol, NO, the hydrogenation of ethylene, and the hydrogenolysis of ethylene, methanol, ethanol on Pt(111), Pt(110)(1x1), Pt(110)(1x2), Pt(100)-hex, Pt(100)(1x1), Pt(210), Pt(511), Pt(331). We find that in general stepped surfaces have different reactivity than closed packed planes, but some stepped surfaces are more active than Pt(111) while other stepped surfaces are less active than Pt(111). There is no correlation between step and kink density and catalytic activity. Calculations are done to understand the variations. We find that in general stepped surfaces relax to more stable geometries. The relaxation process lowers the electronic coordination number of the atoms in the surface of the catalyst so after relaxation, there is not a large difference in the coordination of atoms in stepped surfaces and Pt(111).

9:20am SS2-MoM4 Face Specificity and the Role of Metal Adatoms in Molecular Reorientation at Surfaces, C.C. Perry, S. Haq, University of Liverpool, United Kingdom; B.G. Frederick, University of Maine, U.K.; N.V. Richardson, University of St. Andrews, Scotland, U.K.

Using Reflection Absorption Infrared Spectroscopy (RAIRS), the coverage dependent reorientation of the benzoate species on the (110) and (111) faces of copper is compared and contrasted. Whereas on Cu(110), benzoate reorients from flat-lying to upright orientation with increasing coverage, on Cu(111), at all coverages, benzoate is aligned normal to the surface. The formation of periodic, flat-lying copper-benzoate structures has been attributed to the availability of metal adatoms, which differs dramatically between the (111) and (110) faces. We discuss the face specificity of molecular orientation by comparing calculated formation energies of adatom-vacancies from ledges and kink sites on (100), (110), and (111) faces. Further support for this model is given by the evaporation of sodium, either by pre- or post-dosing, onto low coverage benzoate/Cu(111), which induces benzoate to convert from perpendicular to parallel orientation. Likewise, coevaporation of Cu while dosing benzoic acid onto the Cu(111) surface also results in a majority of flat-lying benzoate species. Finally, for adsorption on the p(2x1)O/Cu(110) reconstruction, benzoate occurs only as the upright species, which is consistent with reducing the copper mobility and availability on the (110)

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face. We therefore suggest the possible role of metal adatoms as a new mechanism in controlling adsorbate orientation, and therefore face specificity, in surface reactions.

9:40am SS2-MoM5 Theoretical Studies of Surface Reactions on Metals: I. Ethyl to Ethylene Conversion on Platinum; II. Photodissociation of Methane on Platinum, J.L. Whitten, North Carolina State University INVITED

An embedding method designed to provide a molecular level understanding of adsorbate energetics and surface reaction mechanisms is presented. Electronic structures, including relativistic effects, are described by an ab initio formalism that permits an accurate determination of energies and adsorbate structure.@footnote 1@ Applications to catalytic and photochemical reactions on transition metal surfaces are reported. I. In the catalytic conversion of ethyl adsorbed on platinum surfaces to ethylene, the minimum energy pathway for the transfer of hydrogen to the metal surface is calculated. A detailed description of the transition state is presented. II. In the photodissociation of methane physisorbed on platinum, results are reported for a methane molecule interacting with an embedded cluster model of Pt(111). Configuration interaction theory is used to sort out states resulting from electron attachment to methane from lower energy states that correspond to metal excitations. Energies of the ground and excited states of the Pt(111)CH@sub 4@ complex are calculated as a function of geometrical distortions and the distance of methane from the surface. Key steps in the photodissociation process are described. @FootnoteText@ @footnote 1@ J. L. Whitten and H. Yang, Surf. Sci. Repts., 218 (1996) 55.

10:20am SS2-MoM7 Chemistry of SO@sub 2@ on Ru(001): Formation of SO@sub 3@ and SO@sub 4@, T. Jirsak, J.A. Rodriguez, S. Chaturvedi, J. Hrbek, Brookhaven National Laboratory

The interaction of SO@sub 2@ with Ru(001) at 300 and 100 K was studied using synchrotron-based high-resolution photoemission, INDO/S MO calculations, and a thermochemical analysis based on the bond-order conservation Morse-potential (BOC-MP) formalism. At 300 K and small exposures of SO@sub 2@, sulfur dioxide completely decomposes (SO@sub 2@ -> S@sub a@ + 20@sub a@). Several coordination modes for adsorbed SO@sub 2@ were examined using INDO/S and the BOC-MP formalism. It was found that adsorption geometries in which the molecule is dicoordinated via O,O or S,O are the most probable precursors for dissociation. For large exposures of SO@sub 2@ at 300 K, SO@sub 3@ and SO@sub 4@ species appear on the Ru(001) surface confirming thus the theoretical predictions derived from the BOC-MP method which indicate that formation of SO@sub 3@ and SO@sub 4@ can take place only when the number of empty adsorption sites is limited. This prediction was also proved during the adsorption of SO@sub 2@ on a O/Ru(001) surface with @theta@@sub O@ = 0.25 ML, producing similar types of species as at saturation of SO@sub 2@ on Ru (S@sub n@+O, SO@sub 4@ and S). When a Ru surface partially covered by sulfur (@theta@@sub S@ = 0.2 ML) was exposed to molecular oxygen at 300 K, formation of SO@sub 3@ and SO@sub 4@ species was not observed. Experiments performed at a surface temperature of 100 K showed a very rich surface chemistry. Five different surface species were observed after SO@sub 2@ dosing: atomic S, S@sub n@+O, SO@sub 2@, SO@sub 3@ and SO@sub 4@. The S 2p spectrum of a Ru(001)surface saturated at 100 K is dominated by a very intensive peak of a multilayer of SO@sub 2@, which entirely disappeared upon annealing to 160 K. Further annealing to 260 K leaves mainly atomic S and SO@sub 4@ on the surface and the latter is completely decomposed by 350 K.

10:40am SS2-MoM8 Low Temperature STM Imaging of Furan Molecules on Pd(111), C.A. Pearson, S. Chiang, A. Loui, D.N. Futaba, University of California, Davis

The cyclotrimerization reaction of acetylene to benzene is known to proceed readily in ultra high vacuum on the Pd(111) surface. Thermal desorption spectroscopy has measured furan (C@sub 4@H@sub 4@O)@footnote 1@ and thiophene (C@sub 4@H@sub 4@S)@footnote 2@ desorbing from the Pd(111) surface following the coadsorption of acetylene with oxygen and sulfur respectively. Using low temperature scanning tunneling microscopy (STM), we have imaged furan molecules adsorbed on the Pd(111) surface. Dosing and imaging of the sample was performed at 200 K. While no changes were evident with low energy electron diffraction (LEED), we observed localized ordering with the STM for monolayer coverage. Furan molecules form ordered rows in three different domains oriented 120° apart. The ordered regions are roughly 50 Å to 100 Å in size. Higher resolution images show individual molecules

within the rows. Measurements of the intermolecular spacing in the images provide information about the molecular tilt on the surface. Images of individual molecules will also be compared with predicted theoretical STM images from extended Hückel molecular orbital theory. @FootnoteText@@footnote1@R.M. Ormerod, R.M. Lambert, Cat. Lett. 6, 121 (1990). @footnote 2@A.J. Gellman, Langmuir 7, 827 (1991).

11:00am SS2-MoM9 Conformation and Orientation of Methyl Pyruvate on Ni(111), P.H. McBreen, M. Castonguay, J.R. Roy, Université Laval, Canada

Both the orientation and molecular conformation of adsorbed layers are determining factors in a variety of properties including chemical reactivity. The question of surface orientation and conformation are particularly important for methyl pyruvate since it possesses both a keto and an ester carbonyl and it can undergo cis-trans isomerization. Its hydrogenation to methyl lactate is one of the very few well documented cases of enantioselective heterogeneous catalysis. To the best of our knowledge this is first report of an investigation of the intrinsic adsorption of this prochiral molecule on a metal surface using surface science techniques. RAIRS data shows that methyl pyruvate is chemisorbed on Ni(111) at all coverages with its molecular plane perpendicular to the surface. Two different adsorption conformations are detected. The full monolayer is found to be exclusively in the bidentate cis-conformation. The results, and DFT calculations, indicate that the keto cabonyl metal surface interaction is stronger than the ester carbonyl metal surface interaction. Comment will be made on the fact that the observed molecular orientation and conformation are at odds with the model usually assumed in rationalizations of the enantioselective hydrogenation of methyl pyruvate.

11:20am SS2-MoM10 Negative and Positive Adsorbate-Induced Reflectance Changes: Formic Acid on Cu(100), C.-L. Hsu, E.F. McCullen, R.G. Tobin, Tufts University

Adsorption on metal surfaces typically reduces the broadband reflectance of the surface, an effect that is usually attributed to diffuse scattering of the conduction electrons by the adsorbate. The resistance of the film typically increases. On the other hand, a dielectric film typically increases the broadband reflectance of a metal. Both effects are observed for the adsorption of formic acid (HCOOH) on epitaxial Cu(100) films at 125 K. Both the dc resistance and the infrared reflectance at 1500 cm@super -1@, away from any vibrational resonances, were measured during dosing. Upon initial exposure to formic acid, the film's resistance increases by 1% and its reflectance decreases by 0.5%. With continued exposure, leading to the growth of a multilayer formic acid film, the reflectance begins to increase and ultimately reaches a level more than 10% greater than the clean-surface reflectance. The resistance, however, scarcely changes after adsorption of the first monolayer. While the results are qualitatively consistent with expectations, there are discrepancies. The resistance and reflectance changes in the monolayer region are not proportional, and the increase in reflectance with thickness is more rapid than expected.

11:40am **SS2-MoM11 Ordering of Chemisorbed PF@sub 3@ on Cu(001)**, *J. Braun, L.V. Goncharova, G.G. Bishop, A.V. Ermakov,* Rutgers University; *D.-M. Smilgies,* Rutgers University, US; **B.J. Hinch**, Rutgers University

PF@sub 3@ adsorbs molecularly on many transition metal surfaces with P bonded at 'on top' positions. On close packed Pt, Ni and Ru crystal faces, PF@sub 3@ has been reported to adsorb with a high density @sr@3 x @sr@3 structure. In these cases steric interactions are believed to be strong enough to prevent rotational motion of the molecules about an axis parallel to the surface normal. On Cu(001), between 140K and 200K, a saturated(4x2) structure with at least two 90° rotated domains has been observed with both helium atom scattering and LEED. We shall discuss the implications of free rotational motion of these molecules in the c(4x2) and a close-packed, uniaxially-compressed, near-hexagonal phase that is found at higher coverages and lower temperatures. Evidence for PF@sub 3@ decomposition on Cu at temperatures above 500K will also be presented.

Nanometer-scale Science and Technology Division Room 321/322/323 - Session NS+EM+SS-MoA

Cross-sectional Scanning Tunneling Microscopy of Semiconductors

Moderator: M. Weimer, Texas A&M University

2:00pm NS+EM+SS-MoA1 Scanning Tunneling Microscopy Studies of Atomic-Scale Structure In Semiconductor Heterostructures, E.T. Yu, S.L. Zuo, University of California, San Diego INVITED

Engineering of advanced heterostructure and nanoscale semiconductor devices requires a detailed understanding of the structure and properties of semiconductor materials and devices at the atomic to nanometer scale. Cross-sectional scanning tunneling microscopy provides unique and powerful capabilities for characterization of structural morphology and electronic properties in semiconductor epitaxial and device structures with spatial resolution at or near the atomic scale. In conjunction with results obtained using complementary characterization techniques, such studies can provide valuable insights into the relationships among epitaxial growth conditions, atomic-scale compositional structure, and various aspects of device behavior. We will discuss a number of recent applications of crosssectional scanning tunneling microscopy to the characterization of III-V compound semiconductor heterostructures. Studies of InAsP/InP heterostructures, currently of interest for optoelectronic devices operating at 1.3-1.55 microns, have revealed that extensive nanoscale compositional clustering occurs, with As-rich and P-rich clusters bounded preferentially by {111} planes forming in the InAsP alloys. Related studies of InNAsP/InP heterostructures, in which low concentrations (~1-2%) of N are incorporated, have provided information about the influence of N on heterojunction band alignments. And STM images of InAsP/InAsSb superlattices of interest for midwavelength infrared emitters have revealed nanoscale compositional fluctuations in these materials consistent with previously reported observations by electron diffraction of partial ordering in InAsSb alloys.

2:40pm NS+EM+SS-MoA3 Growth Asymmetry in InGaAsP/InAsP Superlattices Studied by Scanning Tunneling Microscopy, B. Grandidier, H. Chen, R.M. Feenstra, Carnegie Mellon University; R.S. Goldman, University of Michigan; C. Silfvenius, G. Landgren, Royal Institute of Technology, Sweden

InGaAsP based multiple quantum well structures are increasingly used to fabricate optoelectronic devices. However the strain can lead to lattice relaxation processes during the growth which degrades the optical properties of these structures. To understand the differences in the photoluminescence efficiency of several superlattices composed of InGaAsP quaternary wells, we have investigated a series of InGaAsP/InGaP and InGaAsP/InAsP superlattices using cross-sectional scanning tunneling microscopy (xSTM). These superlattices were grown by metalorganic vapor phase epitaxy, with different number of periods and with or without InP interlayers inserted in the barrier. For InGaAsP/InGaP superlattices, the individual well and barrier layers are well resolved in the xSTM images. In contrast, for InGaAsP/InAsP superlattices, the InGaAsP quantum well and preceding InAsP barrier layers can be clearly seen, whereas the subsequent InAsP barriers are severely intermixed with the quantum wells. Possible mechanisms for this intermixing are described. In addition, the contrast observed in both types of superlattices has been related to the strain which exists in the layers; the compressively strained InAsP barrier protudes outwards from the (110) cleavage plane whereas the tensilely strained InGaP barrier contracts inwards. Finite element computations are used to quantify these elastic relaxation effects of the cleavage surface.

3:00pm NS+EM+SS-MoA4 Microstructure of Mixed-Anion Interfaces Examined with XSTM@footnote 1@, J. Harper, M. Weimer, Texas A&M University; D. Zhang, C.H. Lin, S.S. Pei, University of Houston

The quality of the interfaces between the nearly-lattice-matched 6.1 Å materials (InAs, GaSb, and AlSb) is important for a number of applications, including the development of mid-IR lasers, long-wavelength photodetectors, and resonant-tunneling devices. Cross-sectional scanning tunneling microscopy (XSTM) is a powerful tool for characterizing the heterojunctions in these structures, which pose special challenges for molecular beam epitaxy (MBE) because of the mixed-anion nature of this material system. We have observed a white-noise component in the roughness spectrum of the GaSb-on-InAs interface with XSTM that is associated with the presence of interface point defects; these defects most

likely arise from thermodynamically favored anion exchange reactions that occur during the crossover from arsenide to antimonide growth. Abruptness of the InAs-on-GaSb interface, on the other hand, is limited by antimony segregation that causes compositional grading within the arsenic layers. We have quantitatively characterized the Sb fraction as a function of distance from the arsenide-on-antimonide heterojunction, and find this compositional grading is well described by an exponential profile. @FootnoteText@@footnote1@Work supported by the National Science Foundation (DMR-9633011).

3:20pm NS+EM+SS-MoA5 X-STM Study of InAs/In@sub 1-x@Ga@sub x@Sb/InAs/AISb Laser Structures@footnote 1@, W. Barvosa-Carter, M.J. Yang, L.J. Whitman, Naval Research Laboratory

Strained-layer heterostructures involving the 6.1 Å family of III-V semiconductors (including InAs, GaSb, and AlSb) are being investigated for use in a growing number of high-speed and opto-electronic devices. Recently it was shown in InAs/In@sub 0.73@Ga@sub 0.28@Sb/InAs/AISb mid-IR structures that the photoluminescence (PL) intensity and x-ray superlattice diffraction quality are strongly dependent on MBE growth temperature. These characteristics were shown to be optimized within a rather narrow growth temperature range (410-460°C) and much worse outside of that range. Although the quality of the interfaces in these structures is expected to play a crucial role in determining device performance, little is known about the actual atomic-scale structure of the interfaces. We present an atomic-resolution cross-sectional STM (X-STM) study of these laser structures in order to directly correlate atomic-scale features, such as interface roughness and layer intermixing, with material quality as measured by PL and x-ray measurements on the same samples. Two such laser structures have been examined, one grown at the optimum temperature and another grown at a higher temperature. Interface roughness appears to be larger in the higher temperature structure. In addition, intermixing occurs at the AlSb-on-InAs interfaces which results in electronic structure differences between the InAs-on-AISb and AISb-on-InAs interfaces as observed by X-STM. Based on our X-STM results, we will discuss the atomic-scale sources of device degradation, and present possible routes towards improvement of the growth of these laser structures. @FootnoteText@ @footnote 1@ Funded by the Office of Naval Research and the Air Force Research Laboratory.

3:40pm NS+EM+SS-MoA6 Kinetics of Anion Cross Incorporation in Type-II Heterostructures Characterized with XSTM@footnote 1@, J. Steinshnider, J. Harper, M. Weimer, Texas A&M University; D. Zhang, C.H. Lin, S.S. Pei, University of Houston

We have used cross-sectional scanning tunneling microscopy (XSTM) to examine MBE material quality in the mixed-anion InAs/GaSb/AlSb system under growth conditions (including the use of cracked arsenic and antimony sources) similar to those presently employed for type-II quantum well and interband cascade lasers. Two apparently different anion defects are noted within the antimonide layers. The demonstration of a linear correlation between the defect densities observed with STM and the arsenic valve setting during antimonide-layer growth establishes background arsenic incorporation as the common origin for both of these defects.@footnote 2@ The distribution of As substitutional defects in a (110) cleavage plane is analyzed by way of the two-dimensional pair correlation function. We observe a pronounced attractive correlation in the [110] direction, parallel to the Sb dimer bonds of the (1x3) reconstructed growth surface, whereas the distribution in the orthogonal [001] direction is essentially random. This anisotropic correlation reflects the kinetics of arsenic dimer incorporation during growth and not the equilibrium distribution associated with strain-mediated repulsive interactions. @FootnoteText@ @footnote 1@ Work supported by the National Science Foundation (DMR-9633011). @footnote 2@ J. Harper, M. Weimer, D. Zhang, C.H. Lin, and S.S. Pei, JVST B 16, in press (1998).

4:00pm NS+EM+SS-MoA7 Low Temperature Cross-Sectional Scanning Tunneling Microscope-Induced Luminescence of GaN, S. Evoy, C.K. Harnett, Cornell University; S. Keller, U.K. Mishra, S.P. DenBaars, University of California, Santa Barbara; H.G. Craighead, Cornell University

The GaN system is of interest for applications in the green, blue, and UV spectral regions. Advances in device development have been made in spite of issues such as dislocation densities and defect induced visible luminescence. These issues prompted interest in spatially resolved luminescence studies of the material. Scanning tunneling microscope-induced luminescence (STL) offers nanometer scale resolution and control of the injection bias. In-situ cleaving and cross-sectional imaging is of garticular interest for nanoscale luminescence studies of GaN

heterostructures and interfaces. We recently reported the first low temperature STL of GaN, and the first STL images of this material. We now report the low temperature cross-sectional STL of MOCVD-grown GaN. Optical interference filters are used for semiquantitative spectral analysis. Room temperature top-view experiments reveal faint visible emission at tip biases above 1.5 V, with no clear evidence of UV luminescence. However, a sharp increase of emission in the 350±35 nm range is observed under liquid He cooling at biases above 3 V. The room temperature visible emission may be related to surface issues, suggesting that low temperature is required for the analysis of intrinsic bulk luminescence. Cross-sectional experiments are performed on in-situ cleaved samples. Incompatible cleaving planes between the GaN and the sapphire produce 200-400 nm wide vertical features, yielding an edge roughness of 30-50 nm. Behavior of luminescence is similar to what was observed in top-view. However, close to the sapphire interface, the 350±35 nm band-edge emission is undetected even at low temperature. Images show strong correlation between the remaining visible emission and the cleaved-induced artifacts. We are currently working on our cleaving technique in order to improve the quality of the edge. The technique will also be applied to the study of GaN heterostructures such as InGaN/GaN quantum wells.

4:20pm NS+EM+SS-MoA8 Cross Sectional STM Study on MBE-grown Si/Ge(111) Interface, *H. Hirayama*, *M. Ohmori, K. Takayanagi*, Tokyo Institute of Technology, Japan

We studied the (111) cross sectional surface of MBE grown Si/Ge(111) samples. Samples were cleaved in ultra-high vacuum, and their (111) cross s ection were investigated in-situ by using STM. On the as-cleaved surface, 2x1 reconstruction were observed at both Si and Ge side. After annealing, 2x1 reconstruction changed to 7x7 and c(2x8) on the Si and Ge layer, respec tively. At around the interface, 7x7 reconstruction changed to c(2x8) reconstruction in moving from Si to Ge side. But, the transition from 7x7 to c(2x8) was not abrupt. The transient region of the width of c.a.200nm was obs erved. In the transient region, adatoms arranged with 2x2 and c(2x4) shor t range orderings. Patchy domains of 7x7 reconstruction, which was accompa nied with (110)- oriented grooves and non-double layer height steps, were a lso observed in the sea of 2x2 and c(2x8) arrangement of adatoms. In a det ailed analysis of adatom arrangement, we found that the non-double layer hei ght step was caused by the glide in the (111) plane parallel to the substr ate. The groove was triggered by partial dislocations at the edge of the gild region. The strain field with the glide-induced step and grooves modifi ed the surface strain locally, and caused patchy 7x7 domains.

4:40pm NS+EM+SS-MoA9 Scanning Tunneling Microscopy Characterization of the Depletion Zone of a Si Lateral pn Junction, *M.L. Hildner*, *R.J. Phaneuf*, *E.D. Williams*, University of Maryland, College Park

Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are used to characterize lateral pn junctions fabricated on silicon (100) surfaces. Two separate device structures , one with p@super +@-n and the other with n@super +@-p abrupt junctions, were examined. The STM images of the first set of devices show both an electronic feature and a structural groove on each side of the ion implanted p-type regions. The groove is an etching artifact of the implantation mask fabrication process and was easily avoided in making the second set of devices which show only a similar electronic feature. The electronic feature widens with applied reverse bias with a voltage dependence that closely matches that expected for the depletion zone. However, the width of the electronic feature is much smaller than that of the depletion zone. The STS measurements show that the tip-junction system can be modeled as a series of non-equilibrium metal-insulator-semiconductor (MIS) diodes formed with a semiconductor of spatially variable carrier density. From this model, we qualitatively describe the electronic feature as confined to that portion of the depletion region in which the biasing sense of the MIS junction is switched from the biasing sense when the junction is in the lightly doped neutral region. Thus, the electronic feature commences, as the tip is moved from the lightly doped neutral region into the depletion region, when the majority carrier changes (from electrons to holes for the lightly doped n devices). This work has been supported by the Laboratory for Physical Science, with partial support from the NSF-MRSEC.

Surface Science Division Room 308 - Session SS1+NS-MoA

Novel Surface Probes

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

2:00pm SS1+NS-MoA1 Momentum Resolved ESDIAD, A New Technique, Probing the Low Frequency Motion of Adsorbed Molecules on Single Crystal Surfaces@footnote 1@, J.W. Ahner, D. Mocuta, J.T. Yates, Jr., University of Pittsburgh

A new technique, Momentum Resolved ESDIAD (Electron Stimulated Desorption Ion Angular Distribution), provides a method for taking snapshots of the zero-point position and lateral momentum of particles adsorbed on crystalline surfaces. By employing state of the art electronics and computer technology it is possible to record for each desorbing particle the desorption direction together with the flight time. Highly momentum and directional resolved images are obtained, with time-offlight resolution in the picosecond range and data acquisition rates up to 100 kHz. This enables us to deconvolute spatial and momentum contributions to the ESDIAD pattern and to map the low frequency motion of the adsorbed particles. These maps reflect the adsorbate interactions with the substrate and with neighboring species on the substrate. For selected examples we will present data 'movies' demonstrating how these unique maps of the dynamical behavior of adsorbed species are used in several ways to probe the lowest energy states, as well as to measure the momentum distribution when the particle gains thermal energy. One major opportunity involves dissimilar chemisorbed species which, when imaged together in momentum and real space, give new insights into the first stages of interaction between the species, leading ultimately to a chemical reaction. In addition we present lateral momentum distribution studies for an adsorbed molecule with a rotational symmetry axis showing the rotation of the molecule on its adsorption site about this axis. Such information can be used as a basis for thinking about anisotropies in lateral motion of particles on surfaces. @FootnoteText@ @footnote 1@work supported by DOE/BES.

2:20pm SS1+NS-MoA2 UV Spectroscopy of CO and Benzene on Pt(110), N. Chen, I. Lee, R. Masel, University of Illinois, Urbana

Recently there has been some controversy about the role of d-backbonding in the adsorption of gases on transition metals. People have suggested that the antibonding orbitals should shift, but without any direct measurements, the theory remains controversial. In this paper we use a standard HREELS spectrometer, with modified electronics to measure the equivalent of a UV spectrum for two different systems: CO on Pt(110) and benzene on Pt(110). In the CO case, the UV spectrum shows peaks at 5.41, 5.58 and 7.91 eV independent of coverage. By comparison, gas phase CO shows peaks at 6.04, 6.92, 7.58, and 7.94 eV. The large shifts are indicative of the antibonding orbitals being stabilized, as one would expect from the Blyholder model and recent calculations of Ilias et al, Surface Science 376, (1997) 279 but not with the calculations of Ohsishi and Watarri Phys Rev B 49(1994)14619. In the benzene case we observe two different spectra: a first monolayer spectrum with a broad peak center at 4.71 eV, and a multilayer spectrum with peaks at 3.78, 4.73, 6.11 and 6.82 eV. The multilayer spectrum matches the spectrum of condensed benzene, but the first monolayer spectrum is quite different. Again these results suggest that there is a substantial stabilization of the antibonding orbitals of adsorbed benzene. Together these results show that UV spectroscopy provides useful information about adsorbates on surfaces.

2:40pm SS1+NS-MoA3 Calorimetric Measurements of Metal Adsorption and Adhesion Energies on Clean, Single-Crystalline Surfaces, C.T. Campbell, J.T. Stuckless, D.J. Bald, D.E. Starr, J.E. Musgrove, University of Washington INVITED

The adsorption and adhesion energies of metals on solids are important in many materials and chemistry applications including oxide-supported metal catalysts, bimetallic catalysts, epitaxial thin film growth, metalceramic interfaces in microelectronics, metalization of polymers, composite materials and metal adsorption on minerals in soils. The heats of adsorption of metals have been measured calorimetrically for the first time on clean, single-crystalline surfaces. A pulse of metal vapor from a chopped atomic beam adsorbs onto an ultrathin single crystal's surface in ultrahigh vacuum, causing a transient temperature rise. This heat input is detected by a pyroelectric polymer ribbon, which is gently touched to the back of the crystal during calorimetry. The sticking probability is measured by detecting the reflected fraction mass spectrometrically with a line-of-sight modification of the King and Well's method. The differential heat of

adsorption is thus measured as a detailed function of coverage up through multilayer coverages. The integral heat of adsorption also provides the adhesion energy of the metal film, if the surface free energy of the clean metal surface is known. Adsorption and adhesion energies for metals (Pb or Cu) on the clean Mo(100) surface, on well-defined surface oxides of Mo(100) and W(100), and on clean and hydroxylated MgO(100) thin films will be reported. By comparing a variety of surfaces in Pb and Cu adsorption, an interesting correlation between the growth morphology of thin metal films and the initial heat of adsorption of the metal is revealed. The sticking probability also correlates with the heat of adsorption of the metal.

3:20pm SS1+NS-MoA5 Multispectral Image Classifications of Si(001) Surface Electronic Structure, K.M. Horn, B.S. Swartzentruber, G.C. Osbourn, Sandia National Laboratories

We have imaged the electronic structure of Si(001) surfaces by applying multispectral image analysis techniques to multi-bias STM conductance data. Atomic surfaces are first characterized by recording conductance spectra, C(V), at each point in a 2D scan of the surface. The resulting 3D data set, (x, y, C(V)), is then converted into a series of bias-dependent conductance images. These images are analyzed to produce a single, colorcoded, classed image that reflects the surface's electronic structure. The image analysis is performed by a computed grouping algorithm that identifies pixels sharing common conductance characteristics. The resulting classed images distinguish features not clearly resolved in a topographic image, and reveal stark electronic differences between topographically similar features. We first demonstrate the reliability of this classification technique on simple Si(001) features. Classed surfaces are then presented for various surface defects and Si and Ge structures that have been deposited on the Si(001) surface. These electronic structure images reveal features that are not readily visible or distinguished in a constant-current topograph. Direct comparison of the conductance spectra from these features confirms the classification result. This computer-based data reduction technique may prove useful in defect detection, validating surface models, and in understanding more complicated systems in which atomistic models are derived from a limited number of single-bias topographic images. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S.DOE under contract DE-AC04-94AL85000.

3:40pm SS1+NS-MoA6 A Simple Nulling Technique for Measuring Complex-Valued Nonlinear-Optical Susceptibilities of Interfaces, J.R. Dennis, V. Vogel, University of Washington

For studies of isotropic interfaces by nonlinear optics, a general technique is presented to measure the complete second-order surface susceptibility, up to an overall phase factor. The measurement and data analysis are simple and rapid, with no use of a variable reference phase, and the susceptibility is overdetermined, allowing consistency checks. The technique involves measuring the complete polarization state of the nonlinear-optical signal by nulling the signal, for several linear polarizations of the input beam. Mesurements of second harmonic generation from Langmuir monolayers of the liquid crystal 4'-n-octyl-4-cyano-biphenyl (8CB) have been made with this technique, giving results which agree with previous data, and also revealing a small phase shift between some susceptibility components. This phase shift may be explained by introducing a complex dielectric constant for the monolayer at the second harmonic frequency. Data for the free surface of isotropic 8CB have also been analyzed with this technique. The technique is particularly well-suited to testing or fitting different models of Fresnel factors and local-field factors.

4:00pm SS1+NS-MoA7 Characterization of Near-Field Probes for Enhanced Raman Spectroscopy, *C.E. Jordan*, *L.J. Richter, R.R. Cavanagh, S.J. Stranick,* National Institute of Standards and Technology

Near-field Raman spectroscopy can potentially obtain chemical specificity with the subwavelength resolution of a near-field scanning optical microscope (NSOM). Signals from a single crystal diamond sample have been evaluated to assess the limits of this technique. Three different types of illumination mode fiber optic probes have been used in the near-field Raman experiments: an uncoated probe; a probe coated with a smooth layer of aluminum which has an aperture that is less than 100 nm in diameter; and a probe coated with a smooth layer of aluminum and then overcoated with a rough layer of silver. In order to discriminate between the enhanced contribution to the Raman signal observed in the near-field of the probe and bulk scattering, the Raman intensity from each type of probe is measured as a function of the probe sample separation. Very little change in the Raman intensity is observed as a function of probe sample separation when an uncoated fiber optic probe is used. For an optical probe coated with a smooth layer of aluminum the Raman intensity is about a factor of seven higher when the sample is in the near-field of the probe compared to the intensity measured when the sample is farther than 100 nm away from the probe. Probes that are coated with a rough silver film show a greater enhancement in the near-field Raman intensity than is observed for probes coated only with aluminum.

4:20pm SS1+NS-MoA8 Element Specific Real-Space Imaging Surface Crystallography, *L. Houssiau*, *J. W. Rabalais*, University of Houston

Scattering and recoiling imaging spectrometry (SARIS) extends the technique of time-of-flight scattering and recoiling spectrometry (TOF-SARS) to include both spatial and time resolution of scattered and recoiled particles. SARIS uses a time-resolving, position sensitive, microchannel plate (MCP) detector, resistive anode encoder (RAE), time-to-digital converter (TDC), and a triple axis UHV goniometer to measure the velocityresolved spatial distribution patterns of scattered and recoiled particles produced by a keV beam of pulsed ions from on a crystalline surface. The images combine the advantage of atomic scale microscopy and spatial averaging simultaneously since they are created from a macroscopic surface area but they are directly related to the short-range (< 10 Å) atomic arrangements in the surface. The non-planar scattering features in the images are not normally observed in conventional ion scattering experiments using small-area detectors. The technique is applied to carry out real space imaging of Ni(110) and oxygen chemisorbed Ni(110) with 4 keV He@super +@ ions. A mapping of the entire hemisphere where the ions are reflected was made possible by collecting several images at different angles and merging them together. These maps reveal the blocking cones of surface atoms, which gives a real space image of the crystal surface. After oxygen exposure, the images are modified and reveal the O chemisorption sites. The features of these images can be accurately reproduced by classical ion trajectory simulations using the scattering and recoiling imaging code (SARIC).

4:40pm SS1+NS-MoA9 An Axial Resonant Force Probe for Atomic Force Microscopy, J.A. Harley, T.W. Kenny, Stanford University

A resonant force probe has been constructed which exhibits high force sensitivity from a stiff transducer with a stationary tip. The resonant beam is mounted vertically relative to the surface, as in shear force microscopy. but a tether has been added near the tip. The tether forces the beam to oscillate in a pinned-pinned mode while the tip remains stationary, but does not interfere with axial forces. This configuration has several advantages over current force measurement techniques. First, since the beam is perpendicular to the surface, the probe is not susceptible to force gradient instabilities. Second, the stationary tip provides high spatial resolution in the force measurements. Typical oscillating cantilevers average forces over the oscillation amplitude. Third, since the oscillations can be large, the resonant detection method is not as demanding on the secondary detector, so the force sensitivity in a piezoresistive sensor could approach that of optical lever techniques. Finally, the oscillator could potentially be encapsulated, allowing a high Q resonator in a liquid environment. The beam was constructed out of single crystal silicon, and measures 0.2 x 3 x 200µm, with an implanted piezoresistor to detect the oscillations. The axial spring constant is over 200N/m. Resonant frequency shifts of $30 \text{kHz}/\mu \text{N}$ are detected using a phase-lock loop circuit. In air, the oscillator is heavily damped (Q of 15) but still demonstrates 10nN force resolution in a 1kHz bandwidth. In a moderate vacuum the resonance quality improves to 1200, and10pN force resolution is expected. The design, analysis, and theoretical limitations of these sensors will be discussed.

5:00pm SS1+NS-MoA10 Super Transmission and Resolution Energy Analyzer and Mass-Analyzer System (STREAMS), K. Siegbahn, R. Maripuu, ESCA LASER Lab Institute for Materials Science, Sweden; N. Kholine, Russian Academy of Sciences, Russia; U. Golikov, State Technical University, Russia; M. Larin, Joint Stock Co. CRYOVACS, Russia

A new type of instrument for scientific and technological research is proposed. Its main peculiarity and advantage are the capability to separate charged particles in accordance with their energies and masses on high level of resolution and sensitivity. A basis of the spectrometer is electrostatic axially symmetrical field structure with matched radial and axial potential gradient. The electron optical system can function either in dispersion or time-of-flight mode of operation. The charge particles follow the same trajectories in this field independently of the mode of operation. Electron spectroscopy or mass-spectroscopy information from the same

point of the analyzed sample can be received by switching over to the appropriate potentials of the power source and the detector system. So one and the same instrument can function as a high performance electron spectrometer or a mass-spectrometer. Relative energy resolution better than 0.05% in the energy range of 20-3000 eV and mass resolution more than 5000 in the mass range 1-500 a.e.m. are easily realized for acceptance solid angle of the spectrometer equals to at least 30% out of hemisphere. The diameter of the analyzer is 200 mm, its length is 600 mm. An ultra high vacuum is ensured in the spectrometer at the level 10@super-11@ mbar by oil free pumping system with highly economical cryo condensation-absorption pump cooled by liquid helium. Almost all the spectrometer is made of nonmagnetic materials and first of all from titanium. The surfaces faced into vacuum have special plating with very low absorption-desorption capacity. So ultra high vacuum is achieved without baking out the spectrometer.

Surface Science Division Room 309 - Session SS2-MoA

Surface Chemistry on Model Catalysts

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

2:00pm SS2-MoA1 Adsorption and Mass Transfer Processes on Stepped Metal Surfaces, J.E. Reutt-Robey, University of Maryland, College Park INVITED

We present experiments that explore the role of crystallographic steps in regulating the propagation of surface chemical processes. Using scanning tunneling microscopy as the primary structural probe, we track the evolution of step structures on clean metal surfaces, under chemical adsorption, and under reaction conditions. Substantial step motions are observed during these processes on vicinal Ag(110) and Al(111) substrates, even at room temperature, revealing these steps as efficient adatom sources and sinks. The interplay between these step motions and molecular events is further investigated. Atomically resolved STM measurements of adlayer structures, in conjunction with infrared spectroscopic characterization of the adsorbates, reveal the lateral distribution of adsorbates with respect to the step edge, and their chemical speciation. For the oxidation and hydrogenation reactions that we have investigated on these metallic substrates, steps serve two principal roles: They act as efficient adatom sources for the formation of adsorbatesubstrate complexes. They introduce domain boundaries that facilitate mass flow in both adsorption and reaction.

2:40pm SS2-MoA3 Visualization of Heterogeneously Catalytic Processes,

M. Bode, M. Getzlaff, R. Wiesendanger, University of Hamburg, Germany The goal of this study is to a get deeper insight into the understanding of heterogeneous catalysis by combining the special merits of scanning microscopy/spectroscopy (STM/STS) and tunneling ultra-violett photoemission spectroscopy (UPS). We report on the electronic structure and the development of the adsorption process of hydrogen covered Gadolinium films being exposed to carbon monoxide. Clean Gd(0001) films were epitaxially grown on W(110). These films were exposed to hydrogen which leads to a local quenching of the d@sub z@@super 2@-like surface state being characteristic for the clean Gd(0001) surface. Due to the high spatial resolution of STM and its sensitivity to the local density of states at close to the Fermi-level, the adsorption process can be visualized and directly be correlated to the electronic properties measured by from UPS. The adsorption process at room temperature consists of five steps. At the very beginning the total amount of CO causes a removal of hydrogen from the surface. In the next two steps the rest of the adsorbed hydrogen atoms is removed and carbon and oxygen remains at the surface. In the intermediate regime CO dissociates and carbon and oxygen is adsorbed at or near the surface. This information is corroborated by investigations of clean Gd(0001) being exposed to CO and oxygen, respectively. The last step demonstrates the oxidation to Gd@sub 2@O@sub 3@ acting as catalyst for the transformation of CO to CO@sub 2@ which creates stable carbonate species at the surface.

3:00pm SS2-MoA4 Studies of Oxygen Species on a Heated Silver Membrane, *R.J. Beuhler*, *R.M. Rao*, *M.G. White*, Brookhaven National Laboratory

Oxidation reactions catalyzed by silver are a multi billion dollar enterprise worldwide. Such reactions have been investigated extensively by conventional surface science techniques, however, applications using stateor species-selective laser techniques are difficult to carry out for practical reasons specific to Ag surfaces. For example, the dissociative adsorption cross section of O@sub 2@ on Ag is on the order of 10@super -4@, which means that the high pressure of O@sub 2@ impinging on a silver surface makes state-selective detection of reaction products under collision free conditions nearly impossible. As a step towards understanding of the dynamics of oxidation reactions on Ag, we have undertaken a study of the oxygen species and reactions on the high vacuum side of a heated silver membrane. High surface coverages of O-atoms are produced by dissociative adsorption of molecular oxygen on the high-pressure side of a heated Ag-foil through which the O-atoms diffuse to the surface. Reactions at the high vacuum side can be studied under conditions that allow energy and spectroscopic analysis of the products. Preliminary results have been obtained for the recombination reaction O@sub (a)@ + O@sub (a)@ = O@sub 2(g)@ using (2+1) REMPI laser spectroscopy to probe state and energy distributions of the desorbing molecules. Initial measurements on the yield and temperature dependence of the oxidation reactions of CO and ethylene at intermediate pressures (10@super -5@-10@super -4@ Torr) have also been performed. These results and limitations in the foil experiment will be discussed.

3:20pm SS2-MoA5 Promotion through Gas Phase Induced Surface Segregation: Methanol Synthesis from CO, CO@sub 2@ and H@sub 2@ over Ni/Cu(100), *I. Chorkendorff, J. Nerlov,* Technical University of Denmark, Denmark

The synthesis rate of methanol formation over Cu(100) and Ni/Cu(100) from various gas mixtures of CO, CO@sub 2@ and H@sub 2@ have been studied. It was found that the presence of submonolayer quantities of Ni leads to a strong increase in the rate of methanol formation from mixtures containing all three components whereas Ni does not influence the rate from mixtures of CO@sub 2@/H@sub 2@ and CO/H@sub 2@, respectively. The influence of the partial pressures of CO and CO@sub 2@ on the rate indicates that the role of CO is strictly promoting. From temperature programmed desorption spectra it follows that the surface concentration of Ni depends strongly on the partial pressure of CO. In this way the increase in reactivity was interpreted as a CO-induced structural promotion introduced by the stronger bonding of CO to Ni as compared to Cu. It is suggested that this type of promotional behavior will be of general importance in existent catalysts and perhaps even more relevant in the development of new or improved bimetallic catalyst

3:40pm SS2-MoA6 Carbon-Sulfur Bond Activation in Adsorbed Methylthiolate on Ni(100) with Gas Phase Atomic Hydrogen at 120 K, A.T. Capitano, J.L. Gland, University of Michigan

Low temperature carbon-sulfur bond activation has been observed during reaction with both gas phase atomic and subsurface hydrogen. These results show for the first time that hydrogen can directly induce C-S bond activation in an adsorbed species. This new surface reaction provides exciting new opportunities for examining fundamental mechanisms of hydrodesulfurization on surfaces under UHV conditions. Gas phase atomic hydrogen breaks the C-S bond in methylthiolate resulting in the formation of methane even at 120 K on the Ni(100) surface. These results indicate that the energy for C-S bond activation is furnished by the atomic hydrogen. In contrast, coadsorbed hydrogen causes no C-S bond activation in methylthiolate. For a constant flux of gas phase atomic hydrogen, the rate of methane formation is first order in methylthiolate coverage indicating a direct Eley-Rideal reaction. Some adsorbed methyl and methylthiolate can remain on the surface after reaction, depending on atomic hydrogen exposure. During subsequent TPD experiments, addition of hydrogen to these intermediates results in three methane formation processes. Subsurface hydrogen breaks the C-S bond in methylthiolate at 200 K. Methyl hydrogenation by coadsorbed hydrogen occurs at 250 K. Or, thermal activation of the C-S bond by the surface is observed at 320 K. Taken together, these results demonstrate that energetic forms of hydrogen can break C-S bonds by direct addition to adsorbed thiolates on metal surfaces. The new mechanistic information generated using this approach may have substantial implication in fields ranging from catalytic hydrodesulfurization to stability of microelectronic devices.

4:00pm SS2-MoA7 Propylene Oxidation on the Pt (111) Surface over an Extended Range of Coverages, A.M. Gabelnick, J.T. Sipowska, J.L. Gland, University of Michigan

The reactions of propylene and oxygen coadsorbed on the Pt (111) surface have been characterized over an extended range of coverages using TPRS. Unexpected modification of the oxidation process is observed for high coadsorbed coverages. Initiation of propylene oxidation results in water formation at 200K which appears to involve abstraction of the acid methyl

hydrogens. This low temperature reaction becomes increasingly important for high coadsorbed coverages suggesting that direct interaction between propylene and coadsorbed atomic oxygen may play an important role for high coadsorbed coverages. For the highest coadsorbed coverages and excess propylene we were surprised to observe acetone and acetic acid partial oxidation products. Large coverages of coadsorbed propylene also cause the formation of a new low temperature molecular oxygen peak at 140 K. For both coadsorbed molecular and atomic oxygen, the primary products observed are water, carbon dioxide, and carbon monoxide. Following initial water formation near 200 K, the dominant water peak appears at 300 K over the entire range of coverages. Further increase in temperature results in carbon dioxide formation at 350K. Oxidation of propylidyne has a larger activation energy and occurs in one step at 370K. At higher temperatures further propylidyne oxidation and decomposition resembles that of propylene. Large coadsorbed coverages result in low temperature reaction and modified reaction selectivities.

4:20pm SS2-MoA8 The Catalytic Chemistry of Small Hydrocarbons on Palladium: Cyclization, and Hydrogenation, W.T. Tysoe, H. Molero, M. Kaltchev, University of Wisconsin, Milwaukee

The reaction pathways for acetylene trimerization catalyzed by palladium is investigated using a range of surface-sensitive techniques. It is found that benzene is formed from acetylene via the intervention of a metallocyclic C@sub4@subH@sub4@sub intermediate. This further reacts with a third acetylene to form benzene. However, the catalytic reaction proceeds in the presence of a carbonaceous layer. which consists of vinylidene species. At high pressures, acetylene is formed by reaction between acetylene adsorbed on the vinylidene-covered palladium surface and adsorbed vinylidene itself to form a C@sub4@subH@sub4@sub intermediate. It is shown that the hydrocarbon part of this layer can be removed by reaction in high pressures (several Torr) of hydrogen. The activation energy for this process on molybdenum surfaces is about 6 kcal/mol. Correspondingly, the rate of acetylene cyclotrimerization is found to be accelerated by the addition of hydrogen to the reaction mixture. The implication of these phenomena on alkene and alkyne hydrogenation reactions catalyzed by transition metals will also addressed and a model for hydrogenation reactions under high-pressure conditions is proposed that yield kinetic parameters in good agreement with those measured experimentally.

4:40pm SS2-MoA9 Dehydrogenation of Ethylbenzene Studied on Single Crystalline Iron Oxide Model Catalyst Films, *W. Weiss, D. Zscherpel, M. Ritter, R. Schloegl,* Fritz-Haber-Institut der MPG, Germany

We study the dehydrogenation of ethylbenzene (EB) to styrene over single crystalline FeO(111), Fe@sub3@O@sub4@(111) and @alpha@-Fe@sub2@O@sub3@(0001) model catalyst films grown onto Pt(111) substrates. The epitaxial film growth and their atomic surface structures were studied by STM and LEED. 1-2 ML thick FeO(111) films form oxygen terminated surfaces structures. The Fe@sub3@O@sub4@(111) surface exposes iron atoms in the topmost layer, as determined by a dynamical LEED intensity analysis reveiling a Pendry r-factor of 0.2. The @alpha@-Fe@sub2@O@sub3@(0001) surface exposes two different terminations, iron and oxygen, depending on the ambient oxygen partial pressure. With TDS and UPS a stong chemisorption of EB is observed on the iron terminated Fe@sub3@O@sub4@ and @alpha@-Fe@sub2@O@sub3@ films, wheras only physisorption is observed on the oxygen terminated FeO(111) film. Surface defects on the films were imaged by atomic resolution STM measurements, and the role of the oxide stoichiometry and surface defect concentrations for the model catalyst activities was studied by combining batch reactor experiments at total gas pressures of 1 mbar with pre- and post reaction surface analysis in UHV. No styrene is formed over Fe@sub3@O@sub4@ films. Fe@sub2@O@sub3@ films are catalytically active, and the styrene formation rate increases with increasing surface defect concentration on these films. This reveals Fe@sub2@O@sub3@ as the active oxide phase and atomic surface defects as catalytically active sites thereon. These defects can be steps, vacancies or adatoms. The formation of carbonaceous surface deposits that deactivate the model catalyst films after about 30 min reaction time was monitored with a PEEM microscope. A pattern formation is observed which indicates that the catalyst deactivation is a site selective process, which presumably starts at extended surface defects.

5:00pm SS2-MoA10 Chemisorption on and Modification of Molybdenum Carbide Surfaces, E. Zahidi, C. Morin, H. Oudghiri-Hassani, P.H. McBreen, Université Laval, Canada

Early transition metal carbides and nitrides are materials that combine a wealth of desired mechanical, electrical and chemical properties. Not the

least of which is their catalytic activity and their resistance to poisoning by sulfur. RAIRS, XPS and TPD data will be presented for the interaction of simple molecules with bulk molybdenum carbides. The samples studied were prepared using the method typically used to synthesize high surface area carbide catalysts. Data for isotope labelled NO, CO and ethylene reveal how the carbide carbon may be either removed, replaced or deposited. RAIRS results for the cyclic molecules, cyclopropane, cyclohexane and cyclobutanone provide insight on the ability of molybdenum carbide to activate alkane molecules. The study also reveals methods for cleaning and preparing molybdenum carbide surfaces.

Surface Science Division Room Hall A - Session SS-MoP

Surface Science Division Poster Session

SS-MoP2 Adsorption Dynamics of Monoenergetic Oxygen on Al(111), A.J. Komrowski, Y. Liu, A.C. Kummel, University of California, San Diego

The interaction of oxygen with aluminum has become a prominent system in the study of metal oxidation. An intriguing scanning tunneling microscope (STM) study observed that dissociated O atoms on Al(111) at low coverages are separated by >80 Å when the surface is dosed with thermal O@sub 2@ molecules@footnote 1@. More recently, a detailed energy-resolved sticking probability experiment using supersonic molecular beams reported a strong O@sub 2@ translational energy dependence of the sticking coefficient on Al(111), demonstrating an activated process with no indication of precursor-mediated adsorption@footnote 2@. Further, the sticking measurements suggested that high incident energy O@sub 2@ may access regions of the multipotential energy surface unavailable to thermal O@sub 2@ and therefore chemisorb by a different mechanism. We will present results of the adsorption of monoenergetic O@sub 2@ molecules on the Al(111) surface over a range of incident energies using supersonic molecular beam techniques and STM. We will show how the chemisorption site distribution changes with incident translational energy. @FootnoteText@ @footnote 1@ Brune, H. et. al. J. Chem. Phys. v99, 2128 (1993). @footnote 2@ Österlund, L. et. al. Phys. Rev. B v55, 15452 (1997).

SS-MoP3 Gas Phase Oxidation of Uranium-Niobium Alloys by O@sub 2@ and H@sub 2@O, W.L. Manner, M.T. Paffett, R.J. Hanrahan, Los Alamos National Laboratory

Secondary concentrations of certain transition metals (e.g. niobium, titanium, and chromium) alloyed with uranium are known to improve numerous physical and mechanical properties. One such property is the enhancement of corrosion resistance exhibited by the uranium alloy with six weight percent niobium (denoted as U6Nb) relative to the unalloyed uranium. Despite a tremendous knowledge base concerning the bulk metallurgical properties of this material, very little is known concerning the surface chemistry of U6Nb toward corrosion by O@sub 2@ or H@sub 2@O. Specifically, we seek to understand the role of niobium toward oxidation resistance of this alloy. We have initiated a series of studies using surface-sensitive techniques that include X-ray photoelectron spectroscopy (XPS), thermal desorption-mass spectroscopy (TDMS), and secondary-ion mass spectroscopy (SIMS) in order to better understand the chemistry between this alloy and O@sub 2@ or H@sub 2@O. XPS studies of the oxidation of clean U6Nb by O@sub 2@ at 300 K produces a thin oxide overlayer of stoichiometric UO@sub 2.0@ intermixed with Nb@sub 2@O@sub 5@. While the same stoichiometry is exhibited for uranium when the oxide is prepared at 500 K with O@sub 2@, niobium is much less oxidized showing a mixture of NbO and Nb. Depth profiling studies reveal that oxidation by O@sub 2@ is much greater than that exhibited by H@sub 2@O. Only the first layer or two is oxidized using H@sub 2@O as an oxidant at 300 K (the oxidation by O@sub 2@ is approximately an order of magnitude higher). Formation of a critical density of Nb@sub 2@O@sub 5@ is suggested to be responsible for the enhanced corrosion resistance by preventing diffusion of O@super -@ (O@super 2-@) or OH@super -@ into the oxide/metal interface region.

SS-MoP4 Vibrational Spectra and Structure of Hydrogen Adsorbed on Ni(111), *M. Gostein*, *Q.Y. Yang, S.T. Ceyer*, Massachusetts Institute of Technology

The structure and adsorption site of hydrogen on Ni(111) were investigated using high-resolution electron energy loss spectroscopy. At 0.5 ML coverage where the adsorbed hydrogen forms a (2x2)2H unit cell, the vibrational spectra show a pair of fundamentals at 733 and 791 cm@super -1@ and a pair at 1077 and 1109 cm@super -1@, as well as three overtones at 1260, 1396, and 2180 cm@super -1@. The pair of fundamentals at the lower frequency and the two lower frequency overtones are assigned to H-Ni modes parallel to the surface, while the higher frequency pair and highest frequency overtone are assigned to modes perpendicular to the surface. These assignments are based on the expected anharmonicity of the modes and on the angular distributions of the loss features. The features in each fundamental pair, which are closely-spaced in frequency, are resolved by exploiting their different electron impact energy dependence. Preliminary results indicate that the fundamentals are split into pairs because of different potential energy

surfaces at the hcp versus fcc three-fold hollow binding sites of hydrogen in a structure previously proposed from the observation of a (2x2)2H unit cell.

SS-MoP5 C-C Bond Breaking in Cyclopropane on the Ni(411) Surface, A.J. Guikema, J.L. Gland, University of Michigan

Thermal C-C bond breaking in cyclopropane has been observed on the stepped Ni(411) surface indicating that (111) step sites on a (100) terrace can break C-C bonds both in the presence and absence of coadsorbed hydrogen. Propane resulting from C-C bond activation in the presence of hydrogen is observed near 220 K. With increasing coverages of coadsorbed hydrogen and cyclopropane the yield of propane at 220 K increases. Above half saturation coverages of hydrogen and cyclopropane the yield of propane decreases with increasing coadsorbed coverages. The maximum propane yield corresponds to approximately 25% of cyclopropane saturation coverage. Experiments with coadsorbed deuterium clearly indicate that coadsorbed deuterium participates in propane formation. These observations support a Langmuir-Hinshelwood mechanism for propane formation associated with active sites in the step or near-step region. In the absence of coadsorbed hydrogen, cyclopropane dehydrogenation on the step sites dominates. A small amount of methane and ethane are observed around 120 K indicating multiple bond breaking during disproportionation. No deuterium incorporation is observed for methane and ethane in the presence of coadsorbed deuterium indicating hydrogen intermolecular transfer dominates during that disproportionation. These results indicate that the most reactive disproportionation sites responsible for multiple bond breaking react first and result in formation of about 5% of a monolayer of methane and ethane below 150 K.

SS-MoP6 LEED and STM Measurement of NO/Pt(111) at Low Temperature, *M. Matsumoto*, Institute of Molecular Science, Japan; *T. Yamada*, University of Tsukuba, and CREST, Japan; *N. Tatsumi*, *T. Itoyama*, University of Tokyo, Japan; *K. Miyake*, *K. Hata*, *H. Shigekawa*, University of Tsukuba, and CREST, Japan; *K. Fukutani*, *T. Okano*, University of Tokyo, Japan

The chemisorption of nitric oxide on Pt(111) at low temperature has been studied by electron energy loss spectroscopy (EELS), infrared absorption spectroscopy (IRAS) and low energy electron diffraction(LEED). The vibrational spectroscopy showed that N-O stretching frequency is 1490 cm@super-1@ at low coverage(0.5L).@footnote 1@ At high coverage, 2X2 LEED pattern was observed and its structure was attributed to the fcc hollow site by LEED dynamic theory.@footnote 2@ But there is no reasonable account for the difference of the N-O stretching frequency between low and high coverage regions and the structure is controversial yet. We measured the LEED I-V curves and STM images of NO/Pt(111) surface at several temperature and coverage conditions . At 175K, diffuse 2X2 LEED pattern could be seen even at low dosage(0.05L) and the I-V curve was the same as that at high dosage(1L). This indicates that (2X2)-NO islands grow with coverage increase but the local structure does not change at this temperature region. @FootnoteText@ @footnote 1@M.-B.Song, M.Suguri, K.Fukutani, F.Komori, and Y.Murata : Appl.Surf.Sci. 79/80 (1994) 25. @footnote 2@N.Materer, A.Barbieri, D.Gardin, J.D.Batteas, M.A.VanHove, and G.A.Somorjai: Surf.Sci. 303 (1994) 319.

SS-MoP7 Chemical Contrast by Funtionalized Tips and Movement of Highly Excited "Hot" Adsorbates: LT-STM Experiments with CO on Cu(111), L. Bartels, Paul-Drude-Institut, Germany; G. Meyer, K.-H. Rieder, Freie Universität Berlin, Germany

Chemical Contrast between species looking otherwise very similar in STM images (like CO and oxygen on Cu(111), both of which image as circular indentations) can be achieved by controlled in-situ functionalization of the STM tip apex with a single molecule: Electrons tunneling from a STM-tip to a CO molecule on Cu(111) at a sample bias exceeding 2.4V@footnote 1@ can lead to the excitation of the addressed molecule resulting in its hopping either to the tip apex or to a nearby site on the substrate with approx. 1:3 probability. Thus, tips bearing a CO molecule on their apex can be produced. As putting down the CO molecule from the tip apex is easily accomplished using inverted bias, this technique can be used for a whole range of new manipulation (transfer) experiments. Additionally, imaging with a CO tip the apparent shape of CO molecules is inverted to a protrusion, while the shape of oxygen (and several other molecules) remains unchanged, thus allowing for easy discrimination between them@footnote 2@. It could be shown that the transfer of the CO molecule is achieved by single electron attachment to the CO 2@pi@* level, leading after electronic deexcitation to highly vibrational excited CO molecules. Thus, events, in which the CO molecule does not jump onto the

STM tip but ends up on the substrate surface, can be used to study the diffusion of highly excited ("hot") adsorbates. We found, that their diffusion is limited in 2/3 of the cases to one adsite distance. In case of longer diffusion distance, scattered movement dominates. A Monte-Carlo simulation of the measured distribution of diffusion paths, however, allows to estimate that in 1/3 of the cases an adsite is transgressed, it is transgresses without scattering the movement of the "hot" molecule.@footnote 3@ @FootnoteText@ @footnote 1@ L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl, Phys. Rev. Lett. 80, 2004 (1998) @footnote 2@ L. Bartels, G. Meyer, K.-H. Rieder, Appl. Phys. Lett. 71, 213 (1997) @footnote 3@ L. Bartels, M. Wolf, G. Meyer, K.-H. Rieder, submitted to Chem. Phys. Lett. (1998)

SS-MoP8 Phenyl Containing Radicals on Cu[111], G.S. McCarty, Pennsylvania State University; M.K. Kamna, Intel; P.S. Weiss, Pennsylvania State University

Surface features such as step edges, impurities, and adsorbates cause modification of the local electronic properties of a surface. We are taking advantage of this phenomenon to produce active sites for surface reactions. We explore the atomic scale electronic effects on reactions of phenyl containing species to understand the catalytic properties of copper. Copper catalyzes reactions of phenyl containing species through the Ullmann coupling reaction. A low temperature UHV STM was used to study Cu[111] dosed with iodobenzene, di-iodobenzene, and biphenyl. The dissociation of iodobenzene into iodine and phenyl was observed. The reaction can be driven to produce biphenyl. We observed the intermediate complex pairs responsible for the exquisite specificity of this reaction.

SS-MoP9 Adsorbate Azimuthal Orientation from Reflectance Anisotropy Spectroscopy, B.G. Frederick, University of Maine, U.K.; J.R. Power, R.J. Cole, C.C. Perry, Q. Chen, S. Haq, T. Bertrams, University of Liverpool, United Kingdom; N.V. Richardson, University of St. Andrews, Scotland, U.K.; P. Weightman, University of Liverpool, United Kingdom

We have determined the azimuthal orientation of an adsorbate on a metal surface from an intramolecular-transition-derived feature in reflectance anisotropy spectroscopy (RAS). Adsorption of 9-anthracene carboxylic acid onto p(2x1)O/Cu(110) led to an ordered structure with a strong (2%), derivative-like feature at 4.5 eV. Fresnel theory predicts the measured intensity, functional behavior, and sense of the RAS signal for the molecule aligned along [110]. IR measurements confirm that the molecular plane is perpendicular to the surface and STM measurements support the azimuthal orientation.

SS-MoP10 Nickelocene Adsorption on Single Crystal Surfaces, D.L. Pugmire, M.A. Langell, University of Nebraska, Lincoln

The adsorption and decomposition of nickelocene on Ag(100), Ni(100), and NiO(100) has been studied by high resolution electron energy loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). Nickelocene adsorbs molecularly on less reactive surfaces such as Ag(100) at 140K, and desorbs molecularly at approximately 212K. In contrast to this, more reactive surfaces such as Ni(100) dissociatively adsorb nickelocene at 140K and desorb a variety of metallocene fragments. The orientation of molecularly adsorbed nickelocene as a function of surface coverage and the identification of decomposition products will be presented.

SS-MoP11 Analysis of Desorption Behavior of Sulfur from Pd by Temperature Programmed XPS, K. Dohmae, TOYOTA Central R&D Labs, Inc., Japan

Desorption of sulfur in oxygen gas from polycrystalline palladium plate was investigated by temperature programmed X-ray photoelectron spectroscopy (TP-XPS). The temperature programmed experiments in a range from room temperature to 773K were performed in an ambience of O@sub 2@ gas at 1x10@super -6@ Pa under a base pressure of 2x10@super -8@ Pa. As the initial coverage of sulfur on Pd increases in the range below 0.5 ML, the temperature that the quantity of sulfur on Pd decrease to half of its initial value becomes higher. Over 0.5 ML of the initial coverage of sulfur, the coverage of sulfur on Pd remained more than 0.5 ML at 773K, though the adsorbed sulfur decreases slightly as the temperature went up. The results were compared with calculations of Langmuir-Hinshelwood model with an assumption that the adsorbed sulfur react with the adsorbed oxygen on Pd and desorbe as sulfur dioxide molecule from Pd. The desorption behavior of sulfur in the experiments was well explained by the calculation model. The adsorption and desorption behavior of oxygen did not much agree with the calculations. Though the calculations suggest that the quantity of adsorbed oxygen on

Pd decreased when the sulfur desorbe from Pd, the quantity of adsorbed oxygen did not decrease at the time in the experiments. Furthermore, total quantity of adsorbed sulfur and oxygen on Pd became over 1 ML at higher initial coverage of sulfur than 0.5 ML. They suggest that adsorbed sulfur on Pd affects the ability of adsorption of oxygen onto Pd.

SS-MoP12 Atom Probe Analysis of Dissociation of CO and N@sub 2@ Gas on a W(110) Oriented Tip, T. Shimizu, A. Ohi, H. Tokumoto, JRCAT, Japan

An atom probe (AP) is an attractive mass spectrometer of single-ion sensitivity. But the application of the AP technique to gas-surface phenomena is less advanced than the corresponding study of metallurgical processes. Because the high electric field for desorption induces the dissociation of gases, which hinders us from investigating the gas-surface catalytic phenomena themselves. We measured the dissociative and nondissociative ions and estimated the temperature dependence of the dissociation probability. Here we introduced 10@super -7@ Torr x 10 s of CO and N@sub 2@ gas and investigated the dissociation on a W(110) oriented tip by using voltage-pulsed AP without a probe hole. The temperature of introduced gas was kept at RT and the tip temperature was changed from 50 K to RT. The count of gas ions increased with lowering temperature. Further AP at 50 K could detect two different states by the desorption field strength. A state desorbing at low field strength is related to the physisorption at low temperature, which was not observed at higher temperature. A state desorbing at high field strength is related to the trapping state following the dissociation. The dissociation probability decreased with lowering temperature. But below 100 K, the dissociation probability became almost constant (41% (CO), 45% (N@sub 2@)), which is caused by the field induced dissociation of chemisorbed gas. We postulated the ratio of field induced dissociation is almost constant up to RT and estimated the energy barrier from the trapped to the dissociation state as 30 meV (CO) and 22 meV (N@sub 2@).

SS-MoP13 The Kinetics of Methanol Synthesis by Hydrogenation of CO@sub 2@ Over a Zn-deposited Cu(111) Surface, I. Nakamura, H Nakano, University of Tsukuba, Japan; T. Fujitani, National Institute for Resources and Environment, Japan; T. Uchijima, J. Nakamura, University of Tsukuba, Japan

We have found that Zn deposited on a Cu(111) surface promotes methanol synthesis by the hydrogenation of CO@sub 2@. In this study, we examined the kinetics of methanol synthesis over the Zn-deposited Cu(111) surface by measuring the rates of elementary steps such as formation, decomposition and hydrogenation of formate species to clarify the promotional effect of Zn. The experiments were carried out in an infrared reflection absorption spectroscopy (IRAS) apparatus with a closed-reactor. The formate synthesis was performed using a gas mixture of CO@sub 2@/H@sub 2@=1 at a total pressure of 760 Torr and reaction temperatures of 323-353 K. The formate decomposition was carried out at a constant temperature of 373-403 K under vacuum. The initial formation rate of formate species on a clean Cu(111) surface was obtained by the initial slope of the formate coverage estimated from the peak intensity of the symmetric OCO stretching bands of formate species versus exposure to the CO@sub 2@/H@sub 2@ gas mixture. For example, at 353 K the initial formation rate was estimated to be 8.2 x 10@super -4@ formate molecules/site/sec, which agreed with that measured by the previous XPS experiment under the same reaction conditions. From the arrhenius plot of the initial formation rates, the activation energy for the formate synthesis on the clean Cu(111) surface was found to be 56.7 kJ/mol. The rates of formate decomposition was found to be first-order for the formate coverage and the activation energy was 100.7 kJ/mol. Furthermore, the equilibrium coverage of formate species was calculated by the kinetic data of formation and decomposition, which was in good agreement with experimentally measured coverage.

SS-MoP14 Characterization of CO Oxidation over Au/TiO@sub 2@(110) by Scanning Tunneling Microscopy, X. Lai, Texas A&M University, ••USA•; M. Valden, D.W. Goodman, Texas A&M University

Au clusters of 1-6 nm in diamteter were vapor deposited onto a TiO@sub 2@(110)-(1x1) single crystal under ultrahigh vacuum (UHV) condition, monitored by Auger Electron Spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). Fresh Au clusters on TiO@sub 2@(110) were transferred in situ into a high pressure cell, then exposed in separate experiments to 10 torr CO:O@sub 2@ (2:1), CO and O@sub 2@. STM observed the morphology change of Au clusters induced by reaction mixtures at 300 K, indicating the chemisorption of O@sub 2@ on Au clusters and TiO@sub 2@ substrate even at room temperature. The maximum activity for the oxidation of CO on

Au/TiO@sub 2@ is obtained with Au clusters less than 3.5 nm in diameter and 1.0 nm in height (~300 atoms/cluster) exhibiting an electronic structure characterized by a band gap in the range of 0.2 V - 0.6 V as measured by STM and scanning tunneling spectroscopy (STM/STS), which suggests that CO oxidation over Au/TiO@sub 2@ is structure sensitive.

SS-MoP15 Selective Chemical Reaction of HBO@sub 2@ Molecules on the Si(111)-7x 7 Surface Studied by Scanning Tunneling Microscopy, K. Miyake, K. Hata, University of Tsukuba, and CREST, Japan; R. Morita, M. Yamashita, Hokkaido University, and CREST, Japan; H. Shigekawa, University of Tsukuba, and CREST, Japan

The formation process of boron (B) induced @sr@3x@sr@3 structure by HBO@sub 2@ irradiation was studied by scanning tunneling microscopy (STM). In the chemical reaction of HBO@sub 2@ molecules with Si(111)-7x7 surface, change in the charge density on the adatoms of the 7x7 units during the process play an exceedingly important role, which was analyzed by the bias dependence of STM images, i.e., the adatoms with less charge density become darker in the filled state STM image.@footnote 1,2@ The molecules preferentially reacted with the center adatoms in the unfaulted half units first. This result indicates that HBO@sub 2@ molecules tend to react with the adatoms in less charge density. The center adatoms surrounding the reacted center adatoms became darker compared to those in the normal 7x7 units in the filled state STM images, which indicates some charge redistribution occurred by the reacted center adatoms. Such charge redistribution is supposed to increase the chemical reactivity of the modified center adatoms because HBO@sub 2@ molecules prefer to react with adatoms in less charge density. In fact, center adatoms in the faulted half units, which were adjacent to the firstly reacted center adatoms, reacted subsequently with the HBO@sub 2@ molecules. According to this process, chain structures were formed by the reacted center adatoms. With further irradiation, B atoms were found to form an 1-dimensional network with the same @sr@3x@sr@3 phase, resulting in the formation of an ordered @sr@3x@sr@3 surface. Small off-phase @sr@3x@sr@3 domains remained only in the areas occupied by Si atoms. The remaining Si adatoms were replaced by B atoms with further deposition of HBO@sub 2@ molecules, and a completely ordered @sr@3x@sr@3 surface was formed. @FootnoteText@ @footnote 1@K. Miyake et al., Appl. Phys. Lett. 66, 3468 (1995). @footnote 2@K. Miyake et al., Surf. Sci. 357-358, 464 (1996).

SS-MoP16 Electron-Stimulated Desorption of Na from SiO@sub 2@ Films, B.V. Yakshinskiy, T.E. Madey, Rutgers University

As part of a program to probe the mechanisms by which Na atoms are produced in tenuous planetary atmospheres (e.g., Mercury, The Moon, etc.) we have studied the electron-stimulated desorption (ESD) of sodium ions and neutral atoms from ultrathin amorphous stoichiometric silica films (~100Å thick) grown on a Re(0001) surface. The desorbing neutral Na flux is detected by using a novel surface ionization detector, which also permits measurements of energy distributions of neutral atoms by means of a time-of-flight method. Sodium ions, desorbing from the surface under electron bombardment, are analyzed by a guadrupole mass spectrometer. Approximately the same appearance threshold (~25eV) is found for both Na@super+@ and Na@super0@ desorption, corresponding to O2s core level excitation. A Coulomb pair O@super+@- Na@super+@ forms as a result of intraatomic Auger decay in the oxygen atom, leading to Na@super+@ desorption. The sodium neutral atom desorbs due to Pauli repulsion between Na and the neutralized oxygen ion. The total ESD cross section for Na is ~3x10@super-19@cm@super2@ at an electron energy of 300eV. The yield of Na atoms grows linearly with increasing sodium concentration in the monolayer, whereas the yield of Na@super+@ ions passes through a maximum at ~0.5ML. Velocity and energy distributions of desorbing sodium neutrals demonstrate evidence for the ESD of "hot" atoms, with most probable kinetic energies of ~0.5eV. The results are compared with recent photon stimulated data from oxides, and with observations of Na in planetary atmospheres.

SS-MoP17 Reaction of Atomic Hydrogen and Activated Methane with Si(111) as Precursor for Diamond Nucleation Studied with High Temperature STM, *F. Schaefer*, *H. Bethge*, *A. Bianco*, *U.K. Koehler*, Ruhr-Universitaet Bochum, Germany

An STM has been designed especially for studies under the extreme conditions of hot-filament-CVD diamond growth. As a first step the etchattack of atomic hydrogen and the reaction of activated methane with Si(111) has been investigated by in-situ, time resolved STM in the temperature range between 500°C and 800°C. Gas activation was done by the iongetter pump of the UHV system or by hot filaments. The etch-attack of atomic hydrogen on Si(111) starts at step edges and preferential etching along crystallographic directions is found. The etch-rate has been investigated in dependence on hydrogen flux and substrate temperature. Etching is found to be an activated process with an acitvation energy (E=0.8eV) close to the diffusion energy of Si-atoms on Si(111). Activated methane does not react with Si(111) at temperatures below 500°C. At higher temperatures a layer-by-layer consumption of substrate material and the formation of disordered clusters up to 60 Å height can be seen. Two different contributions to the consumption of Si are discussed: formation of SiC and etching due to the hydrogen supplied by the activated methane. The ratio of consumed substrate material to Si incorporated in the clusters is about 1:1, indicating a consumption of Si due to the formation of amorphous SiC clusters. A quantitative analysis of the nucleation behavior has been carried out. Although the clusters are amorphous their density evolution with growth-rate and temperature can be described according to classical rate equation theories. Different activation energies for nucleation for the two activation methods are found and can be assigned to different species responsible for the growth. As a further step to real hot-filament-CVD diamond growth conditions the reaction of activated methane diluted with hydrogen (1%CH@sub 4@/H@sub 2@) has been investigated for pressures up to 1 mbar.

SS-MoP18 Molecular State Identification of the Adsorbate Present on the Si(111)-(7x7) Surface Reacted with Oxygen. A Cs@super +@ Reactive Scattering Study, K.-Y. Kim, T.-H. Shin, H. Kang, Pohang University of Science and Technology, South Korea

While the interaction of molecular oxygen with a Si(111)-(7x7) surface has been one of the most actively studied surface reactions, the nature of the surface adsorbate, or the precursor state produced during initial oxidation of the Si surface, is still an open question. Interpretation of the experimental results on this system varies from molecular oxygen, either in the peroxide or superoxide form, to atomic oxygen bonded to various sites of the surface. To this surface we have applied a recently developed technique of Cs@super +@ reactive scattering.@footnote 1,2@ From this investigation we have found that oxygen exists on the surface only in the oxide form, and that the molecular oxygen bonded to a surface does not exist. The present finding allows explanation for many of the controversial issues regarding the initial oxidation mechanism of the Si surface. @FootnoteText@ @footnote 1@ M. C. Yang, C. H. Hwang, and H. Kang, J. Chem. Phys., 107, 2611 (1997). @footnote 2@ H. Kang, K. D. Kim, and K. Y. Kim, J. Am. Chem. Soc., 119, 12002 (1997).

SS-MoP19 Reactivity of Hydrogen with Fluorinated LaNi@sub5@, A.R. Layson, C.J. Jenks, Iowa State University

Much interest has been shown in hydrogen storage alloys as possible replacements for cadmium-based rechargeable batteries. Recent work under atmospheric conditions has shown that fluorination of the hydrogen storage material LaNi@sub 5@ substantially improves its ability to adsorb and subsequently desorb hydrogen. We report on studies aimed at understanding the effects of fluorination of LaNi@sub 5@. These are conducted in an ultrahigh vacuum environment using a single crystal of LaNi@sub 5@. Despite LaNi@sub 5@ being notoriously difficult to clean we have developed a method of cleaning which leaves less than 2% impurities at the surface. We follow surface compositional changes with Auger electron spectroscopy and hydrogen release with thermal desorption spectroscopy; these studies are the first such studies on LaNi@sub 5@. We compare results for D@sub 2@ adsorption/desorption on the clean surface to that of an oxidized surface and a surface that has been fluorinated after oxidation. We find that fluorination of the oxidized surface results in a low temperature channel for D@sub 2@ evolution not present on the surface that has only been oxidized. In addition the fluorinated surface enhances the amount of D@sub 2@ dissociation possible.

SS-MoP20 The Study on Activated Chemisorption on Surface of La Thin Film, S.M. Shao, W. Qian, J.P. Song, S.L. Li, Z.Q. Zhuo, G.K. Xi, Nankai University, China

The surface characteristics of evaporated rare-earth metal La thin film were studied by ex-situ and in-situ AES and molecular beam techniques. In case 1, the La thin film was prepared in the vacuum system, then taken out of the system exposing under atmospheric condition and finally put into the UHV chamber to be studied. In case 2, the La thin film was prepared and insitu studied in the UHV chamber. The surface composition by ex-situ AES studies corresponds to mainly La(OH)@sub 3@ which can be attributed to a surface modification by O@sub 2@ and water vapor from the ambient atmosphere. The in-situ AES studies reveals the surface composition of La.

The activated chemisorption of CH@sub 4@ on La thin film was studied in both cases using molecular beam technique.@footnote 1,2@ After surface cleaning treatment of samples, chemisorption probability was measured as a function of translational kinetic energy. The initial sticking probability was found to depend strongly on the incident kinetic energy E,scaling E@sub n@=Ecos@super 2@@theta@@sub i@. The initial sticking probability increases linearly with the translational kinetic energy of the incident molecular beam, but the threshold value and the activated energy were not changed when the surface temperature was increased from 500 K to 700 K.} @FootnoteText@ @Footnote 1@ G. Xi et al., J. Vac. Sci. Technol., A9(3),1688(1991) @Footnote 2@ S. Shao et. al., Chinese Vac.Sci. Technol.,12(2/3),263(1992)

SS-MoP21 Electron Induced Reactions of Ammonia and Nitric Oxide Adsorbed on Si(100), C. Bater, J.H. Craig, J.H. Campbell, University of Texas, El Paso

Electron beam enhanced nitridation of Si(100) by ammonia and nitric oxide was studied using XPS, TPD, ESD and HREELS. At low coverages, both ammonia and nitric oxide dissociatively adsorbed on Si(100) at 120 K while molecularly adsorbed ammonia and nitric oxide were detected by TPD and HREELS at higher exposures. Ammonia condenses on the surface at 110 K. During electron beam irradiation, adsorbed hydrogen atoms were effectively removed from the surface so that the site poisoning effect of adsorbed hydrogen was reduced. The electron stimulated dissociation of the adsorbed NH@sub x@ species enhanced the nitridation process. Enhanced nitride formation occurred when weakly physisorbed and condensed ammonia were present on Si(100) during electron beam irradiation at 110 K. H@super +@ ESD KEDs were used to deduce the surface reaction occurring during electron beam irradiation, and HREELS following electron beam irradiation was used to confirm and enhance the conclusions drawn from the ESD study. The formation of nitride and oxynitride was observed using the peak shifts of the N 1s and Si 2p X-ray photoelectron peaks. From the O@super +@ ESD KED signals, we distinguished O@super +@ originating from NO(a) and O(a), which we used to monitor the surface reaction occurring during electron beam irradiation. Changes in surface chemistry due to different levels of surface nitridation were also studied extensively. From the H@super +@ and O@super +@ ESD decay curves, the ESD cross sections for different surface conditions were obtained.

SS-MoP22 The Interactions of XeF@sub 2@ and F@sub 2@ with Si(100), *M.R. Tate*, *M.F. Bertino*, *S.C. Eckman*, *J.R. Holt*, *S.T. Ceyer*, Massachusetts Institute of Technology

The interactions of molecular fluorine (F@sub 2@) and xenon difluoride (XeF@sub 2@) with Si(100) are model semiconductor etching systems. Despite the similar energetics and chemical nature of these two etchant molecules. XeF@sub 2@ is a much better etchant of Si than F@sub 2@. This comparative study probes the dynamics of the interactions of these two gas-surface systems and seeks to understand the molecular origins of this disparity in reactivity. Using gas-surface scattering techniques, three reaction channels are identified for both etchants including a novel gassurface mechanism, atom abstraction, in which the surface abstracts a fluorine atom from the incident molecule and ejects the remaining particle into the gas phase. The fluorinated silicon surfaces resulting from exposure to F@sub 2@ and XeF@sub 2@ are nearly indistinguishable until the silicon dangling bonds are saturated - that is, only a small fraction of Si-Si lattice bonds are broken until the fluorination of the dangling bonds is complete. Beyond one monolayer of fluorine, however, only XeF@sub 2@ is able to attack the Si-Si lattice bonds, and SiF@sub 4@, an etch product, is observed to desorb. A detailed analysis of the energetics of the scattered products yields insight into the disparate reactivities of F@sub 2@ and XeF@sub 2@ with Si.

SS-MoP23 Atomic Hydrogen Reactions with Si(100) Surfaces, S.K. Jo, J.H. Kang, Kyung Won University, South Korea; B. Gong, D.E. Brown, J.M. White, J.G. Ekerdt, University of Texas, Austin

Chemical reactions of hydrogen atoms with Si(100)2x1 have been investigated over a wide range of substrate temperatures (T@sub s@ = 110 - 635 K) by using temperature-programmed desorption (TPD) and lowenergy electron diffraction (LEED) techniques. Thermal-energy hydrogen atoms generated from a hot tungsten filament were found to react with Si(100) surfaces over the entire temperature regime, resulting in silicon etching, amorphization, and hydrogen penetration into the crystalline substrate. Extensive silicon etching occurred at all substrate temperatures investigated. A large hydrogen uptake of more than 4 monolayers (1 ML = $6.8 \times 10@super 14@$ H atoms/cm@super 2@) and destruction of 2x1 LEED patterns upon H exposure at T@sub s@ = 415 K and 635 K indicate that the etching continues at substrate temperatures where tri- and di-hydride species are not stable. Moreover, in addition to the H@sub 2@ desorption peak at T@sub s@ = 780 K, a new desorption peak at T@sub s@ = 850 K grew in with increasing hydrogen exposure for T@sub s@ @>=@ 415 K. Deuterium exchange experiments suggest that the 850-K peak is due to H@sub 2@ evolution from the crystalline silicon bulk. At T@sub s@ @<=@ 300 K, amorphization as well as etching of Si(100) occurred readily. The observed opposing T@sub s@ effects on the rates of hydrogenation [Si(s) + xH(g) -> SiH@sub x@(a)] and etching [SiH@sub x@(a) + (4-x)H(g) -> SiH@sub 4@(g)] reactions have been elucidated. Terrace etching and step etching have been invoked to explain the observed etching at low (@<=@ 415 K) and high (@>=@ 635 K) substrate temperatures, respectively. Implications for damage-free, dry etching of crystalline silicon surfaces by thermal-energy hydrogen atom beams are discussed.

SS-MoP24 Hydrogen Diffusion and Desorption from the Si(100)-2x1

Surface, E.J. Buehler, J.J. Boland, University of North Carolina, Chapel Hill The mechanisms of hydrogen diffusion on the Si(100) surface and desorption from the 2x1 monohydride surface are being studied using high temperature scanning tunneling microscopy. Several desorption mechanisms have been proposed in the literature to explain the observed first-order kinetics, large energy barrier to adsorption, and similarity between hydrogen molecules desorbing from the decomposition of the mono- and dihydride phases. The possible role of surface defects has also been discussed. Using high temperature imaging conditions at which the tip does not induce desorption, we have observed pairs of vacant dangling bond (DB) sites on the surface following desorption. The spatial distribution of DB's on the surface shows no correlation with the locations of steps and defects. A particular surface feature has been identified, however, which may be a stable intermediate formed during the hydrogen desorption process. The structure and stability of this intermediate are discussed, as is the possible role of this feature in hydrogen desorption.

SS-MoP25 Adsorption and Reaction of H@sub 2@O on GaAs(100), X.M. Wei, Q.P. Liu, Y.T. Wong, H.H. Huang, G.Q. Xu, National University of Singapore, Singapore

The adsorption and reaction of H@sub 2@O on Ga-rich GaAs(100) surface have been investigated using TDS and HREELS. During the H@sub 2@O dosage at 100 K, we believe the adsorption proceeds as follows: initially, molecular H@sub 2@O is adsorbed, probably onto Ga. For a higher exposure at about 0.28 L, a 2-D H@sub 2@O monolayer is built. A subsequent dose increase leads to phase transition from a 2-D monolayer to a 3-D H@sub 2@O multilayer. During heating to 500 K, the desorption follows the reverse scheme. The H@sub 2@O multilayer is first desorbed at about 170 K, as detected by TDS, which makes the surface resemble that prepared by exposure at 0.28 L. On heating to a higher temperature, the remaining H@sub 2@O molecules are desorbed by 250 K. On the other hand, the first monolayer H@sub 2@O dissociates to give hydroxyls and hydrides. Hydroxyls are bound to Ga sites while hydrides tend to occupy As sites. More hydrides are formed from the further dissociation of Ga-bound hydroxyl. These hydrides adsorb onto Ga sites which are left vacant after the recombinative desorption of Ga-bound hydroxyl. At ~500 K, H@sub 2@ gas is also liberated.

SS-MoP26 Sites for Arsine Adsorption on GaAs(001)-(4x2), Q. Fu, L. Li, M.J. Begarney, University of California, Los Angeles; B.-K. Han, University of California, Los Angeles, US; R.F. Hicks, University of California, Los Angeles Arsine adsorption on GaAs(001)-c(8x2) at 298K-693K has been studied by internal-reflectance infrared spectroscopy and x-ray photoelectron spectroscopy. At 298K, AsH@sub 3@ dissociatively adsorbs on terminal Ga sites on step edges and transfers hydrogen to terminal As sites. No gallium hydride was observed during the dosing of AsH@sub 3@ at room temperature. c(8x2) reconstruction was well maintained when GaAs(001) surface was under extended exposure of AsH@sub 3@ between 298K and 573K. Upon dosing AsH@sub 3@ with a dosage of 9600L at 650K, surface reconstruction was converted from c(8x2) to a mixture of c(6x4) and (4x2)domains as illustrated by LEED. XPS also revealed a small increase of As/Ga area ratio after dosing at 650K. Further adsorption of arsine at 650K transformed surface to As rich (2x4) reconstruction. We found that it is necessary to have enough adsorption sites(terminal As) to accomodate hydrogen from arsine in order to incorporate As efficiently during epitaxy growth.

SS-MoP27 A New GaCl Molecular Beam Cell for Surface Dynamic Studies, M. Ohashi, M. Ozeki, JRCAT-ATP, Japan

An understanding of the surface reaction dynamics between source molecules and solid surface is required for the development of an advanced technological base for III-V semiconductor growth. Gallium chloride (GaCl) is one of the most important sources for III-V epitaxial growth. GaCl has an advantage of controlled chemical reaction, because it easily dissociates with H@sub 2@ on GaAs surface in spite of its strong bonding. However it is necessary to produce GaCl in-situ in the production cell, because GaCl preferably exists at higher temperature above 870 K. In order to study the surface reaction dynamics between GaCl molecule and GaAs surface, high purity GaCl molecular beam is necessary. We developed a new GaCl molecular beam cell, where high purity GaCl molecular beam was produced by direct reaction between Ga metal and Cl@sub 2@ gas. We optimized the gas flow rate of Cl@sub2@ gas for the production of GaCl molecular beam and the cell temperature from 920 to 1230 K. The byproduct of GaCl@sub 3@, which is stable and form large particles at low temperature, was observed under excess supply of Cl@sub 2@ gas. Under the optimized condition, which is the gas flow rate of Cl@sub 2@ at .25 ccm, the only GaCl was produced and no Cl@sub 2@ was observed. The Flux density at the sample surface, which is 40 cm away from the nozzle of this cell, was estimated 1.1x10@super 13@ molecules cm@super -2@ s@super -1@. The newly developed GaCl molecular beam cell would be useful for the study of the surface reaction dynamics between GaCl source and GaAs surface. This work is supported by New Energy and Industrial Technology Development Organization (NEDO).

SS-MoP29 Electronic Promotion of Graphite Oxidation in the Presence of Cs Trapped between the Basal Planes, J.R. Hahn, K.-Y. Kim, H. Kang, Pohang University of Science and Technology, South Korea

Oxidation of graphite is investigated by using scanning tunneling microscopy (STM) in the presence of Cs atom trapped between the carbon basal planes. Low energy (< 150 eV) bombardment of Cs@super +@ ions onto a graphite surface produces Cs interstitial defects (Cs-ID), where a Cs atom is trapped between the first and the second graphite layers. Oxygen adsorption onto the defected surface and the subsequent heating at 560 °C inside vacuum leads to formation of the pits with a depth of monolayer and a diameter of several nm. The pit formation starts from the Cs-ID's, indicating its promotion effect on the reaction with oxygen. The average diameter of the pit increases with the amount of supplied oxygen molecule. The experimental results suggest that a Cs-ID donates electron density to the neighboring carbon atoms, making the upper-layer carbons to be reactive with the oxygen molecule. The electron transfer from Cs-ID is the prevailing mechanism for the promoted oxidation, which is different from the direct mechanism proceeding via complex formation between the adsorbed Cs and the oxygen molecule, proposed from the previous studies of the oxidation of graphite covered with Cs.

SS-MoP30 The Penetration Range of Low Energy (50-500 eV) Ar@super +@ and Kr@super +@ lons Impinging onto a Graphite Surface Studied by the Oxidative Etching Method and STM, J.R. Hahn, H. Kang, Pohang University of Science and Technology, South Korea

Penetration of low energy (50-500 eV) Ar@super +@ or Kr@super +@ ions into a graphite surface results in the formation of surface vacancy defect (VD), formed by knock-out of carbon atoms, and interstitial defect (ID) where the incident atom is trapped between the carbon layers@footnote 1@, @footnote 2@, @footnote 3@. Thermal oxidation of the defected graphite surface etches away the carbon atoms surrounding a defect, leading to the formation of a pit of a large diameter and nearly circular shape. The etching process, when occurs from a defect of multi-layer depth, removes the carbons at and above the defect-containing layers simultaneously. Such phenomena enable us to locate the spatial position of the ion-generated defects by measuring the STM topography of the etched pits. The yield for production of multi-layer defect increases with ion collision energy. The depth distribution of the defect obtained by this agrees well the result of theoretical trajectory method calculation@footnote 1@. Lateral displacement of the incident ion inside the basal planes, upon penetration into the first carbon layer, is measured by STM from the distance between the VD and the ID formed in a pair. The average distance of the lateral travel varies with the incidence angle and the mass of ion. @FootnoteText@ @footnote 1@ W. Choi, C. Kim, and H. Kang, Surf. Sci., 281, 323 (1993). @footnote 2@ D. Marton, K. J. Boyd, T. Lytle, and J. W. Rabalais, Phys. Rev. B 48, 6757 (1993). @footnote 3@ J. R. Hahn, H. Kang, S. Song, and I. C. Jeon, Phys. Rev. B 53, R1725 (1996).

SS-MoP31 Scanning Tunneling Microscopy Studies of the Growth of Copper, Silver and Gold Overlayers on TiO@sub2@(110) in Ultrahigh Vacuum, D.A. Chen, K.F. McCarty, R.Q. Hwang, Sandia National Laboratories

The growth of metal films on oxide surfaces has become an area of increasing technological importance for applications involving electronic devices, sensors, catalysis and ceramic joining. We are investigating the growth of copper, silver and gold overlayers on a TiO@sub2@(110) surface in ultrahigh vacuum in order to develop a fundamental understanding of metal-oxide interactions. After annealing at 1000 K in vacuum, the titania substrate is reduced and becomes sufficiently conductive for scanning tunneling microscopy experiments. The resulting (1x1) TiO@sub2@ surface is characterized by low energy electron diffraction, Auger electron spectroscopy as well as STM. Previous work by Diebold and Madey et al. have shown that many transition metals, including copper, grow by threedimensional island formation on titania. Scanning tunneling microscopy is used to study the nucleation, growth and size distributions of the metal islands as a function of annealing temperature and coverage. Furthermore, by comparing the characteristics of copper, silver and gold overlayers deposited on titania, we will investigate how varying the interaction strength between oxygen at the surface and the admetal affects film growth and morphology. This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported in part by the USDOE-OBESDivision of Materials Sciences.

The Science of Micro-Electro-Mechanical Systems Topical Conference

Room 324/325 - Session MM+NS+SS-TuM

Micro-Science and Tribology of MEMS

Moderator: N.E. McGruer, Northeastern University

8:20am MM+NS+SS-TuM1 Making a Bridge to the Nanoworld, S.R. Manalis, S.C. Minne, J.D. Adams, K.B. Crozier, H.T. Soh, T.A. Sulchek, K. Wilder, Stanford University; G.G. Yaralioglu, A. Atalar, Bilkent University, Turkey; C.F. Quate, Stanford University INVITED

Our vision for micro-electro-mechanical-systems (MEMS) is to provide a window to the microscopic world. Scanning probe microscopes with automated cantilever arrays now image surface areas in excess of one square millimeter with atomic resolution. We will present new types of cantilevers and transducers that improve the speed, sensitivity, and simplicity of scanning probe microscopes. Samples are imaged at video rates with an integrated piezoelectric actuator that bends the cantilever over surface topography at high speeds. The deflection sensor, which consists of a micromachined light modulator, monitors cantilever bending with a sensitivity near one percent of an atomic diameter. We also present approaches for microfabricated biological sensors based on mechanical, electrical, and optical methods of transduction.

9:00am MM+NS+SS-TuM3 Nanotribology of Vapor-Phase Lubricants and Their Potential Applications to MEMS@footnote 1@, J. Krim, North Carolina State University INVITED

The concept of lubricating high temperature surfaces with organic vapors has existed for at least forty years, with substantial efforts beginning in the 1980's and continuing on to the present day. Vapor-phase lubricants are advantageous for use at high temperature, as well as in situations where the vapor can be used as a reservoir for replenishment of areas where the lubricant has been depleted in the course of device operation. While work in the area of vapor-phase lubrication has to date focussed on the lubrication of macroscopic systems, vapor lubrication mechanisms may ultimately prove to be of critical importance to sub-micron mechanical systems in cases where lubricant delivery and/or replenishment by other methods proves impractical. In order to examine the viability of vaporphase lubrication at length scales commensurate with submicron-scale machinery, we have constructed a Quartz Crystal Microbalance which operates in combination with a Scanning Probe Microscope so as to form a simple nanometer-scale mechanical system whose response to a number of vapor-phase lubricants can be monitored for nanotribological performance. Our observations of organic and water-vapor films recorded with this device will be discussed. @FootnoteText@ @footnote 1@Work supported by NSF and AFOSR

10:20am MM+NS+SS-TuM7 Vacuum Deposited Fluorinated Alkyl Siloxane Films for Adhesion Control in MEMS Devices, T.M. Mayer, M.P. de Boer, N.D. Shinn, P.J. Clews, T.A. Michalske, Sandia National Laboratories

Monolayer films of polymerized alkyl siloxanes have been employed for surface passivation and adhesion control in MEMS devices. However, reproducible film formation and properties have been difficult to achieve due to process sensitivity to substrate preparation conditions, presence of small quantities of adsorbed water, and the high aspect ratio structures typical of MEMS devices. In contrast to the normal solution coating process using alkyl trichlorosilane precursors, we have developed a vacuum-based film deposition process, using volatile fluorinated alkyl trichloro silane precursors. Reproducible substrate conditions are obtained by UV-ozone oxidation followed by sequential or simultaneous exposure to the chlorosilane precursor and water vapor. Efficient transport of reactants into high aspect ratio structures is accomplished by maintaining Knudsen flow conditions at low pressures. We measure kinetics of film growth by insitu ellipsometric and quartz-crystal microbalance techniques, and evaluate film composition and structure by XPS and IR spectroscopies. We also measure the work of adhesion and surface energy of coated cantilever beams under equilibrium fracture mechanics conditions. We compare results to uncoated structures, and to structures coated from solution with alkyl and fluoro-alkyl siloxane films. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the U. S. Dept. of Energy under contract DE-AC04-94AL85000.

11:00am MM+NS+SS-TuM9 Adhesion Hysteresis of Polysilicon Beams in Controlled Humidity Ambients, *M.P. de Boer, T.A. Michalske, M.R. Tabbara,* Sandia National Laboratories; *R. Maboudian,* University of California, Berkeley; *T.M. Mayer,* Sandia National Laboratories

Auto-adhesion, or spontaneous sticking between MEMS structures, is currently a major limitation in bringing this new class of engineering devices to the broader market. MEMS are particularly susceptible to autoadhesion because the structural members: 1) are constructed in close proximity to each other, 2) are highly compliant due to their extreme length to thickness aspect ratio and, 3) have large surface to volume ratios which increase the relative importance of adhesive surface forces. If the miniature structural members are brought together by surface (capillary, electrostatic) or inertial (shock, rapid air flow) forces, they may remain adhered after the external force is removed. If the structures remain adhered, bonding may increase over time, giving rise to the phenomena known as adhesion hysteresis. In this work we develop mechanical analysis for and report on measurements of adhesion hysteresis in surface micromachined polysilicon beams subject to dry and wet ambients. The electrostatically activated beams used in this study were tested directly after supercritical drying or after the application of hydrophobic molecular octadecyltrichlorosilane coatings such as (ODTS) or perfluorodecyltrichlorosilane (FDTS). Results indicate that both uncoated and coated beams show strong increase in adhesion after an incubation period in humid environments. This incubation time is shorter and occurrs at lower RH for uncoated beams than coated beams. For the case of uncoated beams, we are able to show that a model based on individual asperity contact forces can be used to predict the overall adhesion behavior in micromachined beams. The behavior of coated beams is compared with ellipsometric measurements indicating water adsorption on these nominaly hydrophobic surfaces after extended exposure at high RH conditions.

Surface Science Division Room 308 - Session SS1-TuM

Semiconductor Surface Structure

Moderator: L.J. Whitman, Naval Research Laboratory

8:20am SS1-TuM1 Effect of Tensile Strain on B-type Step Energy on Si(001)-(2x1) Surfaces Determined by Switch-Kink Counting, E. Heller, J.P. Pelz, Ohio State University; D.E. Jones, Y.H. Xie, P.J. Silverman, Company Several years ago Xie et al.@footnote 1@ suggested that applied strain could strongly influence the creation energy of so-called S@sub B@ steps on Si(001)-(2x1) surfaces, which could dramatically affect surface roughening during strain-layer growth. Swarzentruber et al.@footnote 2@ and then later Zandvliet et al.@footnote 3@ showed that step energies on unstrained Si(001)-(2x1) surfaces could be estimated by counting kinks (a kink being a small perpendicular jump in a surface step edge) on samples annealed at elevated temperatures. In order to directly test the proposal of Xie et al., we have used kink-counting in STM images of strained Si(001) surfaces to quantify the effect of strain of the S@sub B@ step energy. For this purpose, we have developed a new kink-counting method (called switch-kink counting), which is more accurate than previous methods when the azimuthal miscut angle changes across the surface. This can be problematic when there is macroscopic surface roughness, due to crosshatch or imperfect surface preparation. I will describe both the method used by Zandvliet et al. and our new method as well as why it is more accurate for non-constant azimuthal miscut angle. I will then give an analysis of data using both of these methods on a large data set we have collected from STM images. We find an energy for these kinks that is significantly higher than that found by Zandvliet et al. for unstrained silicon, and appears to increase with increasing tensile strain, although possibly not as fast as Xie et al. predict. @FootnoteText@ @footnote 1@Xie et al., Phys. Rev. Lett. 73, 3006 (1994). @footnote 2@B. S. Swartzentruber, Y.-W. Mo, R. Kariotis, M. G. Lagally, and M. B. Webb, Phys. Rev. Lett. 65, 1913 (1990). @footnote 3@H. J. W. Zandvliet, H. B. Elswijk, E. J. van Loenen, and D. Dijkkamp, Phys. Rev. B, 45, 5965 (1992).

8:40am SS1-TuM2 Geometry, Energetics, and Electronic Structure of the Dimer Reconstruction on the Carbon, Silicon and Germanium (100) Surfaces, *H.C. Kang, C. Yang*, National University of Singapore, Singapore The ground state geometry of dimers on the C(100), Si(100) and Ge(100) surfaces have been the subject of much study and controversy, particularly in the case of the silicon surface. There are at least two issues which have

not been resolved. First, theoretical calculations for Si(100) have favored both the buckled and unbuckled dimer geometry as the ground state. The most recent cluster calculations favor an unbuckled ground state while the most recent slab calculations favor a buckled ground state. Second, the driving force for dimer buckling is still not well understood. There have been suggestions that slab calculations predict the unbuckled ground state for Si(100) because of the inadequate treatment of electron correlation. We performed density functional cluster calculations for all three surfaces in an attempt to resolve these issues. We find that a number of previous cluster calculations have not dealt satisfactorily with the geometric constraints applied during geometry optimization. Our calculations resolve the differences in ground state geometry, dimer bond length and energetics between cluster and slab calculations. We also find that buckling is driven by a kinetic energy decrease, and that for silicon and germanium this dominates the increase in potential energy with buckling. For carbon the decrease in kinetic energy with buckling is less than the increase in potential energy and, hence, buckling is energetically unfavorable. We can trace this difference in behavior to the small core size of the carbon atom compared to silicon and germanium.

9:00am SS1-TuM3 An Atom-Resolved Dynamical Study of Hydrogen Diffusion on the Si(100) Surface, J.J. Boland, University of North Carolina, Chapel Hill INVITED

A detailed knowledge of the dynamical processes that occurs on surfaces has important implications for materials growth and processing. In the case of low temperature silcon growth hydrogen surface diffusion and desorption are key processes. However, little is known about the behavior of hydrogen on silicon surfaces at high temperatures. In this work we describe in detail the dynamical behavior of hydrogen on the Si(100) surface at temperatures between 600K and 750K. Our starting point for all these studies is a Si(100) surface that is completely terminated with hydrogen. At high temperatures H2 desorption occurs and the dangling bonds that result are initially localized on the same dimer unit. Even though this paired arrangement is stabilized by a weak pi interaction it soon dissociates due hopping of neighborng H atoms into these vacancy sites. Dangling bond motion is largely confined along the dimer row direction but steps act as turning points for this motion. We observe that dangling bonds recombine with surprising efficiency. A statistical analysis indicates that there are configurations other than the paired configuration that are stabilizing and that these promote dangling bond recombination. Missing dimer defects also act a recombination centers and effectively localize dangling bonds about them. Moreover, the residence times of dangling bonds at different surface locations provides a direct measure of the relative energies of the different sites on the Si(100)-2x1 surface.

9:40am SS1-TuM5 Ultra-high B and As Doping during Si(001) Gas-Source Molecular Beam Epitaxy: Growth Kinetics, Dopant-Incorporation, and Electrical Activation, G. Glass, H. Kim, A. Vailionis, J. Soares, P. Desjardins, J.E. Greene, University of Illinois, Urbana-Champaign

Si(001) layers doped with B or As were grown on Si(001)2x1 substrates by gas-source molecular-beam epitaxy using Si@sub 2@H@sub 6@, B@sub 2@H@sub 6@, and AsH@sub 3@ at temperatures T@sub s@ = 500-850 °C. Dopant concentrations ranged from 1x10@super 16@ to 1.2x10@super 22@ cm@super -3@ for B and 1x10@super 16@ to 1x10@super 18@ cm@super -3@ for As. B incorporation was linear with incident B@sub 2@H@sub 6@/Si@sub 2@H@sub 6@ flux ratio for B concentrations C@sub B@ @<=@ 2.5x10@super 20@ cm@super -3@, and increased with higher flux ratios. As incorporation was linear to 3x10@super 17@ cm@super -3@, and subsequently was sub-linear. At T@sub s@ = 550 and 600 °C, B was incorporated into substitutional electrically-active sites for C@sub B@ up to 2.5x10@super 20@ cm@super -3@. At higher B concentrations, there is a large and discontinuous decrease in the electrically active fraction of B, although the total activated B concentration continues to increase. Hall-effect measurements show the As to be fully electrically active for all films in the study. All films were fully strained. TEM investigations revealed that B doped films grown at T@sub s@ @<=@ 600 °C, and all As doped films were highly perfect with no indication of precipitates or dislocations. Deuterium temperature-programmed desorption measurements as a function of increasing C@sub B@ and C@sub As@ show strong surface segregation. The B deactivation behavior can be explained on the basis of a model which accounts for strong B segregation to the second-layer, and the surface formation and subsequent incorporation of electrically inactive B-dimers at higher C@sub B@ values. In contrast, As acts to passivate the surface, resulting in arrested growth as the As coverage approaches 1 ML. The combination of HR-XRD, SIMS and

Hall-effect measurements, show that the Si-B bond length due to B-dimers is 1.99 Å, compared to 2.04 Å for substitutional B atoms.

10:00am SS1-TuM6 Scanning Tunneling Microscopy of B/Si(001), J.F. Nielsen, H.-J. Im, J.P. Pelz, Ohio State University; M. Krueger, B. Borovsky, E. Ganz, University of Minnesota

Previous work has shown that annealing of heavily B-doped Si(001)-(2x1) surfaces produces spontaneous formations of S@sub A@ steps into periodic "striped" patterns,@footnote 1@ consistent with stress relaxation effects considered by Marchenko@footnote 2@ and Alerhand et al.@footnote 3@ However, the exact role of boron in the step formation, as well as the cause for the observed increase in step density with decreasing annealing temperature, are still under investigation. Using detailed bias-dependent STM measurements of various B-induced surface structures, we have (1) determined that the density of B-induced surface structures does NOT change significantly with annealing temperature, leaving unresolved the strong temperature dependence of the step formation, (2) observed direct evidence of boron accumulation at step edges, providing a possible mechanism for boron-induced lowering of S@sub A@-step creation energy, and (3) identified characteristic structural and electronic features of a number of distinct B-induced structures, which indicate a need to reclassify previously reported B-related structures.@footnote 4@ We are currently introducing surface B in a controlled way by decomposing B@sub 2@H@sub 6@ on lightly P-doped Si(001). Initial observations indicate that deposition parameters determine whether B induces the formation of reconstructed islands@footnote 5@ or whether B forms isolated structures equivalent to those observed on bulkdoped samples. Employed as a semiconductor processing step, this process could allow for the controlled production of periodic arrays of nanoscale step structures. @FootnoteText@ @footnote 1@D.E. Jones et al., Phys. Rev. Lett. 77, 330 (1996) @footnote 2@O.L. Alerhand et al, Phys. Rev. Lett. 61, 1973 (1988) @footnote 3@V.I. Marchenko, JETP Lett. 33, 381 (1981) @footnote 4@Z. Zhang et al, J. Vac. Sci. Technol. 14, 2684 (1996) @footnote 5@Y. Wang et al., Phys. Rev. Lett. 74, 403 (1995)

10:20am SS1-TuM7 Halogens Adsorbed on the Ga-rich c(8x2) GaAs(001) Surface: Adsorbtion Sites, Mobility and Overlayer Structure, J.G. McLean, P. Kruse, A.C. Kummel, University of California, San Diego

Chlorine is commonly used to etch the As-rich c(2x8) Gallium Arsenide (001) surface. However, on the well-ordered Ga-rich c(8x2) reconstruction of GaAs(001) at 300 K, Cl@sub 2@ has been found to form an overlayer which passivates the surface against attack by atmospheric gases. Although the clean surface always reconstructs, the Cl@sub 2@ passivated surface yields a sharp (1x1) LEED pattern. A more complete understanding of the Cl chemisorption is desirable both for better control of the etching process and to understand the properties of the passivating overlayer. We have used scanning tunneling microscopy to study the adsorption sites of Cl@sub 2@ on the Ga-rich c(8x2) surface of GaAs(001). The Cl bonds exclusively to the Ga atoms, consistent with expectations based on molecular bonding theory. At low coverage the Cl is mobile along the Ga rows, which is surprising given the strength of the Ga-Cl bond. We have also investigated the overlayer at high coverages, for which STM revealed both c(2x6) and (1x1) structures. In both cases, the structures are inconsistent with the Ga/As ratio of the initial clean c(8x2) reconstruction. This shows that long-range rearrangement of surface atoms has taken place, allowing a bulk terminated surface to form in the case of the (1x1) structure. Tunneling spectroscopy will be used to determine whether this surface rearrangement results in a modified electronic structure, allowing electronic as well as chemical passivation.

10:40am SS1-TuM8 The Role of Dimer-Stacking-Fault Structures in Si(111)

Etching, *M. Fouchier*, *J.J. Boland*, University of North Carolina, Chapel Hill Etching of semiconductors continues to be important from both a fundamental and applied prospective. In this work, we investigated the etching of Si(111) by halogens using Scanning Tunneling Microscopy. It is known that Si(111) etching occurs preferably at steps but also within terraces. We showed that Dimer-Stacking-fault (DS) structures are formed during etching by Bromine at 900K. These structures result from the coalescence of vacancies on the surface.@footnote 1@ These vacancies are produced either thermally or by isolate etching events. These results suggest that DS structures are intermediates in the terrace etching process and that the dimer-rows bounding these structures serve as etch sites. @FootnoteText@ @footnote 1@Marc Fouchier and John J. Boland, Phys. Rev. B 57, 8997 (1998).

11:00am SS1-TuM9 The Structure of Ge Surfaces from (001) to (111), A. Laracuente, S.C. Erwin, L.J. Whitman, Naval Research Laboratory We are studying the structure of Ge surfaces oriented between (001) and (111) using STM and first-principles electronic structure calculations (LDA). Similar to Si,@footnote 1@ Ge surfaces oriented within ~12° of (001) and (111) consist of low-index terraces and steps. Between this range, it appears that only (113) and ~(559) are planar surfaces on Ge, in contrast to Si where (114), (113), and (5 5 12) are planar. Because (113) is the only planar high-index surface common to Si and Ge in this range, its structure is of particular interest. At room temperature, Si(113) has a (3x2) reconstruction that incorporates a highly unusual six-fold-coordinated surface interstitial. The "self-interstitials" occur within every other tetramer (a dimer plus nonrebonded double-layer step), making the otherwise (3x1) surface (3x2). At room temperature the Ge(113) surface consists of an equilibrium mixture of (3x1) domains (~80%) and Si-like (3x2) domains (~20%). In contrast to previously reports, we find that the (3x1) domains have the same structure as Si(113)-(3x2), with the exception that every tetramer includes an interstitial. Extensive LDA calculations confirm that the "self-interstitials" dramatically lower the surface energy on Ge(113). Whereas on Si the (3x1) structure is 2 meV/ Å@super 2@ higher in surface energy than the (3x2), it is approximately degenerate on Ge (in agreement with experiment). Furthermore, calculations of the stability of interstitials at various sub-surface sites indicate that they do not migrate to the surface from the bulk, as previously suggested, but rather originate from surface adatoms (perhaps in a lattice gas). @FootnoteText@ @footnote 1@Baski, Erwin, and Whitman, Surf. Sci. 392, 69 (1997).

11:20am **SS1-TuM10 Structure of Arsenic-Passivated Germanium (100)**, *S. Gan, L. Li, M.J. Begarney, D. Law, C. Li,* University of California, Los Angeles; *B.-K. Han,* University of California, Los Angeles, US; *R.F. Hicks,* University of California, Los Angeles

Arsenic passivation is an important first step in the heteroepitaxy of GaAs on Ge (100). Using scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy and low energy electron diffraction, we have identified the atomic structure of arsenic-terminated Ge (100) surfaces. The germanium substrates were exposed to arsenic in two different ways: (1) by dosing with 500 L arsine in ultrahigh vacuum, and (2) by exposure to 2.0 Torr tertiarybutylarsine and 97.0 Torr hydrogen at 650°C in a CVD reactor. During AsH3 dosing at 25 to 300°C, the As coverage is approximately constant at 0.3 ML. Upon increasing the dosing temperature further, the coverage attains a maximum of 1.0 ML at 425°C, then gradually declines to zero at 600°C. Scanning tunneling micrographs obtained at 1 ML coverage show that the surface has been transformed into a series of flat islands, one atomic layer in height, that are terminated with arsenic dimers. Also, B-type steps are preferred over A-type steps, causing the islands to exhibit narrow rectangular shapes with long straight edges. By contrast, when the surface is treated with tertiarybutylarsine in the CVD reactor, the initial coverage of arsenic is 2.0 ML. Upon annealing these samples in vacuum, the coverage remains constant up to 300°C, then slowly drops to zero as the temperature is raised to 600°C. At more than 1.5 ML of arsenic, the As:Ge (100) surface exhibits an unusual "waffle" pattern, with ridges about 20-50 Å in width crisscrossing the surface in the [110] and [-110] directions. Heating to 425°C, decreases the coverage to 1.0 ML. In this case, the surface is terminated with a series of square, flat islands that are separated by straight step edges one to three atomic layers in height. These surfaces are completely terminated with As dimers. Further heating to desorb the arsenic, causes the Ge (100) surface to transform back into a series of large terraces with their edges composed of equal amounts of A and B steps. The unusual morphology observed after exposure to tertiarybutylarsine in the CVD reactor is attributed to hydrogen-atom etching of the germanium surface.

11:40am SS1-TuM11 STM of Tl Overlayers on Si(111): Structures of a "New" Group III Element, L. Vitali, M.G. Ramsey, F.P. Netzer, Karl-Franzens-Universität Graz, Austria

Thallium is an unusual group III element because it can adopt a monovalent state in addition to the more conventional trivalent state of the other elements of this group. In this study we investigate for the first time the growth and the structure of Tl overlayers on Si(111)7x7 surfaces from room temperature (RT) to 500°C, using STM and STS in conjunction with LEED and AES. At low coverages Tl adatoms adsorb preferentially on the faulted half of the unit cell, covering the surface with an array of triangular adsorbate islands maintaining the (7x7) periodicity. The Tl adatoms are highly mobile at RT as recognised in consecutive STM images. On completion of the first monolayer a low corrugation surface develops at RT, but at 350°C a well ordered (1x1) structure is observed in LEED and with

atomic resolution in the STM. This layer shows a metallic state with a prominent feature at -0.5 eV in STS. Depending on the substrate temperature remarkable contrast phenomena are seen in the STM for the first and the second monolayer of Tl. From RT to 200°C the Si(7x7) substrate arrangement determines the structure of the overlayer, with a network of contrast lines reflecting, presumably, the (electronic?) influence of the (7x7) substrate mesh. Atomic resolution along the lines displays a different distribution of occupied and unoccupied states. From 300-450°C a (6x6) array of broad second layer maxima (~17Å diameter, corrugation ~1Å) on a (1x1) monolayer signals a structural transformation of the overlayer. Tl overlayers on Si(111) thus display a very different structural behaviour to the other group III elements and possible reasons are discussed in terms of valency, bonding geometry and size effects.

Surface Science Division Room 309 - Session SS2-TuM

Noble Metal Catalysis

Moderator: G.B. Fisher, General Motors R & D Center

8:20am SS2-TuM1 Microfabrication and Evaluation of Supported Model Catalysts, B. Kasemo, Chalmers University of Technology, Sweden INVITED Supported catalyst particles and single crystals exhibit differences in catalytic properties which are referred to as the structure gap in catalysis. Experimentally this is addressed by systematic studies of the influence of e.g. particle size and structure, and type of support on the catalytic properties. Modern microfabrication adds new opportunities, complementing the existing ones, to systematically manufacture and evaluate supported model catalysts. In this presentation the advantages and limitations of different microfabrication techniques are briefly reviewed. The use of electron beam lithography (EBL) applied to model catalyst production is described in detail. Specific examples are given of EBL manufactured noble metal catalysts on different supports. Evaluation of these catalysts in catalytic reactions involve (i) studies of morphological changes of the native structures caused by the reaction conditions and (ii) evaluation of the kinetics.

9:00am SS2-TuM3 Chemisorption and Kinetic Studies of Model Low-Temperature CO Oxidation Catalysts: Au/TiO@sub 2@(110), V.A. Bondzie, S.C. Parker, C.T. Campbell, University of Washington

As a room-temperature CO oxidation catalyst, Au/TiO@sub 2@ shows exciting potential in automotive applications. Oxygen does not dissociatively adsorb on bulk Au, although one of the elementary steps in the proposed mechanism for this reaction is the activation of O@sub 2@ at the Au/TiO@sub 2@ interface. No such adsorption sites that react with molecular O@sub 2@ have so far been identified spectroscopically. In order to understand this reaction at the molecular level, O@sub 2@ chemisorption and CO titration over O-covered 2D and 3D Au islands, grown on TiO@sub 2@(110) have been studied. Techniques used included TPD, LEED, XPS and LEIS. A hot filament was used to deposit O adatoms. Subsequent TPD shows O@sub 2@ desorption with a peak maximum shifting from ~650 K (for 2-atom thick Au islands) to ~550 K (for bulk Au). No O@sub 2@ desorption is seen from 2D (i.e., 1-atom thick) Au islands below 770 K. This indicates that as the thickness of the Au islands decreases, the O adatoms bind increasingly strongly to the Au. The kinetics of the titration of oxygen adatoms with CO (CO@sub g@+O@sub a@ ? CO@sub 2,g@) were also measured from O-covered Au particles on TiO@sub 2@(110). The reaction rate on 2D Au islands is slower than on the 3D Au islands, even though CO bonds slightly more strongly on the former. This reflects a higher activation barrier on the 2D Au islands than on the 3D Au islands for the Langmuir-Hinshelwood step (i.e., CO@sub a@+O@sub a@ ? CO@sub 2,g@). This is due to the stronger O-Au chemisorption bond strength on 2D Au islands than on 3D islands. This stronger bond should promote dissociative O@sub 2@ adsorption, which we postulate as the rate-determining step in catalysis.

9:20am SS2-TuM4 Monte Carlo Simulations of Catalytic Reactions on Nanometer-sized Particles, *H. Persson*, *P. Thormählen*, *V.P. Zhdanov*, *B. Kasemo*, Chalmers University of Technology, Sweden

Using a Monte Carlo algorithm, we have investigated the 2A+B@sub 2@@>=@ 2AB reaction both on a nanometer-sized catalyst particle, with interacting facets, and also on an infinite surface, which represents a macroscopic catalyst surface. The reaction mimics practically important catalytic processes such as CO oxidation on Pt, Rh or Pd. In the present work we have studied the role of diffusion between different facets,

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different reaction to diffusion rates and the effect of desorption in these systems. Our results indicate that the kinetics on nanometer-sized particles can be remarkably different compared to the kinetics on a macroscopic catalyst surface.

9:40am SS2-TuM5 Ab Initio Density-Functional Theory Study of CO Oxidation Over Ru(0001), C. Stampfl, M. Scheffler, Fritz-Haber-Institut der MPG, Germany

Under "Realistic conditions" the rate of oxidizing catalytic reactions is very much higher at ruthenium than at any other transition metal, and the dependence on the oxygen partial pressure is qualitatively different.@footnote 1@ Yet, under ultra high vacuum (UHV) conditions Ru is by far the worst catalyst, and the question was frequently raised concerning the relevance of Surface Science studies for real catalysis. Using density-functional theory we show in this contribution that the above noted "pressure gap" phenomenon is only apparent. Thus, if understood, it can be circumvented. In particular, we investigate both a scattering reaction of CO at the O-covered surface [Eley-Rideal mechanism (E-R)]@footnote 2@ and the Langmuir-Hinshelwood (L-H) reaction. In each case the transition state corresponds to a bent CO@sub 2@-complex with an associated bond angle of 131° (E-R) and 125° (L-H). The metastability of a carbonate species is also identified which could act as an intermediory species for CO@sub 2@ production. We attribute the enhanced CO@sub 2@ formation rate at elevated gas pressures (and high coverage) to be due to the notably weaker O-Ru bond strength compared to that at lower Ocoverages as are present under UHV conditions. In this respect we also report results investigating the affect of subsurface oxygen on the energetics of the reaction. Subsurface O has been proposed to be responsible for the very recently reported CO@sub 2@ reaction rates@footnote 3@ that are two orders of magnitude higher than those measured in Ref. 1. @FootnoteText@ @footnote 1@C. H. F. Peden and D. W. Goodman, J. Phys. Chem. 90, 1360 (1986). @footnote 2@C. Stampfl and M. Scheffler, Phys. Rev. Lett. 78, 1500 (1997). @footnote 3@A. Böttcher, H. Niehus, S. Schwegmann, H. Over, and G. Ertl, J. Phys. Chem. 101, 11185 (1997).

10:00am SS2-TuM6 The Effect of Strain on the Reactivity of Metal Surfaces, *M. Mavrikakis*, Technical University of Denmark, DENMARK; *B. Hammer*, Aalborg University, Denmark; *J.K. Norskov*, Technical University of Denmark, DENMARK

Self-consistent density functional calculations for the adsorption of O and CO, and the barrier to CO dissociation on strained and unstrained Ru(0001) surfaces are used to illustrate the general phenomenon of strained metal surfaces having chemical properties drastically different from those of unstrained surfaces. Surface reactivity increases with lattice expansion, following a concurrent upshift of the metal d-states. Consequences for the catalytic activity of thin metal overlayers are discussed.

10:20am SS2-TuM7 In-situ Investigation of the Catalytic Reaction 2 H@sub 2@ + O @sub 2@ @>=@ 2 H@sub 2@O on Pt(111) with Second Harmonic Generation, *F. Gudmundson*, Chalmers University of Technology, Sweden; *F. Eisert*, University of Heidelberg, Germany; *A. Rosén*, Chalmers University of Technology, Sweden

Most knowledge about catalytic reactions is obtained by the use of surface analytical tools, which are restricted to ultrahigh vacuum conditions. The extrapolation to real reaction conditions at ambient pressure however is connected with a relatively high uncertainty. Nonlinear optical techniques like Second Harmonic Generation (SHG) combine the capability of in-situ investigations with an inherent surface sensitivity. We present in-situ SHG investigations of the catalytic reaction 2 H@sub 2@ + O @sub 2@ @>=@ 2 H@sub 2@ O on Pt(111) in the pressure range between 200 mtorr and 10 torr at a catalyst temperature of T=700 K. With SHG the oxygen coverage is determined as function of the hydrogen partial pressure. In the pressure range investigated, the gas flow changes from molecular flow to laminar flow. This transition has a profound influence on the experimental observed oxygen coverages. However, using a kinetic reaction model of the hydrogen oxidation developed by Hellsing, Kasemo and Zhdanov the experimental results can readily be interpreted, if the transition of the gas flow conditions from molecular to laminar flow is taken into account.

10:40am **SS2-TuM8 Suppression of Water Formation by Adsorbed Gold on Pt(335)**, *D.C. Skelton*, Michigan State University/General Motors R & D Center; *R.G. Tobin*, Tufts University; *D.K. Lambert, C.L. DiMaggio, G.B. Fisher*, General Motors R & D Center

Platinum, an excellent catalyst for water formation, has its catalytic activity significantly reduced by a submonolayer coverage of gold. As part of a

larger study on surface reactions on modified electrodes for chemical gas sensors, temperature programmed reaction on a stepped platinum surface, Pt(335), at three gold coverages was studied. Reactive surfaces were prepared in UHV with systematic doses of hydrogen and oxygen to obtain submonolayer coverages of adsorbed atomic hydrogen and oxygen. Gold coverage was measured by comparing the relative intensities of the 64 and 69 eV Auger peaks of platinum and gold, respectively. At low coverages gold adsorbs into the step sites on Pt(335) [4(111) × (100) in terrace step notation] and fills in to form islands which merge into a semi-continuous surface with openings to the platinum approximately 50 to 100 @Ao@ in diameter at 0.7 monolayers. This presumably leaves 30% of the surface platinum atoms available for chemisorption. However, hydrogen and oxygen in adsorption are reduced to 15% and 9% of their values on bare Pt(335), respectively, and bonding in step sites is reduced to 3% and 6%, respectively. Neither molecule bonds to the gold covered areas. The temperature-programmed reaction data for both Pt(335) and 0.7Au/Pt(335) show that this reduction in reactant coverage accounts for only part of the reduction in water production. Blockage of step sites by gold eliminates a major low-temperature reaction pathway seen on Pt(335) and a slight reduction in the desorption temperature of terrace hydrogen shifts hydrogen desorption into the same temperature range as water formation. At intermediate coverages (40% of the maximum hydrogen coverage and 50% of the maximum oxygen coverage) on each surface, the resulting competition between desorption and reaction lowers the reaction probability per hydrogen atom from 0.6 on Pt(335) to 0.2 on 0.7Au/Pt(335).

11:00am SS2-TuM9 Isothermal Kinetic Study of the Catalytic Reduction of Nitric Oxide over Rh(111) Surfaces, G. Chinnakonda, F. Zaera, University of California, Riverside

The kinetics of the thermal decomposition of NO and of its catalytic reduction to molecular nitrogen on Rh(111) surfaces was probed by isothermal measurements using an extension of the so-called King and Wells collimated beam method. Initial NO TPD studies corroborated previously reported results, including the development of two distinct molecular nitrogen desorption peaks at 460 and above 500 K, the first of which displays apparent first-order kinetics. In the isothermal experiments the rate of molecular nitrogen production was found to be significant above 450 K, and to be controlled by the recombination of atomic nitrogen below 600 K. In addition, the adsorption of NO was found to not be affected significantly by the presence of coadsorbed nitrogen and/or oxygen atoms at any temperature below 900 K. There is an induction period during which the surface concentrations of nitrogen and oxygen atoms build up before the recombination reaction starts. When performing the experiments with NO alone oxygen deposition on the surface eventually poisons the system and stops the reaction, but when using CO + NO mixed beams that oxygen is removed and a steady-state catalytic regime is reached. In any case, the experimental data could not be reproduced in a satisfactory manner by any empirical rate law unless the order in nitrogen coverage was set to less than unity, an observation that is interpreted here as being the result of the slow diffusion of nitrogen atoms across the surface prior to their recombination. A strong additional effect due to lateral repulsions between nitrogen and/or oxygen atoms was also observed.

11:20am SS2-TuM10 Surface Species and Desorption Products from NO Exposure on Clean and (Rh,Pt) Loaded Surfaces of Highly Oriented CeO@sub 2@ Characterized by SXPS and TPD, S.H. Overbury, D.R. Mullins, D.R. Huntley, Oak Ridge National Laboratory

Adsorption and reaction of NO on ceria, both with and without Rh or Pt additions, was studied by soft x-ray photoelectron spectroscopy and temperature programmed desorption. The results demonstrate the complexities and interactions which may occur in supported catalysts involving reducible substrates. Growth in UHV of thin films of CeO@sub 2@ on a Ru(0001) substrate allowed creation of oriented films with variable oxidation state, quantitatively determined by valence band and Ce 4d photoemission. Following NO exposure various N containing surface species were observed by N 1s photoemission, and their distribution depended upon surface oxidation state, exposure and adsorption temperature. These species included N@sub 2@O, NO, NO@super +@ and three states believed to be associated with NO@super -@ or atomic forms of N. Occurrence of adsorbed N@sub 2@O at 100 K indicates that NO dissociation and reaction occurs readily at low temperature. N@sub 2@ is evolved during adsorption from above 100 K to at least 600 K indicating that some NO direct decomposition occurs over a wide range of temperatures and coverages. Adsorption of NO at 150 K is predominantly

molecular while exposure to NO at 400 K leads to a low binding energy atomic state which desorbs at temperatures above 500 K. NO adsorbed on oxidized ceria yields a molecular state at a higher binding energy than on reduced ceria and thus is associated with NO@super +@. Adsorption of NO on reduced ceria is oxidative resulting in strongly non-Langmuirian adsorption behavior. Deposition of Rh or Pt on these surfaces alters the observed NO chemistry, and the extent of reduction of the ceria in turn modulates the activity of the noble metal for NO dissociation. Greater dissociation probability of NO and increased stability of the resulting N atoms is observed for the noble metal deposited on a reduced compared to a fully oxidized support. Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy

11:40am SS2-TuM11 An Investigation of the NO@sub x@ Storage Mechanism, M. Skoglundh, H. Persson, E. Fridell, P. Engström, S. Ljungström, Chalmers University of Technology, Sweden

In order to reduce nitrogen oxides (NO@sub x@) from lean burn vehicles, NO@sub x@ storage catalysts are used. The key idea is to first store NO@sub x@ in the catalysts during lean conditions (oxygen in excess) and then the NO@sub x@ is released and reduced during short periods of fuel rich conditions. In the present study we systematically investigate the sequence of mechanistic elementary steps in the NOx storage cycle, by using different experimental techniques in combination with theoretical modelling. As a model system we have used a NO@sub x@ storage catalyst containing Pt, @gamma@-Al@sub 2@O@sub 3@ and BaO as the storage component. Our results suggest that an intermediate peroxide step (BaO@sub 2@) is essential for storing NO@sub x@ as Ba(NO@sub 3@)@sub 2@. Furthermore, the relative importance of direct NO@sub x@ storage via gas phase or NO@sub x@ storage via Pt spillover is discussed.

Biomaterial Interfaces Group Room 326 - Session BI+AS+MM+NS+SS-TuA

Nanoscale to Mesocale Biomaterial Structures

Moderator: M.J. Tarlov, National Institute of Standards and Technology

2:00pm BI+AS+MM+NS+SS-TuA1 Self-Assembly of a Multidomain Protein: Fibronectin at Lipid Model Interfaces, V. Vogel, G. Baneyx, University of Washington INVITED

Fibronectin, an adhesion protein with multiple recognition sites, mediates cell attachment to synthetic and biological surfaces. In solution, fibronectin exists in a globular state where most of its recognition sites are buried in the protein core. Surface adsorption induces conformational changes in the protein that expose many of these sites. Furthermore, it is known that on the surface of cells fibronectin assembles into detergent insoluble fibers, which are considered to be the main functional form of the protein. Fibronectin is hence a prime example of a protein with multiple recognition sites that can be regulated through environmental control. Unfortunately, the molecular pathways of activation and self-assembly are still poorly understood. We have recently found that fibronectin can self-assemble into fibrillar networks at receptor-free phospholipid monolaver interfaces under physiological conditions. This is a crucial observation since the paradigm in biology is that fibril assembly of fibronectin is mediated by membrane-bound receptor molecules. Availability of a simplified model system allows investigation of the molecular pathways by which appropriate surfaces can activate fibronectin and facilitate self-assembly.

2:40pm BI+AS+MM+NS+SS-TuA3 Nanofabricated Substrates for Probing Single Biomolecules by Surface Enhanced Raman Scattering, *S. Petronis, L.K. Hedberg, H. Xu, M. Käll, B. Kasemo,* Chalmers Univ. of Technology and Univ. of Gothenborg, Sweden

The effect of Raman scattering enhancement when coherent laser light interacts with molecules attached to rough surfaces and microscopic metal domains has been known for more than two decades and is called Surface Enhanced Raman Scattering (SERS). The intensity of the Raman signals for such molecules is frequently enhanced by a factor 10@super 5@-10@super 6@ at best.@footnote 1,2@ However recently much larger enhancement factors, in the range 10@super 14@-10@super 15@, have been observed for molecules adsorbed on colloidal silver particles of specific dimensions.@footnote 3,4@ This giant enhancement allows the recording of vibrational spectra from a single molecule for the first time, instead of the ensemble averaged spectra from many molecules, which are normally obtained in optical spectroscopies. Here we report on an attempt to use nanolithography to fabricate structures of silver in the size range 100 - 200 nm and having different shapes in order to explore the size and geometry dependence of the SERS effect. Microfabricated structures which give the highest enhancement could be used for probing different biomolecules and perhaps designing a biosensor. SERS active substrates were prepared as arrays of silver particles on a Si wafer. Within each array the silver particles had a constant shape, size and separation. Three particle shapes (circular, triangular and square), two particle sizes (100 nm and 200 nm), and five different particle separations (10, 50, 100, 150 and 200 nm) were produced by electron beam lithography with a double-layer resist system and "lift-off" procedure. A reference area of uniformly deposited Ag film mimicked an infinite silver surface. The final structures and the chemical composition of the silver particles were characterized by Scanning Electron Microscopy (SEM) and Auger electron spectroscopy (AES), respectively. Preliminary Raman scattering experiments have been performed on the dye-molecule Rhodamin 6G adsorbed on the nanofabricated substrates. A giant enhancement of the Raman signal was observed on all patterns, but not on the Ag film or the Si surface. @FootnoteText@ @footnote 1@M.Moskovits, Rev. of Mod. Phys., vol. 57, No 3, 1985, pp 783-826 @footnote 2@A.G.Mal'shukov, Phys. Rep., vol 194, Nos 5&6, 1990, pp 343-349 @footnote 3@K.Kneip et al., Phys. Rev. Lett., vol. 78, No 9, 1997, pp1667-1670 @footnote 4@S.Nie, S.R. Emory, Science, vol. 275, No 21, 1997, pp 1102-1106

3:00pm BI+AS+MM+NS+SS-TuA4 Nanostructured Surfaces for Biorecognition - A Novel Templating Approach, H. Shi, B.D. Ratner, University of Washington

Materials that specifically recognize proteins may find a variety of applications in separations, sensors and medical materials. Molecular imprinting provides an intriguing approach to plastic antibodies against small molecules, but the use of proteins as templates has been less successful in making protein recognition materials. In this study, nanostructured surfaces with tailored protein-binding cavities are prepared

by an imprinting technique based on RF-plasma deposition of organic thin films. A polysaccharide-like surface with protein-imprinted nanopits allows only the template protein to fill the pits, and to bind strongly, because the nanopits are complementary to the template protein in shape and in the distribution of functional groups. The bound protein in its pit is prevented from exchange with protein in the solution due to a strong binding and steric hindrance, while the non-template protein that is weakly adsorbed on the surface is displaceable. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) showed that nanometer-sized pits, in the shape of imprinted proteins, were created on the surfaces of our protein-imprinted polymer films. Imprinting fidelity was confirmed by AFM analysis of imprints of monodisperse colloidal gold nanoparticles. Electron spectroscopy for chemical analysis (ESCA) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) indicated that template proteins were washed off the surfaces of protein imprints while sugar molecules were covalently incorporated. Radiolabeled -protein adsorption showed that a protein imprint recognized its template protein from a binary mixture with a high specificity. This study illustrates a novel templating strategy for biological molecules that can be exploited for fabrication of biorecognition materials.

3:20pm BI+AS+MM+NS+SS-TuA5 Sensing and Analyzing Single Molecular Interactions with Microfabricated Devices@footnote 1@, J.-B.D. Green, G.U. Lee, Naval Research Laboratory INVITED

There is an intense effort to create new tools for manipulating and characterizing single macromolecules because of the power that these techniques can bring to the analysis of biological macromolecules. Due to the high force and displacement sensitivity of the atomic force microscope (AFM) it has been used to measure inter- and intramolecular forces between model ligand-receptors, i.e., streptavidin-biotin, complimentary strands of DNA, and biologically relevant supra-molecular structures, i.e. titin. With the success of these measurements, there are efforts to obtain even more detailed force measurements and to establish these techniques in the biotechnology laboratory. Our efforts focus on: 1. Designing force transducers with force (10@super -12@N), time (10@super -5@s) and spatial (10@super -9@m) resolutions that push the thermal noise envelope. 2. Developing immobilization strategies that produce more reliable force measurements. We will discuss two new microfabricated devices under development in our laboratory. The first microfabricated apparatus offers an excellent platform for detailed measurements of intermolecular interactions and possibly even analysis of combinatorial arrays. The second is an ultra-sensitive detector based on piezoresistive force transduction and magnetic microparticles. The future of these and similar devices will be considered. @FootnoteText@ @footnote 1@This work has been conducted in collaboration with Alexey Novoradovsky, Jonah Harley, Mohan Natesan, Steven Metzger, David Baselt, and Richard Colton.

4:00pm BI+AS+MM+NS+SS-TuA7 Nanomechanical Properties of Cellular Components Determined by Interfacial Force Microscopy, P.R. Norton, K de Jong, J.F. Graham, N.O. Petersen, University of Western Ontario, Canada The cell membrane is the contact surface between the cell's internal environment and the outside world. Increasingly it is recognized the there is strong active coupling between mechanical properties and cellular functions in properties such as locomotion and adhesion and in cytoskeletal diseases such as muscular dystrophy.@footnote1@ There is therefore an urgent need to understand the mechanical properties of cells and cellular subcomponents at length scales << 1µm. We will describe our initial experiments to achieve this goal. We have used three different imaging techniques in our investigation of the nanomechanical properties of larynx cells. First, immunofluorescent labelling was used to permit visualization of specific cell components in the confocal microscope, for example to determine whether the cell nucleus was removed in a shearing process. The same cell was then imaged in the atomic force microscope (AFM), permitting identification of components involved in motion such as microspikes. The nanomechanical properties of cells were then studied by using nanoindentation the interfacial force microscope (IFM).@footnote2@ While we have not yet succeeded in imaging and measuring the same cell used in the confocal and atomic force microscopies, we have demonstrated the feasibility of our approach and have obtained quantitative force-distance curves on different regions of a single cell fixed in paraformaldehyde, sodium periodate and lysine, which cross-links the proteins. From these data we can derive the elastic modulus, hardness etc of the specific region of the cell. The modulus of such a cell was ~ 3GPa, comparable to a soft polymer. Similar measurements are planned on unfixed cells. @FootnoteText@

@footnote1@Chen, C.S., et al. Science 276, 1425 (1997) @footnote2@Warren, O.L., et al. Physics in Canada 54, 122 (1998)

4:20pm BI+AS+MM+NS+SS-TuA8 Unbinding Force of NTA-M@super 2+@--Histidine Complexes. The His-Tag Immobilization Force, J.G. Forbes, P. Yim, University of Maryland, College Park

A sequence of six or more histidines will bind tightly to a Cu, Ni, or Co complex. The compound typically used to immobilized the metal is N-(5amino-1-carboxypentyl)iminodiacetic acid (NTA). Most proteins will not bind to the complex unless there is a sequence of histidines, which is readily added using recombinant DNA techniques. The histidine tag may be removed from the metal complex with a high concentration of imidazole or by protonating the histidines at a pH below 6. We have studied the the unbinding strength of this interaction with the atomic force microscope (AFM). To perform this measurement, we have functionalized silicon nitride AFM tips with NTA-M@super 2+@. A glass slide was coated with recombinant DNAse I with a his-tag on the C-terminus. Unbinding force measurements were made in phosphate buffered saline (PBS) to reduce electrostatic interactions. We find that the unbinding force for the NTA-M@super 2+@/His-tag interaction to be ca. 85~pN for each of the metal complexes. Interestingly, 0.5~M imidazole does not remove the interaction, but only changes the distribution of the measured forces. This is a result of the non-equilibrium condition of the tip being forced into the protein coated surface. The interaction is almost completely removed by lowering the pH to 5.0 where the histidines are protonated and can no longer coordinate with the nickel. The remaining interaction forces are due to the histidines which are exposed when the tip presses into the surface. These results provide a quantitative measurement of mechanical strength of binding of proteins to surfaces functionalized with NTA-M@super 2+@.

4:40pm BI+AS+MM+NS+SS-TuA9 Sieving of DNA Molecules in Nanofluidic Channel, J. Han, H.G. Craighead, Cornell University

Entropic trapping and sieving effect of long DNA molecules was studied in variable thickness nanofluidic channels. We used photolithography and etching techniques to define fluid channels on Si wafers, and anodic bonding method to seal the channel with a thin pyrex glass coverslip. The channel consists of alternating regions with two different channel thicknesses(~100nm and 1.6µm). We studied electrophoretic motion of lambda phage DNA in this channel by epi-fluorescence microscopy. Since the radius of gyration of a typical long DNA molecule is larger than the smaller gap of the channel, the shallow part of the channel can be an entropic barrier for DNA motion. Therefore, DNA molecules were retarded when they entered into the thin region from the thick region. We measured the mobility of DNA molecules in these channels and observed that below a certain electric field, mobility of DNA molecule decreased to near zero drastically, showing that DNA molecules be entropically trapped and sieved. The threshold electric field was mainly dependent on the geometry of channel(e.g. gap size) and the length of DNA driven. This suggests a new type of separation device for DNA and other polymers.

5:00pm BI+AS+MM+NS+SS-TuA10 Detection of Molecular Ion and Quantification of Pentapeptide on Plasma Hydroxylated Fluoropolymer by Time of Flight Secondary Ion Mass Spectrometry, J.A. Gardella, L.M. Sun, State University of New York, Buffalo

Abstract: Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) was modified by a hydrogen/methanol radio frequency glow discharge plasma. Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) was employed to characterize the modified FEP surface and three pentapetides (YGGFM, YGGFL, YIGSR) which were microsyringe deposited on the modified FEP film. New fragments of OH (CF@sub 2@)n in negative ion SIMS of the modified FEP film indicated that -OH functional group had been incorporated on the FEP surface after plasma treatment. In the positive ion SIMS of three pentapeptides on the hydroxylated FEP film, protonated molecular ions were dominant signals from the peptides whereas not many fragments were observed either from the peptides or the impurity. Sodium and potassium adduct molecular ions were detected as well as oxidized protonated molecular ion of YGGFM in the positive ion SIMS spectrum. Negative ion SIMS of YGGFL yielded a deprotonated molecular ion. The mixture of these three pentapetides was also studied by TOF-SIMS. The relative intensity of protonated molecular ions of YGGFL, YGGFM and YIGSR showed the possibility of quantification on the hydroxylated fluoropolymer by TOF-SIMS. As a study of substrate effects, TOF-SIMS spectra of these peptides on oxidized Ag substrate were recorded. Comparing SIMS results of pentapetides on Ag and on modified FEP film, fewer fragments occurred from the FEP film than that from the Ag substrate. A substrate like the FEP

fluoropolymer might be beneficial for the quantification of peptides because of the intensity of parentlike species in SIMS measurement.

Surface Science Division Room 308 - Session SS1-TuA

Semiconductor Surface Chemistry

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

2:00pm SS1-TuA1 The Effect of Phosphorus and Germanium on Silicon Surface Chemistry, *J.E. Crowell*, *M.L. Jacobson*, *G.J. Batinica*, *M.C. Chiu*, University of California, San Diego

Our studies focus on the deposition surface chemistry of Group IV semiconductors. We have examined the effect that adatoms such as P, Ge, and both P/Ge have on (i) the Si precursor chemisorption behavior and (ii) the hydrogen desorption behavior. Surface phosphorus contains a lone pair of electrons rather than a dangling bond and is thus passive to adsorbing gas molecules, and acts as a site blocker to species diffusing on the surface. In contrast, Ge adatoms contain a dangling bond and behave in a way similar to Si. However, both adatoms modify the surface chemistry of silicon. This presentation will describe TPD, AES, and MIRIRS studies aimed at determining the effect of pre-adsorbed P and Ge on the reactivity of Si(100) and Si(111) surfaces. For example, disilane (Si@sub 2@H@sub 6@) reacts with the Si(100) surface at 300K to form a mixture of SiH@sub x@ species. At higher temperatures, recombination reactions occur which produce silane (SiH@sub 4@) and H@sub 2@ that subsequently desorb. The reactivity of the Si(100) surface decreases with increasing P coverage, as determined by the increase in the selectivity of the Si@sub 2@H@sub 6@ reaction toward SiH@sub 4@ production over H@sub 2@ production. The H@sub 2@ desorption temperature increases with increasing P coverage while the SiH@sub 4@ desorption temperature decreases. A similar increase in H@sub 2@ desorption energy was seen upon H atom exposure of the P/Si surface, whereas Ge pre-adsorption decreases it. These results, a comparison of the (100) and (111) Si surfaces, and the combined effect of P and Ge will be discussed within the framework of electronic and morphological modifications of the surface and ensemble size effects caused by the presence of these pre-adsorbed adatoms.

2:20pm SS1-TuA2 In situ Boron Doping of Si(100): Effects of Low Boron Concentration on Hydride Surface Reactions, *B. Gong, D.E. Brown,* University of Texas, Austin; *S.K. Jo,* Kyung Won University, South Korea; *J.G. Ekerdt,* University of Texas, Austin

Hydrogen desorption and hydride adsorption will potentially control film growth rates during in situ doping of Si(100) in chemical vapor deposition processes involving hydride gases. The reactions of hydrogen and disilane with boron-doped Si(100) have been studied with temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS) and low energy electron diffraction (LEED). Recent studies by our group have been conducted in the boron concentration range from 0.001 to 0.05 monolayer (ML) to illustrate the kinetic effects of in situ doping, which has a typical doping level of 10@super 16@-10@super 20@ cm@super -3@. With ~0.001 ML boron, TPD and HREELS show essentially no dihydride formation on the boron doped surface. After H-passivation, the boron doped surface (@theta@@sub B@~0.001 ML) shows a 2x1 reconstruction by LEED, while the H induced reconstruction on a clean surface at the same conditions shows a 3x1 reconstruction. This inability of the H-passivated Si(100) to undergo the 3x1 reconstruction is associated with the subsurface boron-induced silicon dimer vacancy defects. At slightly higher @theta@@sub B@, monohydride starts to be suppressed and decreases with increasing @theta@@sub B@. At @theta@@sub B@= 0.01 ML, monohydride formation decreased 15% and then more slowly with increasing boron coverage due to islanding. A boron electronic effect that deactivates silicon dangling bonds reduces active sites on the surface, which in turn shows less monohydride adsorption with increasing @theta@@sub B@. The saturation coverage of disilane decreases with increasing @theta@@sub B@ due to less dangling bonds as a result of the boron deactivating effect. However, the disilane adsorption rate increases with @theta@@sub B@ while the hydrogen desorption rate is not affected by the addition of boron. We propose that the boron effects on silicon deposition rate is a result of enhanced disilane adsorption rather than enhanced hydrogen desorption.

2:40pm SS1-TuA3 Chemical Modification of Semiconductor Surfaces: Functionalization Using Cycloaddition Reactions, S.F. Bent, New York University INVITED

Due to the increasing importance of organic-based electronic and optical devices, there is much interest in developing attachment chemistries to join organic structures with inorganic semiconductor substrates. In this presentation, the use of unsaturated hydrocarbons to form the initial organic layer by direct bonding to silicon and germanium surfaces in vacuum will be discussed. A series of unsaturated molecules, both cvclic and non-cyclic, have been investigated using various methods including multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy, near-edge X-ray absorption fine structure (NEXAFS), and temperature-programmed reaction/desorption (TPR/D). Conjugated dienes such as butadiene can undergo Diels-Alder-like [4+2] cycloaddition reactions on both Si(100)-2x1 and Ge(100)-2x1 surfaces, whereas nonconjugated dienes and alkenes react by direct [2+2] addition. The relative reactivity of Si(100)-2x1 and Ge(100)-2x1 toward unsaturated molecules will be compared. An overview of the bonding and thermal reactivity of the different compounds will be presented, and the potential for these types of cycloaddition reactions in future applications will be discussed.

3:20pm SS1-TuA5 Cycloaddition Reactions at Germanium Surfaces, S.W. Lee, L.M. Nelen, University of Missouri, Columbia; H. Ihm, University of Texas; C.M. Greenlief, University of Missouri, Columbia

The adsorption and reaction of a number of cyclic unsaturated hydrocarbons with the Ge(100) surface is investigated. It is shown that well-defined ordered organic layers can be formed on semiconductor surfaces. On semiconductor surfaces the majority of the reactions with hydrocarbons occur at or near the dangling bonds of the reconstructed surface. The dangling bonds on a Ge(100)-(2x1) surface are arranged in surface dimers. This arrangement of dangling bonds means that it is possible to form a molecularly ordered thin film that is covalently bound to the surface, provided that one can have the reaction occur at the dangling bond sites. In this paper we present an investigation of the structure and chemical bonding of the organic film/semiconductor interface. Data are obtained for a number of different starting precursor molecules using photoelectron spectroscopy, high resolution electron energy loss spectroscopy and temperature programmed desorption. The molecules investigated include 1,3-cyclohexadiene, 1,4-cyclohexadiene, and cyclohexene. The possibility of a surface Diels-Alder [4+2] cycloaddition, as well as, a [2+2] cycloaddition reaction are explored. Either cycloaddition reaction leads to an organic layer that is ordered with respect to the germanium surface.

3:40pm SS1-TuA6 Binding Energies of Hydrogen on Flat and Vicinal Silicon Surfaces, *M.B. Raschke*, *U. Höfer*, Max-Planck-Institut für Quantenoptik, Germany

Despite the importance of hydrogen interaction with silicon in many technological applications and its role as a model system for chemisorption on semiconductor surfaces, the binding energy of hydrogen on silicon surfaces is not well known. In a novel experimental approach, a bakeable UHV-guartz apparatus was used to establish thermal equilibrium between molecular hydrogen and well-defined Si(111) and Si(001) surfaces at gas pressures of 10@super -5@ 1 mbar and temperatures of 770 - 980 K. Under these conditions, continuous dissociative adsorption and recombinative desorption of H@sub 2@ lead to an equilibrium hydrogen coverage on the surfaces which is measured sensitively using optical second-harmonic generation (SHG). The resulting adsorption isotherms allow for the accurate determination of the hydrogen binding energies and their dependence on surface coverage. In the case of H/Si(111)7x7, the binding energy increases from 2.9 eV to 3.1 eV in the investigated coverage range between 0.05 ML and 0.3 ML. The Si-H bond is thus found to be considerably weaker than hydrogen bonding in silanes (3.7-3.9 eV). The values are compatible with a large barrier (0.9 eV) for phonon-assisted sticking of H_2/Si.@footnote 1@ They are in good agreement with theoretically predicted Si-H bond strengths at the adatoms and restatoms of this surface.@footnote 2@ Exploiting substantial differences in reactivity between the step and terrace sites towards molecular hydrogen, equilibrium and non-equilibrium hydrogen coverages on vicinal Si(001) could also be investigated. From measurements for various surface temperatures on samples with different angles of miscut it is inferred that the steps are thermodynamically favored by approximately 0.2 eV. @FootnoteText@ @footnote 1@P. Bratu and U. Höfer, Phys. Rev. Lett. 74 (1995) 1625. @footnote 2@H. Lim, K. Cho, I. Park, J. D. Joannopoulos, and E. Kaxiras, Phys. Rev. B 52 (1995) 17231

4:00pm SS1-TuA7 The Reactions of Trimethylgallium and Ammonia on GaN(0001), H.-T. Lam, J.M. Vohs, University of Pennsylvania

The reactions of trimethylgallium and ammonia on MOVPE-grown GaN(0001) were studied using temperature programmed desorption, highresolution electron energy loss spectroscopy, Auger electron spectroscopy, and Rutherford backscattering spectrometry. The results of this study show that TMGa dissociates on GaN(0001) to form monomethylgallium (MMGa) and/or dimethylgallium (DMGa) and surface methyl groups at temperatures above 250 K. The MMGa/DMGa species either desorb between 250 and 450 K or undergo further dissociation forming adsorbed methyl groups and Ga atoms. For low TMGa coverages, surface methyl groups desorb near 600 K producing gaseous methyl radicals. At higher coverages a fraction of the methyl groups undergo dehydrogenation produces methane at 590 K and surface carbon atoms. The reaction of ammonia on GaN(0001) was found to proceed via dissociation to form surface NH@sub x@ species and atomic hydrogen above 300 K.

4:20pm SS1-TuA8 An Investigation of the Surface Reaction Mechanisms of Alternating-Grown Ordered Layers: CdS on ZnSe(100), *M. Han, Y. Luo, J.E. Moryl, R.M. Osgood, Jr.*, Columbia University

In previous experiments we have found that ordered layers of CdS on ZnSe(100) substrate were formed by a binary surface reaction sequence using gas-phase dosing of the substrate with (CH@sub 3@)@sub 2@Cd and with H@sub 2@S. This system provides a prototypical example of the interplay between reaction and desorption in such a binary sequence. In this talk we report a careful investigation of the surface chemistry using TPD. The experiments were performed in a UHV chamber, which is also equipped with AES, LEIS and LEED. Analysis of the TPD spectra show clearly that adsorbed DMCd irreversibly dissociates on ZnSe(100)-c(2x2) surface, and that the previously reported self-limiting reaction results from a methyl-termination of the surface. At ~ 370K, DMZn desorbs from this surface due to a methyl exchange reaction. This desorption temperature is independent of coverage, indicating a first-order reaction. In addition, at high DMCd exposures, the adsorption and desorption process leads to replacement of surface Zn by Cd. The experiments have also examined the reaction of the methyl-terminated surface with H@sub 2@S. This reaction is also self-limiting, yielding desorbed CH@sub 4@ and forming a sulfurhydride-terminated surface. Studies of surfaces formed by more than one binary reaction sequence showed that the alternating growth surfaces are also terminated with either methyl group or sulfur-hydride. The methylpassivated surface above the first layer preferentially desorbs methyl radicals at ~390K instead of metal-alkyl species. For the sulfur-hydrideterminated surface the recombinative reaction of HS species causes desorption of H@sub2@S at 480K. In this case, the symmetric peak shape and its shift to lower temperature with increasing the coverage suggest a second-order reaction mechanism. In more general terms the above results indicate that the relative strengths of bonding energy for methyl-metal(II) and metal-VI element play an important role in the surface reactions.

4:40pm SS1-TuA9 Competition Between Passivating and Etching in Halogen Reactions with III-V Semiconductor Surfaces, W.K. Wang, University of California, Riverside; W.C. Simpson, Pacific Northwest National Laboratory; J.A. Yarmoff, University of California, Riverside

Halogen adsorption on III-V semiconductor surfaces with certain reconstructions leads to the formation of an ordered overlayer, while other III-V surfaces become disordered and etch. It has been suggested that the initial atomic structure and stoichiometry play important roles in determining whether a surface passivates or etches. A single crystal face of a given III-V material can have many surface reconstructions, each of which has a slightly different stoichiometry in the outermost few atomic layers. In this study, a direct comparison is made of the adsorption of halogens on different reconstructions of the same material. From the results, the microscopic mechanism underlying the predilection for ordering or disordering can be ascertained. Synchrotron-based soft x-ray photoelectron spectroscopy and low energy electron diffraction were employed to investigate surfaces following reaction. These techniques provide information about the chemical bonding and ordering on the surface. For example, for I@sub 2@ reaction with the In-terminated InAs(100)-c(8x2) surface, a well-ordered (1x1) structure forms and all of the iodine attaches to In. The As-terminated InAs(100)-c(2x8) surface, on the other hand, becomes disordered and iodine attaches to both In and As atoms. This can be explained by a preference for iodine to initially bond with the electron-deficient group III In atoms. In contrast, I@sub 2@ reaction produces ordered structures on both the Ga-terminated and Asterminated GaAs(100) surfaces. Cl@sub 2@ reactions almost always lead to etching after sufficient exposures, no matter what the initial surface

structure, although following small exposures some ordered structures may form. In this presentation, the microscopic mechanisms underlying this behavior will be discussed.

5:00pm **SS1-TuA10 A Scanning Tunneling Microscopy Study of [(tbutyl)GaS]@sub 4@ Adsorption on GaAs,** *R.I. Pelzel,* University of California, Santa Barbara, U. S. A.; *B.Z. Nosho,* University of California, Santa Barbara; *B. Fimland,* Norwegian University of Science and Technology, Norway; *W.H. Weinberg,* University of California, Santa Barbara

Gallium sulfide layers grown using the single-source molecular precursor [(t-butyl)GaS]@sub 4@ have shown promise in providing long-term chemical and electrical surface passivation for GaAs.@footnote 1@ With this in mind, we have conducted an ultrahigh vacuum investigation of the initial stages of [(t-butyl)GaS]@sub 4@ adsorption on GaAs(100)-(2x4) and (4x2). Adsorbing [(t-butyl)GaS]@sub 4@ at elevated surface temperatures (> 650 K) results in carbon-free adsorption as judged by Auger electron spectroscopy. For low coverages on both reconstructions, low energy electron diffraction (LEED) data indicate that both the (2x4) and the (4x2) surface reconstructions remain intact. Scanning tunneling microscopy (STM) images show that the adsorption of submonolayer coverages of [(tbutyl)GaS]@sub 4@ disorders the surface reconstructions. Subsequent deposition results in further disordering until a coverage of approximately 1 ML where a weak (2x1) LEED pattern is observed. The (2x1) surface order is not observable in STM prior to annealing to a temperature of approximately 780 K. The (2x1) surface observed using STM following annealing is well-ordered, and images will be presented. Possible models of GaS growth achieved using [(t-butyl)GaS]@sub 4@ will be discussed. @FootnoteText@ @footnote 1@ P. P. Jenkins, A. N. MacInnes, M. Tabib-Azar, and A. R. Barron, Science 263, 1751 (1994); A. N. MacInnes, M. B. Power, A. R. Barron, P. P. Jenkins, and A. F. Hepp, Appl. Phys. Lett. 62, 771 (1993); M. Tabib-Azar, S. Kang, A. N. MacInnes, M. B. Power, A. R. Barron, P. P. Jenkins, and A. F. Hepp, Appl. Phys. Lett. 63, 625 (1993).

Surface Science Division Room 309 - Session SS2-TuA

Morton M. Traum Student Award Session

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

2:00pm SS2-TuA1 Hot Ethene Desorption by Dissociative Electron Attachment of Adsorbed Halocarbons, A.S.Y. Chan¹, R.G. Jones, University of Nottingham, United Kingdom

The electron stimulated reactions of adsorbed 1,2-dihalocarbons have been studied by measuring the time-of-flight (TOF) velocity distributions of the ethene product ejected from the surface. Both 1,2-dichloroethane (DCE) and 1-bromo-2-chloroethane (BCE) have been found to undergo dissociative electron attachment from secondary electrons generated by a pulsed 2 keV electron beam impinging on the Cu(111) surface, leaving chemisorbed halogens and ethene desorbing in the gas phase. The TOF distributions of the ethene product from both adsorbate molecules are quite similar; both exhibit a bimodal distribution with a hyperthermal channel of ~ 1200 K and a slow channel of ~ 200 K. When the distributions obtained from identical coverages of DCE and BCE are compared, a consistently smaller intensity of the slow channel is observed from the latter molecule. This slow component appears to grow with increasing number of adsorbed layers, indicating that it is most likely due to ethene molecules that have thermalised by interactions with the adsorbate. By comparing the possible dissociation dynamics of the two molecules, we discuss the possibility that a direct dissociation of the adsorbed molecule after electron capture, rather that a surface-mediated energy transfer mechanism, may be responsible for the high translational energy of the hyperthermal ethene.

2:20pm SS2-TuA2 Combined Experimental and Quantum Chemistry Study of the Disproportionation of Dimethylalane on Aluminum Surfaces, *B.G. Willis*², *K.F. Jensen*, Massachusetts Institute of Technology

A combined experimental/theoretical approach has been employed to study the decomposition reactions of trimethylaluminum and dimethylalane on aluminum surfaces. Together with UHV surface science experiments, plane wave pseudopotential density functional theory calculations have been implemented to augment the experimentally derived reaction mechanism. The plane wave surface calculations provide additional details of the surface reactions not easily probed with experiments, and where the two approaches overlap, comparisons are made. Dimethylalane is found experimentally to decompose on aluminum via a disproportionation reaction to produce trimethylaluminum. Trimethylaluminum follows the same reaction pathways on aluminum, but due to the difference in stoichiometry there is no net growth, and a dynamic equilibrium exists between the gas phase and surface at low temperatures. Based on the experimentally observed mechanism, the calculations are employed to generate thermodynamic heats of reaction for each elementary reaction step, and a complete mechanism is presented for the surface reactions. Results suggest exothermic steps for breaking down the dimethylalane and trimethylaluminum monomers to surface monomethylaluminum fragments. Further decomposition of these fragments, the desorption of hydrogen, and additional recombination reactions are found to be endothermic. The overall heat of reaction is calculated to be approximately -16 kcal if written in terms of monomeric gas phase units. If it is considered that trimethylaluminum and dimethylalane may exist as dimer gas phase units, the reaction is endothermic by approximately 16 kcal. At high temperatures both dimethylalane and trimethylaluminum share a strongly activated pathway for methyl dehydrogenation which produces a carbon contaminated surface. The experimental barrier is found to lie near 40 kcal for the methyl decomposition reaction. Theoretical calculations of this impurity incorporation pathway predict a methyl decomposition activation barrier near 40 kcal, in good agreement with experiments. The full ab initio model includes elementary reactions leading to growth, surface diffusion of the active methyl groups, methyl decomposition reactions to produce surface carbon, and the alternative (not experimentally observed) surface reaction pathway to form methane. Comparisons are made where both theory and experiment overlap and agreement is found to be good (within approximately ±5 kcal).

2:40pm **SS2-TuA3 Low-Symmetry DFT Diffusion Barriers and Dimer Dynamics in Homoepitaxial Growth of Al(111)**, *A. Bogicevic*³, *J. Strömquist*, *P. Hyldgaard, G. Wahnström, B.I. Lundqvist*, Chalmers Univ. of Tech. and Göteborg Univ., Sweden

From fractals to compact islands, epitaxial growth offers an exotic variety of surface morphologies that emanate from a handful of elementary atomic diffusion processes. Adsorption calculations have hitherto been limited to high-symmetry configurations, or to semi-quantitative methods. Using extensive density-functional calculations on parallel computers, we map out barriers for self-diffusion at steps, kinks, and corners on Al(111). The results include an unexpected exchange mechanism at kinks and a large barrier anisotropy at corners. Using transition state theory we are able to transform the barriers into a set of activation temperatures and hereby predict various growth modes as a function of temperature. New STM experiments confirm four of our main results in great detail, including the fractal-compact island transition and the transition to equilibrium shaped islands. The central role dimer stability and mobility plays during nucleation and in later stages of growth has motivated us to study Al dimer diffusion at 0 and 5% compressive strain. The smooth potential energy surface enables a long-ranged attraction between the dimer atoms, leading to a substantial temperature window in which dissociation is frozen and fascinating dimer dynamics takes place. Surface relaxations play a prominent role in the uncovering of unexpected ground states, which should be easy to verify with, e.g., STM measurements of dimer height or dimer direction. A new diffusion mechanism is found, where dimers migrate by concerted sliding. The effect of elastic strain on dimer diffusivity is addressed, and its impact on the epitaxial growth mode is discussed.

3:00pm SS2-TuA4 STM and LEIS Study of Oxygen-Induced Restructuring of Rutile TiO@sub 2@(110)(1x1) Surface, M. Li⁴, W. Hebenstreit, Tulane University; D.R. Jennison, Sandia National Laboratories; U. Diebold, Tulane University

The rutile TiO@sub 2@(110) surface is one of the most-popular substrate in the surface science of metal oxides. We show that the exact surface preparation conditions critically influence the surface structure and morphology of this material in a rather unexpected way. TiO@sub 2@(110) surfaces, prepared by sputtering and annealing at 850 K in UHV, exhibit a (1x1) surface termination and flat, several hundred Å wide terraces. After exposure to oxygen at elevated temperatures (onset ~470 K), the surfaces are covered with small (typically tens of Å wide) terraces with monoatomic step height and the same (1x1) structure. On top and in between these

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terraces appear patches of an irregular network consisting of interconnected rosettes (width ~ 7 Å) with pseudohexagonal symmetry. The positions of atoms within the network are consistent with an incomplete TiO@sub 2@(110) layer. Ab-initio LDA calculations support the stability of the proposed structural model. It contains undercoordinated atoms with an electronic structure that is distinctly different from (1x1) terminated surfaces. LEIS measurements of surfaces annealed in @super 18@O@sub 2@ clearly show that new TiO@sub 2@ layers are formed through outdiffusion of interstitial Ti cations from the reduced bulk to the surface where they react with ambient oxygen. The kinetics of this 'restructuring' mechanism as well as possible implications for the surface chemistry of TiO@sub 2@ are discussed.

3:20pm SS2-TuA5 A Study of the Relationship Between Si/SiO@sub 2@ Interface Charges and Roughness, *L. Lai*¹, *K.J. Hebert, E.A. Irene*, University of North Carolina, Chapel Hill

This study examines the correlation between interface micro-roughness and charges. Atomic force microscopy (AFM) and a newly developed area roughness function, A(RMS,D@sub F@)@footnote 1@ which couples two roughness parameters, root mean square (RMS) and fractal dimension (D@sub F@), are used to reliably and accurately characterize surface micro-roughness. For the common surface area computation methods, this leads to large round-off errors. This new area roughness function obviates this problem, and it is not only a sensitive roughness parameter, but also a reliable area extracting tool for surfaces with micro-roughness. Microroughness has a small vertical magnitude relative to the large horizontal data sampling interval. Interface charges (D@sub it@ and Q@sub f@) are measured using high frequency and quasistatic capacitance-voltage methods. These charges are reported in per unit area, so in order to obtain reliable charges levels, one must know the area. This study is divided into three parts where smooth, purposely roughened, and purposely smoothened Si substrates are used to make MOS capacitors. For smooth samples, we found that interface charges decrease as the oxidation time increases. Purposely roughened substrates show that there is a correlation between interface roughness and charges. When the correct area, A(RMS,D@sub F@), is used, the excess interface charges due to roughness are accounted for. Roughened then smoothened substrates show that the rate of decrease of the corrected charges with respect to oxidation time become about the same as those from smooth substrates. We conclude that the increases of D@sub it@ and Q@sub f@ with Si roughness are due entirely to the area increase and orientation changes that result from roughness. @FootnoteText@ @footnote 1@ L. Lai and E. A. Irene, J. Vac. Sci. Technol. A. submitted (1998).

3:40pm SS2-TuA6 The Chemistry and Formation of Ordered Organic Molecular Films on Silicon (001)-2x1 Surfaces, J.S. Hovis², R.J. Hamers, University of Wisconsin, Madison

We have recently developed a novel method for growing ordered organic films on the technologically important Si(001)-2x1 surface. The reaction involves the interaction of a surface Si=Si dimer with a C=C double bond from an unsaturated alkene, resulting in the formation of two new Si-C @sigma@ bonds. Due to the directional nature of @pi@ bonds the Si=Si dimer bond is able to act like a template, controlling the locations and rotational orientation of the individual adsorbed molecules. One unique aspect of this growth method is the fact that the molecules adsorb without dissociation, leading to a well defined interface between the silicon substrate and the organic film. We find that a number of molecules, including cyclopentene, 1,5-cyclooctadiene, and 1,3,5,7-cyclooctatetraene form films that exhibit in-plane optical anisotropies on the length scales of centimeters when adsorbed on 4°-miscut (single-domain) wafers. The molecules 1,5-cyclooctadiene and 1,3,5,7-cyclooctatetraene form monolayers that terminate with ordered arrays of C=C double bonds at the vacuum-surface interface and the ability to grow further layers will be discussed. We have also examined the adsorption of 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene on the Si(001) surface. These molecules can form two different products on the surface; one of which is more thermodynamically favorable. Our studies show that both possible products are formed, indicating that kinetics play a larger role in the adsorption probability than do thermodynamics. Experimental evidence using scanning tunneling microscopy (STM), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) will be shown as will the results of ab inito calculations.

4:00pm SS2-TuA7 ToF-SIMS Characterization of the Interaction Between Vapor-Deposited AI Atoms and an Ordered Array of Organic Functional Groups, G.L. Fisher³, A.E. Hooper, The Pennsylvania State University; R.L. Opila, Bell Laboratories, Lucent Technologies; D.L. Allara, N. Winograd, The Pennsylvania State University

The room temperature vapor deposition of up to 4Å of Al metal onto monolayers of @omega@-functionalized alkanethiolate molecules, of structure HS-(CH@sub 2@)@sub n@-X, self-assembled on polycrystalline Au was studied using static ToF-SIMS, XPS and IRS. Deposited AI was found to be highly reactive with methylester organic functional groups (OFGs). The data indicate a titration of one Al atom per methylester OFG, and the ether bonds appear to be unperturbed. Thus, deposited Al reacts solely with carbonyl oxygen of the OFG forming a uniform dielectric with an Al-O-C bonding arrangement. Upon saturation of methylester OFGs with deposited AI, further deposition results in formation of metallic overlayers. Deposited Al was found to be unreactive with methyl OFGs. Instead, the deposited AI diffuses through the monolayer to the monolayer/Au interface via thermally activated transient defects. Here, the Al atoms are observed to disrupt the Au-S bonding to form stable Au-Al-S bonds that quench further transient defect formation. As the deposition progresses deposited Al is observed to form islands on top of the monolayer. Island formation in this case is a result of physisorbed AI; no chemical reaction is observed. Penetration of deposited Al through the methylester-terminated monolayer to the monolayer/Au interface was not observed. Reaction between deposited AI and the methylene backbone of methyl-terminated and methylester-terminated monolayers was not observed.

4:20pm SS2-TuA8 The Reactivity of Surface Defects on the MoS@sub 2@(0001) Basal Plane: Methanethiol and Thiophene Reactivity Studies, *C.G. Wiegenstein*⁴, *K.H. Schulz*, Michigan Technological University

Molybdenum disulfide based materials are important industrial catalysts for the removal of aromatic organosulfur compounds from petroleum feedstocks. The removal of sulfur compounds is important since sulfur is a known catalysts poison. Although there have been significant amounts of study on the structure of the industrial hydrodesulfurization catalysts, there is still a significant amount of uncertainity as to the surface chemistry and reactivity of the organosulfur compounds on the catalyst surface. Information on surface intermediates and adsorbate structures is hindered by the high pressures used in commercial HDS reactors. MoS@sub 2@ grows large sheets of sulfur terminated planes which are not catalytically active towards thiophene. Wiegenstein and Schulz@footnote 1@ attempted to prepare basal surfaces with large defect densities using deuterium adsorption, but were not successful. Although defects were produced by adsorption of deuterium atoms on sulfur anions which subsequently desorbed as deuterium sulfide, no significant changes were observed in the population of ethyl-thiolate surface species following repeated sample exposures to atomic deuterium. However, reactive MoS@sub 2@(0001) surfaces have been prepared using short ion bombardment times. Three different surface preparation treatments were used: a freshly cleaved surface; a 30 second ion-bombarded surface; and a 60 second ion-bombarded surface. An increase in the population of the higher temperature state was observed as ion-bombardment time was increased. AES results demonstrated that surface sulfur was preferentially removed via ion-bombardment, and thus, the higher temperature state has been identified as arising from methyl-thiolate adsorption at defect sites thought to be sulfur vacancies. This paper will give the details of these studies, and will report on present efforts examining thiophene decomposition on ion-bombarded MoS@sub 2@(0001) surfaces. Finally, the usefulness of the defective basal plane as a model HDS catalyst will be discussed. @FootnoteText@ @footnote 1@Wiegenstein and Schulz, Surface Science, 396 (1998) 284.

4:40pm SS2-TuA9 The Influence of Chlorine on the Dispersion of Cu Particles on Cu/ZnO(0001) Model Catalysts, A.W. Grant⁵, University of Washington; A. Jamieson, Massachusetts Institute of Technology; T. Evans, University of Manchester, United Kingdom, UK; G. Thornton, University of Manchester, United Kingdom; C.T. Campbell, University of Washington

Adsorbed chlorine is thought to affect the dispersion of metal catalysts on oxide supports. We have studied this by vapor depositing thin films of Cu onto Zn-terminated ZnO(0001), both with and without a pre-exposure of Cl@sub 2@. First, the adsorption of Cl@sub 2@ was studied on ZnO using XPS, LEIS, work function, and band-bending. A close-packed monolayer of

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Cl adatoms forms at saturation with 0.31 Cl adatoms per Zn site. The work function increase of 2.2 eV indicates anionic Cl@sub ad@. Without Cl@sub ad@, vapor-deposited Cu grows in two-dimensional islands that cover ~33% of the ZnO, after which these islands thicken (i.e., as 3D Cu particles) while the clean ZnO between these Cu islands gets covered with Cu only very slowly. The presence of Cl@sub ad@ decreases the fraction of the surface that is covered by Cu islands by ~3-fold, so Cl@sub ad@ either decreases the number of 2D Cu islands or their critical area before thickening. This is consistent with weaker binding of Cu to the Cl covered surface than to the clean ZnO. In addition, Cl@sub ad@ not only covers the surface of the ZnO, but also covers the surface of the Cu islands, as suggested by the constant CI-LEIS signal during Cu deposition. This was verified further by following the formate-derived TPD features from HCOOH adsorption, which are distinctly different for Cu and Zn sites on Clfree Cu/ZnO(0001). Pre-dosed Cl virtually eliminated the 575K Zn-formate peak. When Cu was vapor-deposited onto a Cl-precovered surface, neither the Zn- nor Cu- formate peaks were observed. Apparently, Cu displaces some of the Cl adatoms from Zn sites, and they subsequently cover the Cu islands.

5:00pm SS2-TuA10 Modeling Molybdenum Carbide-Based Hydrodesulfurization (HDS) Catalysts Using Carbon and Sulfur-Modified Mo(110) Surfaces, C.L. Roe¹, K.H. Schulz, Michigan Technological University Mo@sub 2@C catalysts have shown potential for commercial use in hydrodesulfurization (HDS) processes. Although these molybdenum carbide catalysts look encouraging as replacements for MoS@sub 2@based catalysts, questions remain regarding the fundamental surface chemistry associated with the HDS of organosulfur molecules on carbided and sulfided molybdenum catalyst surfaces. Previous surface science studies examining HDS reactions have focused on using Mo(110) and Mo(100) surfaces as model catalysts, but have not been extended to include models of the newer Mo@sub 2@C-based materials. To further investigate the suitability of Mo@sub 2@C for HDS applications, the interaction of sulfur-containing molecules with molybdenum surfaces was examined by utilizing carbon and sulfur-modified Mo(110) single crystals as model catalysts. Specifically, the reactivity of ethanethiol, 1,2ethanedithiol, and thiirane were studied on the clean Mo(110) and p(4x4)-C/Mo(110) surfaces as a function of sulfur coverage. Ethanedithiol TPD experiments performed on the clean and carbon modified Mo(110) surfaces produced similar reaction products, although changes were observed in selectivity. On the clean Mo(110) surface, the major products observed during TPD experiments were acetylene, ethylene, vinyl thiol, and ethanethiol. However, the reaction of ethanedithiol on the p(4x4)-C/Mo(110) surface produced acetylene, ethylene, and ethanedithiol. Product molecules are thought to arise from two distinct types of surface intermediates: 1) a monodentate thiolate species and 2) a bidentate organosulfur metallocycle. We propose that vinyl thiol and ethanethiol are produced via C-S bond scission and subsequent hydride elimination of the thiolate intermediates, and that the surface metallocycles undergo C-S bond scission to yield acetylene and ethylene. On the carbon-modified surface, complete desulfurization of ethanedithiol occurs upon decomposition, yielding only hydrocarbon products. With increasing sulfur coverage, a decrease in reactivity and a shift in desorption features to lower temperatures is observed for ethanedithiol on the clean and carbonmodified surfaces. Additionally, experimental results on the reaction of ethanethiol and thiirane on the Mo(110) and p(4x4)-C/Mo(110) surfaces will be discussed.

Surface Science Division Room 314/315 - Session SS3-TuA

Photon- and Electron-Induced Chemistry

Moderator: R.G. Tobin, Tufts University

2:00pm SS3-TuA1 Photon Driven Chemistry of Adsorbates, J.M. White, University of Texas, Austin INVITED

The photon driven chemistry of adsorbates on Ag(111) will be illustrated using results from sulfur dioxide, trifluoromethyl iodide and, in greater detail, methyl nitrite. The focus of the presentation will be a discussion of the angular and velocity distributions of nitric oxide moieties ejected from irradiated methyl nitrite. The dependence of these properties on photon energy (3 to 6 eV) and coverage (submonolayer to thick multilayer) is interpreted in terms of direct excitation of methyl nitrite with negligible

contributions from substrate mediated processes. Comparisons with gas phase photochemistry of methyl nitrite will be made.

2:40pm SS3-TuA3 Negative Ion Enhancement in Transport of Low Energy F@super -@ Ions Through Rare-Gas (Xe) Films, Q.B. Lu, T.E. Madey, Rutgers, The State University of New Jersey

As part of a program to understand the energy-transfer and chargetransfer processes that affect ion transport through surface layers, we have studied the transmission of low energy (<10 eV) F@super -@ through ultrathin Xe films (up to several monolayers (ML)). The ions are created by electron-stimulated desorption from CF@sub 2@Cl@sub 2@-covered Ru(0001) at ~25 K, and their yields and angular distributions are measured by a digital detector with time-of-flight (TOF) capability. Our new findings include the following. (i) A strong enhancement is observed as 0.5~1.0 ML Xe is deposited onto a fractional monolayer CF@sub 2@Cl@sub 2@ covered surface, and most strikingly, the magnitude of enhancement depends on the intensity of incident electron current. (ii) The negative ion enhancement decreases with increasing precoverage of CF@sub 2@Cl@sub 2@. (iii) The angular distribution of F@super -@ is centered along the surface normal under all conditions. These results will be discussed in terms of several different mechanisms: dielectric screening of the Xe overlayer, coupling between an anionic exciton (Xe@super *-@) and a [CF@sub 2@Cl@sub 2@]@super *-@ state, and charge transfer between a Xe@super *-@ and a F atom.

3:00pm SS3-TuA4 Atomic Scale Femtochemistry: Electron Induced Manipulation of Single CO Molecules on Cu(111) @footnote 1@, L. Bartels, G. Meyer, K.-H. Rieder, Freie Universität Berlin, Germany; D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Low Temperature STM experiments on the excitation dynamics of isolated CO molecules on Cu(111) were performed. CO molecules adsorb on-top on Cu(111). By injection of electrons at a minimum sample bias of 2.4V hops of an adsorbed CO molecule can be induced. These hops either lead to the transfer of the CO onto the STM tip or to its diffusion on the sample with a probability of approx. 1:3. It was found that at constant bias the hopping rate linearly depends on the rate of electron tunneling from tip to sample (i.e. the tunneling current), thus bearing witness of a one-electron excitation at the heart of this process. However, the corresponding quantum yield of approx. 10@super -11@ is ultra-low only. Increasing the bias from 2.4V to 3.0V this rate increases. Spectroscopy with the STM reveals in the given energy range an increased density of states of CO-Cu(111) with reference to bare Cu(111). This was confirmed by two photon photoemission spectroscopy (2PPE) to correspond to the 2@pi@* level of CO. Estimating the energy barrier for CO transfer to the tip from the known CO-Cu vibrational energy, the known gap-distance and the know desorption barrier it comes out to be only insignificantly lower than the desorption barrier itself. This allows to treat this STM-induced excitation process in terms of a stimulated desorption experiment. Then the MGRmodel can be applied to deduce the electron attachment rate from the net quantum yield, if an isotope effect can be found. Carefully comparing the hopping rates on mixed coverages of @super 12@C@super 16@O and @super 13@C@super 18@O an isotope effect of 2.7 can be estimated. This allows to estimate that 0.5% of the tunneling current passes through 2@pi@*. Parametrization of the isotope effect in a semiclassical model with the lifetime of the excited state and its potential slope only yields correct results, if a lifetime of the excited state of less than 3.5fs is assumed. This is in good agreement with the rang of 0.8-5fs obtained by time-resolved 2PPE. @FootnoteText@ @footnote 1@ L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl, Phys. Rev. Lett. 80, 2004 (1998)

3:20pm SS3-TuA5 Surface Femtochemistry: Electrochemistry with Ultrafast Lasers and/or Slow Nanostructures?, J.W. Gadzuk, National Institute of Standards and Technology

Inelastic resonance scattering of hot electrons is the fundamental mechanism underlying many electron-stimulated f-sec processes such as desorption or dissociation of molecules adsorbed on metal surfaces. The hot electrons may be produced by an ultrafast laser pulse or by a solid state tunnel device ("slow nanostructure"). Theoretical reaction rates or yields are given as an integral product of the energy distribution of the flux of incident hot electrons with the the inelastic electron scattering cross section (which contains the influence of the fs intra molecular dynamics). For fixed laser fluence, the temporally narrowest pulses produce the hottest electrons. The flux of laser-generated hot electrons incident upon the surface is given by an electron-temperature-dependent expression that

is akin to the oldtime Richardson equation for thermionic emission. The all important consequences of this fundamental quantum statistical mechanical constraint on our current understanding of the so-called twotemperature model of DIMET (M=Multiple) will be discussed in detail. In contrast, the incident electron flux produced by the tunnel device may be given by the (again oldtime) Fowler Nordheim equation for field emission. In either case, what is important is the energy of the incident electron relative to the energy level position of the acceptor/LUMO/negative-ion resonance of the reactant. But this is exactly one of the fundamental problems in both hardcore electrochemistry and its contemporary embodiments. Implications of the full circle linkage between venerable electron emission/electrochemistry and ultra-modern Surface Femtochemistry will also be visited.

3:40pm SS3-TuA6 Photodesorption of Atomic Hydrogen from Si(100) at 157 nm, X.-Y. Zhu, T. Vondrak, University of Minnesota

Irradiation of the Si(100)-(2x1):H monohydride surface by 157 nm light results in the breaking of the H-Si surface bond and the desorption of atomic hydrogen. This process can be attributed to the resonant photoexcitation of the sigma-sigma* transition of H-Si at the photon energy of 8 eV. The photodesorption cross section is 3×10 @super -21@ cm@super 2@, independent of surface hydrogen coverage. Time-of-flight (TOF) measurement of the photodesorbed atomic hydrogen yields a mean translational energy of = 74 meV. Such a low translational energy is indicative of the short lived electronic excitation on the semiconductor surface. This short-time dynamic process is further explored by wavepacket simulation on ab initio potential energy surfaces.

4:00pm SS3-TuA7 Study on Photon Energy Dependence of Laser-Induced Chlorine Reaction on Si(111), S. Haraichi, F. Sasaki, Electrotechnical Laboratory, Japan

A photo-induced etching is considered as a powerful candidate of the nextgeneration device fabrication process from the view point of extremely low damage. However the atomic mechanism of the photo-induced surface reaction has not been well understood. We have investigated photon energy dependence of laser-induced chlorine reaction on Si(111) to elucidate the resonant reaction of this system using surface reflectance spectroscopy (SRS) and second-harmonic generation (SHG). In the SRS study, reflectance spectra from an initial oxidized, a cleaned 7x7, and a chlorinated Si(111) surface have been measured by the p-polarized light at the incident angle of around 74°, which is Brewster angle of silicon, with the photon energy ranging from 3.0 to 5.0 eV. Reflected lights themselves have a peak at around 3.4 eV involving the direct band gap transition E@sub 1@ in bulk silicon, however, the peak intensity shows no significant change due to the variation of the surface condition. On the other hand, the reflectance spectra have a peak at around 4.4 eV whose value changes remarkably due to the surface condition and is probably concerned with some surface states. The threshold laser fluency of etching reaction dependence on the photon energy ranging from 1.5 to 2.5 eV has been studied by the SHG method. The threshold fluency shows the minimum value at around 2.15 eV whose SH energy of 4.3 eV is almost equal to the above surface originated peak of the reflectance spectra. The time constant of the on- and the off-resonant reaction will also be discussed.

4:20pm SS3-TuA8 Photoinitiated Electron Transfer to Selected Alkyl Bromides Physisorbed on GaAs: The Effects of Alkyl Chain Length on Dissociation Cross-Sections and Fragment Dynamics, *R.M. Osgood Jr., K.A. Khan, N. Camillone III, J.E. Moryl,* Columbia University

Brominated hydrocarbons adsorbed on semiconductor surfaces serve as ideal model systems for investigating the photoinduced chemistry of oriented molecules in the condensed phase. These adsorbates dissociate via attachment of photoexcited substrate electrons giving rise to energetic alkyl and surface-bound bromine fragments. We will describe the effect on the dissociation cross-section and fragmentation dynamics due to systematic variation of the complexity (alkyl chain length) of the adsorbate. The enhancement in the dissociation cross-section with increased chainlength will be discussed in the context of substrate-mediated dissociativeelectron attachment (DEA). Comparison of these observations with those made in the gas-phase DEA of similar haloalkanes allows us to consider the role of the surface in this dissociation process. Increasing the length of the alkyl chain also leads to distinct changes in the alkyl fragment angular distributions. For methyl bromide, the angular distribution is dominated by a focused beam of hyperthermal methyl radicals at 45° (in the [-1,0] direction) from the surface normal. For ethyl and propyl bromide, inelastic scattering of the fragments results in increased importance of a slower diffuse cos@super n@ @theta@ desorption. In addition, significant

retention of alkyl fragments is detected by post-irradiation thermal desorption measurements. Increasing the number of degrees of freedom of the adsorbate dramatically alters the energetics of the ejection of the photofragments from the surface. Velocity distributions of the fragments clearly demonstrate that the energy partitioned into translational motion is strongly reduced when the number of rovibrational degrees of freedom is increased. Quantitative variations in the energy and angular distributions are discussed in terms of changes in energy partitioning with alkyl chain length.

5:00pm SS3-TuA10 Surface Modification on GaAs(110) Induced by 100-3000 eV Electrons, B.Y. Han, K. Nakayama, J.H. Weaver, University of Minnesota

Atomic level modification of semiconductor surfaces induced by 100-3000 eV electrons is demonstrated for the first time. Scanning tunneling microscopy results reveal that single-layer deep vacancies are created randomly on GaAs(110) terraces under conditions typical for low-energy electron diffraction and Auger electron spectroscopy. Small regrowth structures resulting from Ga and As atoms ejected onto the terrace are observed. Surface modification is related to electronic excitations, and we discuss the mechanisms in view of the rate of production of defects at various electron energies. We also discuss the consequences of this electron-induced surface modification.

Applied Surface Science Division Room 307 - Session AS+BI+SS-WeM

Organized Molecular Monolayers

Moderator: H.G. Tompkins, Motorola, Inc.

8:20am AS+BI+SS-WeM1 Structural Characterization of the Outermost Surface Monolayers of CH@sub 3@ and CF@sub 3@ Terminated n-Alkanethiol Monolayers Self-Assembled on Au(111), L. Houssiau, J.W. Rabalais, University of Houston

Time-of-flight scattering and recoiling spectrometry (TOF-SARS) was used for surface elemental and structural characterization of hexa- and heptadecanethiols (C@sub 16@ and C@sub 17@ for short) and of 16,16,16trifluorohexadecanethiol (FC@sub 16@) self-assembled monolayers (SAMs) on a Au(111) surface. The substrate was also characterized after insitu sputtering and annealing by TOF-SARS and LEED in order to identify its crystalline orientation. The azimuthal angle scans performed on the C@sub 16@ samples displayed unique features, indicating well-ordered structures. The recoiling intensities of the H and C atoms exhibited a clear 60° periodicity, with H recoil maxima and C recoil minima displayed at 30° from the substrate nearest-neighbor directions. Several models were tested by means of classical ion trajectory simulations using the scattering and recoiling imaging code (SARIC). The molecular length, tilt angle, and twist angle were varied in the simulations. Good agreement between the experiments and simulations for both C and H signals was obtained for a (@sr@3x@sr@3)R30 structure of SAM lattice, with the molecules tilted along the substrate nearest-neighbor directions by 35° from the surface normal. Moreover, a twisting of the molecular plane by 55° from the plane normal to the surface had to be considered in order to reproduce the H angular variations. Similar measurements on the C@sub 17@ samples showed much weaker variations for the H and C recoil intensities. This is believed to be due to the high tilt angle of the end methyl group. The FC@sub 16@ samples showed the presence of C and F atoms in the surface layer. No evidence for H and C recoil azimuthal variation was observed on the FC@sub 16@ samples, although a weak azimuthal periodicity was noticed for the F recoils.

8:40am AS+BI+SS-WeM2 Fundamental Studies of Phase Transitions in Functionalized Amphiphile Monolayers, *G.E. Poirier*, National Institute of Standards and Technology

Alkanethiol molecules chemisorb strongly to noble metal surfaces. Intermolecular dispersion forces compress the molecules into a dense, commensurate, crystalline film that spontaneously terminates growth at one molecular monolayer. The thickness of the film, its dielectric constant, and the physical properties of the exposed surface can be controlled by changing the length of the alkyl chain, its degree of saturation, and its terminal functional group, respectively. These systems are therefore desirable in any application requiring control of the adhesive, tribological, or electron transfer properties of metal surfaces. This talk will outline experiments in which methyl-terminated alkanethiol monolayers were prepared by vapor deposition onto clean Au(111) in ultra-high vacuum and characterized in-situ using molecular-resolution scanning tunneling microscopy.

9:00am AS+BI+SS-WeM3 Characterization of Fluorinated Monolayers, D.G. Castner, University of Washington INVITED

Self assembly processes have made it possible to prepare organic monolayers with well-defined surface structures and chemistries. The ability to systematically vary the surface structure and chemistry of these self-assembled monolayers (SAMs) provide an excellent method for examining the relationship between the surface properties of a film and its performance in a given application (e.g., cell culture). To develop these relationships requires detailed characterization of the surface composition, molecular structure, orientation, and topography of the films with techniques such as XPS, ToF SIMS, NEXAFS, and STM. How the methods and molecules used to form fluorinated films affect the resulting film structure will be discussed. The degree of ordering and relative orientation in SAMs prepared with perfluoroalkyl thiols depend on the length of the fluorinated tail. Although SAMs prepared from thiols with long perfluoroalkyl tails are highly ordered, their stability is limited by the single point attachment of the Au-S bond. This stability can be increased by using grafted copolymers containing both perfluorinated and alkanethiol side chains to generate multipoint attachment of each polymer chain. However, this method of increasing film stability also results in a decreased degree of film orientation. Typically films prepared using polymers with perfluorinated side chains are highly disordered. Only at high

concentrations of perfluoroalkyl side chains (>50%) is any ordering detected in polymeric monolayers. Other methods, such as trifluoroacetic anhydride derivatization of hydroxyl-terminated alkanethiols can also be used to produce fluorinated surfaces. Depending on the derivatization system, the high degree of ordering in the starting SAM can be retained after derivatization.

9:40am AS+BI+SS-WeM5 Controlling Defects in Self-Assembled Monolayers, J.J. Jackiw, J.J. Arnold, J.A. Johnson, T.D. Dunbar, T.L. Spiva, D.L. Allara, P.S. Weiss, The Pennsylvania State University

Much is known about the formation, structure, stability, and properties of alkanethiolate monolayers on Au (111). We have begun to explore the effects of changing the molecule-surface linkage. In the cases of alkanethiolates and alkaneselenolates, monolayers can be made respectively from: thiols and selenols, disulfides and diselenides, and by deprotecting alkanethioacetates and alkaneselenoacetates, which are less prone to oxidation. Our experiments probe monolayer structures and defects resulting from the deposition of dodecanethiol, didodecane disulfide, didodecane diselenide, dodecaneselenol, and in situ deprotected dodecanethioacetate and dodecaneselenoacetate. We compare the structures and defects in the resulting monolayers. The defect identities and densities are important in determining the properties of the films, especially our ability to manipulate their structures and compositions.

10:00am AS+BI+SS-WeM6 New Preparation Methods for Self Assembly of Alkanethiolates on III-V Semiconductor Surfaces, C.K. Mars, D.L. Allara, Pennsylvania State University

The ability to control the chemical composition of III-V surfaces is vital in semiconductor technology. Alkanethiolate monolayers prepared from thiol melts at temperatures near 100°C have been shown to mimic the improved electronic passivation properties seen on III-V semiconductors with Na@sub 2@S and NH@sub 4@S@sub x@ treatments. We have developed a new process by which these films can be grown reliably in a highly organized state from millimolar ethanol solutions near 50°C. In addition, by adding controlled amounts of base to these solutions, the degree of organization as determined by IR spectroscopy and contact angle measurements, can further be improved. This new process has allowed us to deposit a wide variety of films including aromatic and functionalized molecules as well as layers anchored by other chalcogenide elements.

10:20am AS+BI+SS-WeM7 The Effect of Solvents and Electrical Fields on the Molecular Conformation in Organic Monolayers, *M. Grunze*, *M. Buck*, *F. Eisert, M. Zolk, P. Harder*, University of Heidelberg, Germany; *A. Pertsin*, Russian Academy of Sciences, Russia; *H.J. Kreuzer*, Dalhousie University, Canada INVITED

The molecular conformation in self-assembled monolayers (SAMs) of functionalized alkanethiols is affected by the presence of solvents. The polarity and ability of the solvent molecules to form hydrogen bridge bonds, and the lateral density in the SAMs determines the orientation of the terminal functional moiety at the organic film/solvent interface. We will discuss our in situ Sum Frequency Generation (SFG) and protein adsorption experiments on methyl- and oligo(ethylene glycol)-terminated self-assembled alkanethiolate monolayers, and present atomistic force field calculations to explain our data. These results show that spectroscopic measurements taken in vacuum or ambient atmosphere are not necessarily representative for the molecular structure and chemical nature of organic surfaces immersed in a liquid.

11:00am AS+BI+SS-WeM9 Nanometer-Scale Design and Fabrication of Polymer Interfaces using Polydiacetylene Monolayers, *M.D. Mowery*¹, *M. Cai*, University of Michigan; *H. Menzel*, University of Hannover, Germany; *C.E. Evans*, University of Michigan

The selective control of polymer interfacial characteristics such as viscoelasticity and electronic properties is crucial for numerous important applications from sensor design to device fabrication. In this work, robust interfacial polymer films are successfully fabricated within a single molecular layer with nanometer-scale control of the polymer physical structure. The formation of these unique polymer films is accomplished by the spontaneous assembly of alkyl disulfide precursors containing conjugated diacetylene groups at the gold-solution interface. The resultant well-defined monomer assembly is covalently linked through UV photopolymerization, forming a highly conjugated polymer backbone parallel to the surface. Nanometer-scale control of the interfacial structure is accomplished by manipulating the vertical position of the polymer

backbone within the single layer assembly. Additionally, photo-templating affords lateral control over the formation of polymer domains. These subtle variations in physical structure have a profound impact on the global electronic and viscoelastic properties of the polymer interface. The impact of these structural variations is demonstrated by surface infrared and Raman spectroscopy as well as electrochemical capacitance, heterogeneous electron transfer, and reductive desorption measurements. Furthermore, AFM is utilized to physically image the interfacial structure and evaluate the polymer viscoelastic properties. Finally, the application of these monolayer polymers for lithographic applications and the implications for interfacial design are discussed.

11:20am AS+BI+SS-WeM10 Bias-dependent Contrast in STM Images of Phenyloctadecylethers, *I.H. Musselman*, *H.S. Lee, S. Iyengar*, University of Texas, Dallas

A homologous series of para-substituted phenyloctadecylethers (X-POEs, X = H, Cl, Br and I) was prepared and characterized using @super 1@H NMR and GC/MS. Scanning tunneling microscopy (STM) images were acquired from monolayers of the ethers physisorbed onto highly oriented pyrolytic graphite. The contrast exhibited by the X-POE molecules in these images varied as a function of tip-sample bias. For example, STM images acquired at biases of approximately -0.5 to -0.6 V (sample negative) exhibited a dim alkyl tail and a series of bright spots corresponding to functionalities in the head group (e.g. halogen, phenyl group, oxygen). However, at biases more negative than -1.2 V, the largest contribution to contrast was observed for the alkyl tail (e.g. octadecyl group). A comparison of STM images of the adsorbed X-POE molecules with electron density contours calculated using HyperChem suggested a bias-dependent participation of individual bonding molecular orbitals to tunneling. A resonance tunneling mechanism between the tip and molecular orbitals adjacent to and including the highest occupied molecular orbital (HOMO) is proposed.@footnote 1@ @FootnoteText@ @footnote 1@ The support of this research by a grant from the Robert A. Welch Foundation is gratefully acknowledged.

11:40am AS+BI+SS-WeM11 Self-Assembling Trichloro- and Trimethoxysilanes on TiO@sub 2@(100) Crystal, *R. Magnée*, *J.-J. Pireaux*, LISE -Facultés Universitaires Notre-Dame de la Paix, Belgium

Trichlorosilanes (CH@sub 3@(CH@sub 2@)@sub n@SiCl@sub 3@, n = 1, 7, 17) and trimethoxysilanes (CH@sub 3@(CH@sub 2@)@sub n@Si(OCH@sub 3@)@sub 3@, n = 2, 7, 17) SAM's were deposited by dipping a TiO@sub 2@ (100) crystal in a 10@super -3@M toluene solution for 4 hours. The titanium dioxide surface was prepared by Ar@super +@ sputtering, annealing in UHV to get a clear LEED (1x3) pattern, then exposed to atmosphere before dipping. Silane molecules need H@sub 2@O or a hydroxylated surface to react but it was not necessary to hydroxylate the TiO@sub 2@ because of the air exposure. Hydroxylation was confirmed by FT-IR and XPS. X-Ray and Ultra-violet Photoelectrons Spectroscopy (XPS, UPS) were then used for the SAM's charaterization. We expect a siloxane network to appear at the interface in addition to the Ti-O-Si bonds. XPS results show that the silane groups do indeed bind to the TiO@sub 2@ surface but that some defects are also present at the interface: for n=17 the amount of OH groups is 4 % of the total oxygen signal while this value is doubled for n=7. Probably due to the higher reactivity of chlorine atoms, trichlorosilanes present less defects than trimethoxysilanes. By comparison with theoretical calculations,@footnote 1@ UPS provides information on the alkane chain conformation: we show that longer silane molecules (n=17) are grafted in a zigzag planar conformation, while n=7 molecules seem to present chain defects. This is consistent with the self-assembling process that depends on long-range interchain interactions. For the smallest chains (n=1,2), the XPS C/Si ratios are always too high, suggesting some contamination: this is probably due to solvent incorporation in the layer. HREELS analysis (not yet performed at the date of abstract submission) may help to get more information on the order of the layers. @FootnoteText@ @footnote 1@ A.-S. Duwez, S. Di Paolo, J. Ghijsen, J. Riga, M. Deleuze, J. Delhalle, J. Phys. Chem. B, 101 (1997) 884.

Surface Science Division Room 308 - Session SS1-WeM

Physics of Semiconductors

Moderator: J. Krim, North Carolina State University

8:20am SS1-WeM1 Medard W. Welch Award Lecture - Optical Spectroscopy of Surfaces and Interfaces: Progress and Opportunities, D.E. Aspnes¹, North Carolina State University INVITED

9:00am SS1-WeM3 Chemistry and Intermolecular Interactions of Nitridation and Oxidation Precursors on Si(100)-(2x1), K.T. Queeney, Bell Laboratories, Lucent Technologies; A.B. Gurevich, Columbia University; X. Zhang, E. Garfunkel, Rutgers University; J. Eng, Jr., B.B. Stefanov, K. Raghavachari, Y.J. Chabal, Bell Laboratories, Lucent Technologies

The manner in which various molecules adsorb, dissociate and interact on silicon surfaces can dramatically affect their subsequent incorporation into the silicon substrate and thus the nature of compounds formed at higher temperatures.@footnote 1@ We have studied mechanisms leading to oxidation, nitridation and oxynitridation of silicon via investigations of the structure and reactivity of H@sub 2@O, NO, NH@sub 3@ and N@sub 2@H@sub 4@ on Si(100)-(2x1). Dissociation of these molecules on a single Si-Si dimer yields well-defined structures which are identified using highresolution infrared absorption spectroscopy in a new, sensitive transmission geometry, together with density functional cluster calculations. This powerful combination of theory and experiment also reveals subtle frequency shifts associated with the inter-dimer interactions of surface intermediates. For example, in the case of water adsorption, hydrogen bonding between two hydroxyl groups on neighboring dimers leads to splitting of all the observed vibrations (@nu@(SiO-H), @nu@(Si-H), @delta@(Si-H), @delta@(Si-OH) and @nu@(Si-O)). The magnitude of these splittings (@>=@ 10 cm@super -1@) allows definitive characterization of these interactions with infrared spectroscopy. For instance, two @nu@(OH) peaks corresponding to coupled hydroxyls appear at 3675 and 3660 cm@super -1@, well resolved from the uncoupled O-H stretch at 3684 cm@super -1@; likewise, the two @nu@(Si-O) features of coupled hydroxyl groups are split to 14 cm@super -1@ above and 12 cm@super -1@ below @nu@(Si-O) of the uncoupled species. Similar effects are observed after co-adsorption of water and ammonia. Such interactions provide a natural mechanism for local oxygen and nitrogen agglomeration during the thermal evolution of these surfaces, observed by monitoring changes in @nu@(Si-H) as well as Si-N and Si-O vibrations as atomic nitrogen and oxygen insert into Si backbonds at higher temperatures. @FootnoteText@ @footnote 1@M. K. Weldon, B. B. Stefanov, K. Raghavachari and Y. J. Chabal, Phys. Rev. Lett. 79, 2851 (1997).

9:20am SS1-WeM4 Spectromicroscopy Evidence of Lateral Inhomogeneities for Metal-(III-VI) Semiconductor Interfaces, *M. Zacchigna*, *H. Berger*, Ecole Polytechnique Federale, Switzerland; *G. Lorusso*, *F. Cerrina*, University of Wisconsin, Madison; *G. Margaritondo*, Ecole Polytechnique Federale, Switzerland

We exploited the very high lateral resolution of the MAXIMUM beamline on ALS to study microscopic lateral variations of semiconductor interface barriers. The capability to analyze the chemical properties with high lateral resolution often reveals unexpected overlayer-substratechemical reactions and links between such reactions and lateral barrier inhomogeneities. The experiment first studied lateral band bending changes in metalsemiconductor junctions for several interfaces between Au or Al and different III-VI compounds. By taking photoemission spectra on a series of microscopic spots along the interface is possible to detect the band bending with high lateral resolution. A novel way to perform this type of measurements, giving the "image" of the band bending, will be presented. The second and more interesting part of our study concerns the search for inhomogeneities in the first steps formation of metal-(III-VI) interfaces. We did discover such inhomogeneities in several prototypical interfaces, expanding and corroborating preliminary data on Au-GaSe interface. Furthermore, for the first time we did establish the sought link between barrier fluctuations and local chemical properties

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9:40am SS1-WeM5 Direct Determination of the Interplay between Gas-Surface Reactivity, Thin Film Strain and Alloy Surface Segregation: Growth of Strained Heteroepitaxial Si@sub 1-x@Ge@sub x@ Thin Films on Si(100), A.M. Lam, Y.J. Zheng, J.R. Engstrom, Cornell University

Silicon-Germanium alloys have attracted attention for more than a decade. The addition of Ge to Si epitaxial films leads to a variety of effects and phenomena, some well understood, some not. Almost untouched are phenomena related to the dissociative adsorption of the relevant thin film precursors on surfaces of the growing alloy. Knowledge of the corresponding sticking coefficients is key to developing relationships between gas phase, surface and sub-surface/bulk compositions. Concerning alloy (Ge) segregation, virtually all work conducted to date has relied on a single in situ experimental probe. We shall present here a comprehensive study of the heteroepitaxial growth of Si@sub 1x@Ge@sub x@ alloys on Si(100) employing no less than 3 complementary in situ probes: supersonic molecular beam scattering, x-ray photoelectron spectroscopy (XPS), and low-energy ion scattering spectrometry (LEISS). Our results for the first time demonstrate the importance of strain in determining gas-surface reactivity in these heteroepitaxial alloys-- the reactivity of the strained Si@sub 1-x@Ge@sub x@ overlayers is not simply an appropriate combination of pure component (bulk, relaxed) reactivities. On the other hand, use of the complementary in situ surface analyses of XPS and LEISS has allowed us to determine both the extent and nature of Ge surface segregation, and its dependence on film growth conditions. In all cases the surface Ge concentration exceeds that found in the bulk (often by an order of magnitude). A two-site model (involving surface and bulk) cannot account for both the XPS and LEISS results, rather a model invoking Ge enrichment in the subsurface layers is required to explain the data.

10:00am SS1-WeM6 Ballistic Electron Emission Microscopy Studies of Tunneling to Surface and Bulk States on Cu (111) Thin Films, W.H. Rippard, M.K. Weilmeier, R.A. Buhrman, Cornell University, US

Thin bilayer films consisting of a thin Au layer and an overlayer of Cu have been grown on the surface of hydrogen passivated Si (111) and Si(100) wafers. UHV STM measurements reveal that these bilavers consist of ~10 nm grains with surfaces that are either atomically flat or transversed by only a few atomic step-edges. X-ray diffraction indicates that these films, for both substrates, consist nearly completely of (111) normal oriented grains. When ballistic electron emission microscopy (BEEM) measurements are made on these systems, a strong contrast is seen between the BEEM current when the STM tip is over a flat surface and when it is positioned at a grain boundary or step edge, with the higher BEEM current occurring in the latter case. This contrast in current can be as much as a factor of three, depending on the sharpness of the STM tip, and occurs for both (100) and (111) oriented substrates. STM spectroscopy measurements indicate the presence of pronounced surface states on the flat areas of the Cu surface and an absence of thes states at grain boundaries and steps. We conclude that the low BEEM current which occurs when the STM tip is positioned over a Cu surface mesa is the result of tunneling predominately to empty surface states, while at grain boundaries and step edges the STM tip is able to tunnel more strongly to the empty bulk states of the Cu, which enhances the BEEM signal. This observation provides a strong demonstration of the role of the metal band structure in determining the amplitude of the BEEM signal, even in the case of the noble metals, and demonstrates a new means by which the degree of coupling between bulk and surface states on the (111) normal surface of Cu, Au and Ag can be determined by BEEM.

10:20am SS1-WeM7 Current-Voltage Measurements of Ultrathin Metal-Si(111) Sensors, *H. Nienhaus*, *H.S. Bergh*, *B. Gergen*, University of California, Santa Barbara; *A. Majumdar*, University of California, Berkeley; *E.W. McFarland*, *W.H. Weinberg*, University of California, Santa Barbara

A novel microfabricated Si-based device structure was developed in order to characterize the transport properties of thin metal films on Si(111) ranging from 10 Å to 150 Å. Metals were evaporated onto the device under ultrahigh vacuum conditions. The evaporation temperature was varied between 130 and 180 K. The design of the device allowed zero-force electrical contacts to the very thin metal films on silicon for current-voltage (I/V) measurements. The resulting I/V curves were analysed within the thermionic emission theory. The change of Schottky-barrier height, ideality factor and serial resistance was monitored as a function of film thickness and temperature. Cu, Ag and Fe films were investigated on Si(111). Generally, an improvement of the rectifying properties was observed with increasing thickness. To study the temperature dependence, Cu films of about 60 Å were annealed to room temperature. This treatment led to a significant increase of the barrier height from 0.45 to 0.65 eV and a decrease of the ideality factor from about 2.5 to values close to 1.

Subsequent cooling of the annealed samples conserved the excellent rectifying properties. This finding indicates that annealing of low-temperature deposited films reduces the inhomogeneity of the contact barrier height. Further evaporation of Cu onto annealed diodes led again to lower barrier heights and larger ideality factors. First results suggest that the devices are suitable sensors for detecting hot charge carriers created by gas-surface reactions.

10:40am SS1-WeM8 Electroless Deposition of Au onto H-Si(111), I. Suni, R. Srinivasan, Clarkson University

Electroless deposition of Au from aqueous HF onto p-type H-Si(111) has been studied by electrochemical methods, atomic force microscopy (AFM), Rutherford backscattering (RBS), and surface second harmonic generation (SHG). The H-terminated Si(111) surface is prepared by HF etching prior to Au deposition. We have found evidence that Au deposition occurs by a two-step process, where initial deposition of AuCN is rate-limited by diffusion, while subsequent reduction of Au is rate-limited by surface reaction involving a fluoride-containing species. The growth of Au nanoclusters can be monitored by SHG through the development of the surface plasmon resonance, which occurs above a threshold cluster size of about 2 nm. The SH signal goes through a temporal maximum and then declines again due to interdiffusion of Au and Si. Surface kinetics can then be analyzed by manipulating the solution phase equilibria and following the effects on Au reduction by SHG. This analysis reveals that HF, not HF@sub 2@@super -@, is the mechanistically important species and that Au reduction is half-order in HF.

11:00am SS1-WeM9 Growth of Si@sub 1-x@Ge@sub x@ on Si(011): Kinetics, Surface Structure, and Morphological Evolution, N. Taylor, H. Kim, T. Spila, P. Desjardins, J.E. Greene, University of Illinois, Urbana-Champaign

Strained Si@sub 1-x@Ge@sub x@/Si(011) heterostructures provide additional degrees of freedom over the more common Si@sub 1x@Ge@sub x@/Si(001) system for bandgap engineering. The maximum film/substrate conduction band offset is predicted to be substantially larger, the optical bandgap decreases more rapidly with increasing x, and optical selection rules allow hole-intersubband transitions to be excited by light parallel to multiple quantum well layers. In this investigation, Si@sub 1-x@Ge@sub x@ layers with x @<=@ 0.35 were grown on Si(011) by gassource molecular beam epitaxy (GS-MBE) using Si@sub 2@H@sub 6@ and Ge@sub 2@H@sub 6@ at T = 400-950 °C. The growth kinetics are a function of the following complex surface reconstructions: 16x2 at x < x@sub c@ and 2x8 at x > x@sub c@. The critical Ge concentration x@sub c@ ranges from 0.10 at T = 475 °C to 0.06 at T = 650 °C. As the temperature is raised from 650 to 725 °C, the surface gradually transforms to a 1x1 reconstruction for all x. Temperature-programmed desorption (TPD) measurements show that the 16x2 unit cell consists of 16 adatoms and 8 pi-bonded dimers, resulting in 32 dangling bonds compared to 64 for the 1x1 surface. In the surface-reaction-limited growth mode at T < 500 °C, the rate-limiting growth step is hydrogen desorption from the Si and/or Ge monohydride. The surface structure consists of uniformly-sized terraces, according to atomic force microscopy (AFM) measurements. In the fluxlimited regime at T = 500-650 °C, the growth rate is limited by the surfacedependent reactive sticking coefficient and the morphology is characterized by extensive faceted pitting. At T > 650 °C, the growth rate rises with temperature as the dangling bond coverage increases with the surface transformation to a 1x1 reconstruction. At these high temperatures, the surface morphology consists of long ridges oriented along the [100] direction.

11:20am SS1-WeM10 Surface Structural Study of Ultra-Thin Si (111) on SiO@sub 2@, M. Noh, University of Tennessee and ORNL; A.P. Baddorf, Oak Ridge National Laboratory; H.H. Weitering, University of Tennessee and ORNL

Si on insulator (SOI) material is important for extension of metal-oxide silicon (MOS) technology development in the next generation of microelectronics. Technological requirements have led to interest in very thin SOI layers. The surface structure of ultra-thin layers of (111) oriented SOI has been investigated for the first time, using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). SOI samples were prepared using the Separation by Implanted Oxygen (SIMOX) method, then characterized by Rutherford backscattering spectrometry (RBS) to determine the thickness and quality of the Si overlayer. LEED observations from a 2000 Å thick Si layer on 5000 Å SiO@sub 2@ reveal a sharp 7x7 diffraction pattern, well known for bulk Si (111) surfaces. STM images of the same surface show nearly defect free 7x7 surface reconstructions with

terrace lengths exceeding 1000 Å. These observations reveal that the surface of a thin Si (111) film on SiO@sub 2@ can be fabricated with a comparable degree of structural perfection as the (111) surface of bulk Si. The quality of the (111) SOI surface was monitored as a function of Si top layer thickness after thinning by dry oxidation and stripping. Results are compared to previous images of (100) SOI surfaces.@footnote 1,2@ @FootnoteText@ @footnote 1@K.C. Lin, O.W. Holland, L.C. Feldman, and H.H Weitering, Appl. Phys. Lett. 72 (1998) 2313. @footnote 2@Oak Ridge National Laboratory (ORNL) is managed by Lockheed Martin Energy Research Corp. for the U. S. DOE under contract number DE-AC05-96OR22464.

11:40am SS1-WeM11 Reconstructed Oxide Structures Stable in Air: Monolayer Silicate on Hexagonal SiC Surfaces, U. Starke, J. Schardt, J. Bernhardt, K. Heinz, University of Erlangen-Nuernberg, Germany

Ultrathin oxide layers on hexagonal SiC surfaces were studied using lowenergy electron diffraction (LEED) and Auger electron spectroscopy (AES). SiC(0001) and SiC(000-1) samples were ex situ prepared using thermal hydrogen etching or microwave powered hydrogen plasma treatment. A well ordered (@sr@3x@sr@3)R30° reconstructed surface is observed by LEED immediately upon introduction into vacuum. The samples contain oxygen of approximately one layer equivalent bonded to Si atoms as indicated by AES. By a full dynamical LEED structure analysis carried out for the SiC(000-1) surface the crystallographic structure is determined: The silicon oxide is arranged as a silicate (Si@sub 2@O@sub 3@) layer ontop of the SiC substrate forming rings of the (@sr@3x@sr@3)R30° periodicity with twofold coordinated oxygen atoms in the topmost position. The oxygen incorporation into the surface is presumably caused by a rapid oxidation in air of the well ordered topmost substrate bilayer. The extreme stability of the resulting surface reconstruction is caused by the absence of dangling bonds in the surface terminating silicate layer. Similar results are indicated for the SiC(0001) surface by preliminary LEED calculations.

Surface Science Division Room 309 - Session SS2-WeM

Gas-Surface Dynamics

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

8:20am SS2-WeM1 Monte-Carlo Simulation of the Adsorption and Desoption of CF@sub 4@ on Cu/CuO(110), *M. Hohage*, University of Wisconsin, Madison; *V. Diercks*, Forschungszentrum Jülich, Germany; *P. Zeppenfeld*, Universität Linz, Austria; *M.G. Lagally*, University of Wisconsin, Madison

The unique adsorption and desorption dynamics of CF@sub 4@ on the Cu/CuO(110) stripe phase is reproduced by a Monte-Carlo simulation to reveal the underlying processes on the molecular scale. As observed by means of thermal energy atom scattering (TEAS), at temperatures above 20K CF@sub 4@ adsorbs preferentially on the CuO stripes.@footnote 1,2@ A comparison of these adsorption measurements with a Monte-Carlo simulation is used to determine the parameters of the CF@sub 4@ diffusion on Cu and on CuO. With the knowledge of these diffusion parameters the more complicated desorption of CF@sub 4@ is analyzed. TEAS and TDS measurements show that annealing the sample with a rate of 1K/s leads to desorption between 55K and 70K@sub 2@. Two wellseparated peaks occur. The peak at lower temperature is related to the desorption from the Cu stripes, whereas the peak at higher temperatures is related to the desorption from the CuO stripes. This desorption behavior as well as shifts of the desorption peaks in dependence of the composition of the surface (amount of O on the surface) is reproduced by a Monte-Carlo simulation including the previously determined diffusion parameters as a fixed input. The different features of the desorption spectra, i.e. peak positions, peak shifts, and peak shapes, are assigned to binding energies and diffusion barriers on the molecular scale. This allows the development of a consistent model of the CF@sub 4@ adsorption and desorption dynamics. *Supported by NSF and by the Alexander von Humboldt-Stiftung @FootnoteText@ @Footnote 1@P. Zeppenfeld, V. Diercks, Ch. Tölkes, R. David, and M. A. Krzykowski, Appl. Surf. Sci. (1998) in print. @Footnote 2@V. Diercks, Ph.D. thesis, Bonn 98

8:40am SS2-WeM2 Adsorption, Absorption, and Abstraction of Hydrogen on Cu(111) Surfaces, Th. Kammler, J. Küppers, Universität Bayreuth, Germany

The interaction of H(D) with Cu(111) surfaces and the abstraction of D adsorbed on Cu(111) by H was studied with thermal desorption

spectroscopy and direct product rate measurements. H atoms were produced in a W tube heated at 2000 K. H atoms directed at clean Cu(111) surfaces at 85 lead to H adsorption with an initial sticking coefficient of 0.19. After completion of the adsorbed layer with a saturation coverage of 0.25, further H uptake leads to H absorption. Adsorbed H desorbs as H@sub 2@ via a second order process in the temperature range 250 to 400 K. Absorbed H desorbs as H@sub 2@ starting at 150 K and peaking around 200 K in a first order process. The interaction of H atoms with a saturated D layer, @THETA@=0.25, at 85 K leads to the formation of gas phase HD and D@sub 2@. The kinetics of HD formation as a function of H atom fluence follows a strict Eley-Rideal-type phenomenology: a HD rate jump at reaction start and a subsequent exponential decay of the HD rate. However, the D@sub 2@ product suggests that the reaction mechanism is not of an Eley-Rideal but of hot atom type. An analysis of the abstraction kinetics in terms of hot-atom mechanisms reveals that on Cu(111) the reaction probability of hot atoms is of the same magnitude as their sticking probability at empty surface sites. About 1% of the adsorbed D appears in the D@sub 2@ reaction channel. The abstraction cross section towards HD is 2.3 Å@super 2@. The HD yields and rate steps scale with the D coverage at reaction start, the D@sub 2@ yields and rate steps scale with the square of the D coverage. Absorbed D cannot be abstracted by gas phase H. The kinetics of HD formation is independent of the H flux.

9:00am SS2-WeM3 A Comparison of State-Resolved Studies of Reaction and Inelastic Scattering for H@sub 2@ with Palladium and Copper Surfaces, E. Watts, University of Texas, Austin; M. Gostein, Massachusetts Institute of Technology; G.O. Sitz, University of Texas, Austin INVITED We report results of molecular beam experiments of hydrogen scattering from single crystal palladium and copper surfaces. These two materials represent a reactive and unreactive substrate, respectively, for hydrogen dissociation at low (50-70 meV) incident energy. Because the reaction has strong geometrical and dynamical requirements, features of the potential energy surface are evidenced in the inelastic scattering of those molecules which do not react. This will be demonstrated by comparing scattering distributions for the two surfaces. In addition we have observed efficient loss of initially vibrationally excited H@sub 2@, and have measured the probability that this loss occurs via relaxation into the ground vibrational state for selected final rotation states. For scattering from Pd, an energy balance for the H@sub 2@ degrees-of-freedom indicates that a substantial amount of energy is lost to the surface during the relaxation.

9:40am SS2-WeM5 Energy Dependent Al(111) Oxidation Kinetics, H. Ternow, I. Zori@aa c@, M. Zäch, B. Kasemo, Chalmers University of Technology, Sweden

We have investigated the oxidation kinetics of the Al(111) surface at different O@sub 2@ kinetic energies, using molecular beam technique, Auger electron spectroscopy, AES, and surface plasmon spectroscopy. The central issue we concentrate in this report is how the oxide growth kinetics depends on kinetic energy of the impinging O@sub 2@ molecules. A series of oxygen uptake experiments, a la King and Wells, were performed for two oxygen beam energies yielding low (0.8) initial dissociative sticking probabilities. The total coverage (chemisorbed plus oxidic oxygen) was increased in steps of 0.1 ML until the surface was saturated with oxygen. Between each step the surface was analyzed by AES and surface plasmon measurements. Al(LVV) transitions influenced by oxygen chemisorption and oxide formation were measured as a function of the total amount of oxygen on (in) the sample for different oxygen beam energies. We find the appearance of oxide in a submonolayer regime at a threshold coverage which depends on oxygen beam energy. Furthermore, the growth kinetics of the oxidic phase is also energy dependent. We attribute the latter to energy and coverage dependent dissociation dynamics, resulting in an energy dependent distribution of oxygen atoms among available adsorption sites. Surface plasmon spectroscopy (plasmon energy and lifetime dependence on total oxygen coverage) also reflects the existence of the well defined threshold for oxide appearance as well as heterogeneous distribution of chemisorbed and oxidic phases on the surface. A simple kinetic model which accounts for these observations is presented.

10:00am SS2-WeM6 Initial Stages of Al(111) Oxidation by Oxygen -Temperature and Surface Morphology Effects, V. Zhukov, I. Popova, J.T. Yates, Jr., University of Pittsburgh

The mechanism of oxygen chemisorption and the oxidation of aluminum is again of interest in the light of recent STM studies on Al(111).@footnote 1,2@ We have used X-Ray Photoelectron Spectroscopy (XPS) and High Resolution Electron Energy Loss Spectroscopy (HREELS) to carefully

examine the temperature dependence of the AI(111) oxidation kinetics in the range 95-773 K. The onset of oxide formation was detected near 473 K at the low oxygen coverages investigated here. Both activated and nonactivated adsorption channels have being found depending on surface temperature and the degree of oxide formation, causing nonmonotonic behavior of the sticking coefficient versus temperature. These results are discussed in terms of a one-dimensional potential energy diagram. Surface defects along with the presence of the oxide structures have been found to influence the kinetics of O@sub 2@ adsorption. The importance of careful surface preparation and smooth surface morphology for the reproducible adsorption measurements are demonstrated in this work. Coverage sensitive HREELS measurements are highly dependent upon surface conditions, and these results may rationalize contradictions present in the literature. Work supported by AFOSR. @FootnoteText@ @footnote 1@H. Brune, J. Wintterlin, J. Trost, G. Ertl, J. Wiechers, R.J. Behm, J. Chem. Phys., 99 (1993) 2128. @footnote 2@J. Trost, H. Brune, J. Wintterlin, R.J. Behm, G. Ertl, J. Chem. Phys., 108 (1998)1740.

10:40am SS2-WeM8 Comparison of Chemical Selectivity and Kinetic Energy Release in Si@sub (s)@ + ICl@sub (g)@ and H@sub (g)@ + ICl@sub (g)@, K.A. Pettus, T. Ahmadi, E. Lanzendorf, A.C. Kummel, University of California, San Diego

The chemisorption of ICI on the Si(111)-7x7 surface is comparable to the gas reaction of ICI and hydrogen. ICI chemisorbs onto Si(111)-7x7 by two mechanisms: dissociative chemisorption and abstractive chemisorption. Abstractive chemisorption, in which one halogen atom of ICI bonds to the silicon surface while the other is ejected into the gas phase, is the dominant chemisorption mechanism for ICl/Si(111)-7x7. Multiphoton ionization (205 nm MPI) spectroscopy and time-of-flight (TOF) mass spectrometry were used to determine that the ratio of iodine-selective abstraction to chlorine-selective abstraction is at least 34 +/- 4 :1. Furthermore, the chemical selectivity of ICl + Si(111)-7x7 is greater than the chemical selectivity of the gas phase reaction of H +ICl where the ratio of formation of HI to HCl is 4:1.@footnote 1@ In both reactions, the iodine atom of ICI molecules is more reactive than the chlorine atom because the pi @sub x,y@ @super *@ antibonding orbital (the orbital that reacts with any other species) consists primarily of atomic iodine orbitals.@footnote 2@ The difference in the chemical selectivities of the silicon surface and gaseous hydrogen reactions with ICl is due to the ability of the silicon surface to rotationally steer ICI molecules and the inability of silicon to migrate between the iodine and chlorine atoms in ICl . The median translational energies of the abstracted halogen atoms were determined to be 0.18 +/- 0.04 eV for chlorine atoms and 0.53 +/-0.27 eV for iodine atoms which are a small fraction (14% for ejected iodine atoms and 9% for ejected chlorine atoms) of the total reaction exothermicities. The low translational energy of ejected atoms is due to the fact that the iodine-chlorine bond of ICI lengthens as the Si-I bond contracts and there is little repulsion energy attributed to the Si-I-Cl transition state. @FootnoteText@ @footnote 1@J.C. Polanyi, Chemica Scripta, 27, 229 (1986) @footnote 2@J.D. McDonald, P.R. LeBreton, Y.T. Lee, and D.R. Herschbach, J. Chem. Phys., 56, 769 (1972)

11:00am SS2-WeM9 Hydrogen Atom Induced Decomposition of Water Adsorbed on Si(100), L.M. Struck, National Institute of Standards and Technology, US; S.A. Buntin, National Institute of Standards and Technology The reaction of incident atomic hydrogen with water adsorbed on Si(100) is investigated using multiple internal reflection infrared (IR) spectroscopy. The clean Si(100) surface is exposed to water forming a half monolayer of both SiH and SiOH surface species. Atomic hydrogen is generated by hot filament decomposition of molecular hydrogen. The evolution of the adlayer is probed with IR spectroscopy by following the silicon hydride and hydroxyl stretch features as a function of atomic hydrogen exposure for different isotopic reaction combinations (e.g., incident D atoms on adsorbed H@sub 2@O). The results show a concomitant decrease in the Si-H and O-H stretch features with increasing D atom exposure, indicating the involvement of both the surface hydride and hydroxyl species in the initial adlayer decomposition. The implications of these results with regard to the reaction mechanism will be discussed.

11:20am SS2-WeM10 Nonthermal Effects of Photon Illumination on Surface Diffusion, E.G. Seebauer, D. Llera-Rodriguez, University of Illinois, Urbana

The presence of an energy bandgap in semiconductors together with their ability to support significant separations in charge offer the potential to observe surface phenomena not seen on metals. For example, several years ago this laboratory predicted the possibility of photon-influenced surface diffusion on semiconducors by nonthermal mechanisms. The present work reports the first experimental confirmation of this prediction for Ge, In, and Sb diffusion on Si(111), using second harmonic microscopy as the measurement probe. At modest illumination intensities of 2 W/cm@super 2@ or less, we have observed substantial changes in diffusional activation energy E@sub diff@ and prefactor D@sub o@. For all the adsorbates on p-type Si, illumination increases E@sub diff@ by about 0.3 eV (out of 2.4) and increases D@sub o@ by nearly two orders of magnitude. However, use of n-type substrates causes decreases of the same magnitude. All effects remain independent of illumination wavelength as long as the photon energy remains higher than the substrate bandgap energy. We can explain most of these effects by extending our adatom-vacancy model for surface diffusion at the experimental temperatures (400 to 1000 C) to incorporate charging of the surface vacancies, in direct analogy with vacancy behavior in bulk semiconductors. Charging of the vacancies requires electron transfer to or from surface quasi-fermi levels, whose positions are modified by illumination as in surface photovoltage spectroscopy. Our results have significant implications for semiconductor manufacturing steps performed by the lamp illumination of rapid thermal processing.

11:40am SS2-WeM11 The Role of Surface Reconstruction in the Photofragmentation Dynamics of Oriented Methyl Bromide Adsorbed on GaAs, K.A. Khan, N. Camillone III, R.M. Osgood Jr., Columbia University; J.A. Yarmoff, University of California, Riverside

Our previous work has detailed the UV-initiated dissociation of CH@sub 3@Br physisorbed on GaAs(110), both by numerous experimental techniques and theoretical calculations. The substrate-electron-mediated dissociation yields energetic (1.4eV) methyl fragments whose dynamics are governed by surface-alignment forces acting on the adsorbate. The anisotropic angular distribution of the methyl fragments reflects the surface corrugation of the 1x1 reconstruction of GaAs(110). In this paper we demonstrate that significant changes are observed in the fragment dynamics upon modifying the surface reconstruction via well-controlled surface preparation protocols. Specifically, to further explore and understand the role played by the surface morphology in fragmentation dynamics, we have compared the photodissociation of methyl bromide on two different surface reconstructions of the (100) face of GaAs. In contrast to the (110) surface, mass and angle-resolved time-of-flight measurements show the ejection of methyl fragments from the (100) surface to be symmetrical about the surface normal. Photoinduced fragmentation of monolayers of methyl bromide on c(8x2)-reconstructed Ga-rich and c(2x8)reconstructed As-rich GaAs(100) surfaces also reveals a striking difference between these two surface structures. On the Ga-terminated surface we observe desorption of intact CH@sub 3@Br as well as methyl fragments formed by photoinduced dissociation. Only methyl fragments are detected leaving the (110) surface and the As-terminated (100) surface. As in the (110) case, the mechanism for C-Br bond cleavage in the (100) cases is photo-initiated electron attachment from the surface to the molecule. However, the energetics of the methyl fragments are quite different on the three surfaces suggesting site-specific dissociation. Therefore, the energetics of the methyl fragments will be discussed in terms of the surface texture and stoichiometry of the three surfaces.

Surface Science Division Room 314/315 - Session SS3-WeM

Surface Dynamics and Roughening

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

8:20am SS3-WeM1 The Atomic Steps of Oxygen Adsorption on Pt(110)-(1x2), S. Helveg, S. Horch, I. Stensgaard, E. Laegsgaard, F. Besenbacher, Aarhus University, Denmark

The dissociative adsorption of Oxygen on the Pt(110)-(1x2) surface is studied using a variable-temperature, fast Scanning Tunneling Microscope. The dynamic information extracted from the STM movies direct reveal how the O structures develop as function of O coverage. A variety of new and novel O structures are observed on the atomic scale. These initial structures develop at higher O coverage into [110] oriented stripes which self organize into highly regular and periodic bands. From an interplay between these STM results and theoretical GGA calculations a new and coherent picture evolves for O adsorption on Pt(110). This picture deviates significantly from previously proposed structural models but we can within the new picture explain all previous experimentally obtained results.

8:40am SS3-WeM2 Etching of the Si(001) Surface with Molecular Oxygen, J.B. Hannon, M.C. Bartelt, N.C. Bartelt, G.L. Kellogg, Sandia National Laboratories

We have investigated the growth and decay of two-dimensional pits, or vacancy islands, at the Si(001) surface using low-energy electron microscopy (LEEM). The vacancy islands nucleate near the centers of large (10 micron diameter) terraces when the surface is exposed to molecular oxygen at elevated substrate temperature. At sample temperatures above about 1000 K, oxygen does not accumulate on the surface, but desorbs in the form of SiO, leading to a net removal of Si from the surface. In our experiments, the vacancy islands grow monotonically during oxygen exposure. The growth rates of the individual vacancy islands depend on the distribution of neighboring islands and steps. We quantify this dependence using both Monte Carlo simulations and a diffusion equation analysis. The vacancy-island growth rates can be described using a simple model of the etching process: during oxygen exposure, Si atoms are removed from the surface at a temperature-dependent rate, leaving behind surface vacancies. The vacancies diffuse on the terrace until they encounter an island edge, where they are irreversibly incorporated. The sensitivity of the vacancy-island growth rates to the island configuration is a consequence of the fact that vacancy terrace diffusion is slow compared to vacancy incorporation at steps. By measuring the growth rates as a function of temperature and oxygen pressure, we are able to determine both the mechanisms by which oxygen etches the surface as well as the activation energy associated with the etch rate. We find that the temperature dependence of the etch rate, at constant oxygen pressure, obeys an Arrhenius form with an activation energy of about 2.0 eV. This work was performed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000

9:00am SS3-WeM3 Surface Morphology Induced on Metal Surfaces by Ion Sputtering, S. Rusponi, G. Costantini, C. Boragno, U. Valbusa, University of Genova, Italy

Ion sputtering can be used not only to clean or to analyse a surface, but also to construct regular patterns on amorphous, semiconductor and metals surfaces. We studied the formation of these patterns in different metal single crystals by using a variable temperature UHV STM. By accurately dosing the ion energy, flux and fluence and by selecting the appropriate crystal temperature, we can tune the final morphology, changing the shape of holes and islands, their density and thickness. Different examples will be reported: on Ag(110)@footnote 1@ and Cu(110)@footnote 2@ a ripple structure can be induced, with an orientation respect to the surface directions depending mainly on the temperature, while on Ag(001)@footnote 3@ a checkerboard morphology with a square simmetry has been found. It has been found that many properties of the sputtered surfaces follow simple scaling laws. A general model, based on the competitive role of surface diffusion and erosion can well explain the reported results. @FootnoteText@ @footnote 1@S. Rusponi et al., Phys. Rev. Lett. 78 (1997) 2795 @footnote 2@S. Rusponi et al., Phys. Rev. Lett., submitted @footnote 3@S. Rusponi et al., Surf. Sci., submitted

9:20am SS3-WeM4 Direct Observation of Etching Mechanisms of Cu Surfaces with STM, C.Y. Nakakura, E.I. Altman, Yale University

Scanning tunneling microscopy movies of the halogenation and subsequent etching of Cu(100) and Cu(11 1 0) were recorded. Adsorption of both Br@sub 2@ and Cl@sub 2@ resulted in a c(2x2) structure on the Cu(100) terraces. As the adsorbate coverage approached saturation, the substrate steps faceted to align along the close-packed directions of the adlayer. The faceted steps were the Cu atom source for subsequent halide formation and etching. For Cl@sub 2@, the reaction was initiated at facet corners and proceeded by stripping away rows of atoms parallel to the steps. In contrast, Br@sub 2@ could also react perpendicular to the step edge creating channels etched into the terraces. For both Cl@sub 2@ and Br@sub 2@, the halide formed by reaction diffused across the surface, nucleating and growing halide clusters independently of the reaction step. At room temperature, three-fold symmetric CuBr(111) islands were observed that grew by addition of CuBr units to island edges. Remarkably, the presence of these islands did not block further reaction of the underlying Cu surface. The CuBr islands formed at room temperature roughened either with time or annealing. At temperatures above 440 K, the halide formed by reaction sublimes resulting in etching. Under these conditions, a new CuBr morphology was observed: four-fold symmetric islands. These square islands nucleated at step edges and then sublimed at rates far in excess of those of similar sized three-dimensional clusters,

suggesting that controlling the morphology of the CuBr can lead to reductions in etching temperatures.

9:40am SS3-WeM5 How Predictable Is Surface Morphology?, N.C. Bartelt, Sandia National Laboratories INVITED

One way people are beginning to probe the mechanisms of surface dynamics is to compare the histories of particular surface configurations obtained using microscopy with predictions from simulations. An advantage of this technique over the usual method of studying the time dependence of quantities averaged over the surface is that it allows the direct determination of how individual surface defects (such as steps) move in response to their local environment. A fundamental question about this approach is how well, and for how long, can one expect to account for the evolution of the complicated surface configurations which are typically observed in experiments. At small enough length scales, unpredictable thermal fluctuations begin to play a role. In this talk I discuss the basic theory and implications of the breakdown of deterministic equations of motion of surface morphology caused by these fluctuations. I will illustrate the issues involved. for several systems: First, given a configuration of surface steps. I will discuss how well one can predict where, and in what sequence, islands nucleate during epitaxial growth. I will compare theory with experiments of vacancy island nucleation during O etching of Si(001) which show that nucleation gets less predictable as the temperature (and critical nucleus size) gets smaller. Second, I will discuss how long one can in principle expect to account for the structure of adsorbed layers during domain coarsening and for island configurations during ripening. I will give theoretical and experimental examples of how sensitive histories of such complicated structures are to chance events and the knowledge of initial conditions

10:20am SS3-WeM7 Restructuring of Non-Square Vacancy and Adatom Clusters and of Indentations and Protrusions at Step Edges for Ag/Ag(100), C.R. Stoldt, A.M. Cadilhe, C.J. Jenks, J.W. Evans, P.A. Thiel, Iowa State University

During metal(100) homoepitaxy, near-square 2D islands (which are nucleated on broad terraces) first grow and merge, forming rectangular and dumbbell shaped clusters. Approaching a coverage of one monolaver. vacancy regions remain in the first layer which display a variety of unusual compact and worm-like shapes. Also, any extended step edges advance during deposition, incorporating islands in the process, and acquiring an irregular structure with many protrusions and indentations. The rearrangement of these non-equilibrium structures, if sufficiently rapid, can significantly influence multilayer growth. Thus, we present roomtemperature STM studies for Ag/Ag(100) adlayers which provide a comprehensive characterization of the restructuring dynamics: (i) for adatom and vacancy clusters with rectangular and dumbbell shapes, and for worm-like vacancy regions; and (ii) for square, triangular, and other shapes of protrusions and indentations at extended step edges. In particular, we assess the dependence of restructuring rates on feature size and shape (or on local step edge orientation), and compare behavior for "mirror-image" adatom and vacancy structures. Behavior is elucidated by comparison with theoretical studies of "perimeter diffusion" models for step edge evolution.

10:40am SS3-WeM8 Evolution and Structure of the Stripe Phase Reconstruction of Cu/Ru(0001), *H. Zajonz*, *D. Gibbs*, Brookhaven National Laboratory; *A.P. Baddorf*, *D.M. Zehner*, Oak Ridge National Laboratory

X-ray scattering studies of the structure of Cu layers deposited on Ru(0001) substrates during growth and versus substrate temperature have been initiated. The nearest-neighbor spacing in bulk fcc Cu is 5.8% smaller than that in hcp Ru. Earlier STM studies,@footnote 1@ established that the first layer of Cu on Ru(0001) adopts a pseudomorphic structure, but that the two-layer film exhibits a stripe-phase reconstruction which consists of an uniaxial modulation of Cu chains along [100]. Measured x-ray intensities provide evidence that the first layer does not remain pseudomorphic in the stripe phase. Our experiments also involve characterizing the appearance and evolution of the stripe-phase reconstruction peak as a function of Cu coverage and substrate temperature. At 720 K, x-ray scattering confirms a pseudomorphic Cu structure for coverages up to about one monolayer, followed by the growth of a stripe-phase reconstruction between one and two layers. In the stripe phase, the average Cu spacing along the rows is that of Cu bulk, however between rows the spacing is equivalent to that of Ru. At two monolayers coverage, there is an abrupt contraction of the average Cu spacing by an additional ~0.5% which can be attributed to an increase in the amplitude of the transverse modulations with layer completion. This phenomenon has not been observed previously for an

interfacial reconstruction. ORNL is managed by Lockheed Martin Energy Research Corp. under U.S. Department of Energy contract DE-AC05-96OR22464. Work at BNL is supported by DOE, under contract DE-AC02-98CH10886. @FootnoteText@ @footnote 1@ C. Günther et al., Phys. Rev. Lett. 74, 754 (1995)

11:00am SS3-WeM9 Dynamics of the Striped Nanostructure of the Oxidized Cu(110) Surface: A Momentum-Resolved ESDIAD Study, D. Mocuta, J.W. Ahner, J.-G. Lee, S. Denev, J.T. Yates, Jr., University of Pittsburgh

The striped structure of the partially oxidized Cu(110) surface has been studied using a novel technique, Momentum-Resolved ESDIAD. Long ... O-Cu-O... strings oriented in the direction and exhibiting attractive interactions with each other form periodically arranged stripes with widths in the nanometer range.@footnote 1,2@ Two different oxygen sites were detected, leading to a two-fold symmetrical four beam O@super +@ ESDIAD pattern with tilting of the beams of 22° in the azimuth (A) and 8° in the azimuth (B) directions. The relative intensities of the four beams have been compared for a wide range of oxygen coverages leading to a model in which the A beams correspond to O@ super +@ ions desorbing from the edges of the stripes and the B beams from the internal regions of the stripes. This model is confirmed by studying the effect of the coadsorption of Ar at 32 K on the oxidized structure. The dynamical motion of the onedimensional ...O-Cu-O... oscillator chains situated at the edges of the stripes has been studied by Momentum-Resolved ESDIAD measurements over a broad range of temperatures (70 K- 650 K). In addition, this striped surface has been used as a template for the adsorption of other species, whose interactions with the ...O-Cu-O... chains are revealed. @FootnoteText@ @footnote 1@D. J. Coulman, J. Wintterlin, R. J. Behm, G. Ertl, Phys. Rev. Lett. 64 (1990) 1761. @footnote 2@K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. George, G. Comsa, Phys. Rev. Lett. 67 (1991) 855.

11:20am SS3-WeM10 Evidence and a Model for a Chemically Mediated Roughness Transition, *E.A. Irene, C. Zhao, Q. Liu*, University of North Carolina, Chapel Hill

In our previous research we have followed the changes effected by oxidation on purposely roughened and initially smooth Si surfaces via atomic force microscopy (AFM) and spectroscopic ellipsometry (SE) and a new technique called spectroscopic immersion ellipsometry (SIE).@footnote 1,2@ For initially rough surfaces both thermal and plasma oxidation yield smoother surfaces and this can be understood from the changes in the local free energy at asperities, viz. the Kelvin equation. What was surprising was that initially smooth Si surfaces roughen upon oxidation. These results are not contradictory, since the roughness magnitudes do not cross, but these results strongly suggest a limiting roughness. Furthermore, a chemically mediated roughening transition explains the observations although this mechanism is not yet proven. The experimental and modeling results will be presented. @FootnoteText@ @footnote 1@Q. Liu, L. Spanos, C. Zhao and E.A. Irene, J. Vac. Sci. Technol. A, 13, 1977 (1995). @footnote 2@C. Zhao, Y.Z. Hu, T. Labayen, L. Lai and E.A. Irene, J. Vac. Sci. Technol. A, 16, 57, (1998).

11:40am SS3-WeM11 Reconstruction of Bimetallic Systems: Ultrathin Films of Rh, Pt and Pd on W(211), K. Pelhos, I.M. Abdelrehim, C.H. Nien, T.E. Madey, Rutgers University

The (211) face of tungsten is found to undergo an (nx1) reconstruction when covered with a thin film of Rh, Pt or Pd, followed by annealing. A combination of low energy electron diffraction, Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) experiments indicate that the reconstruction occurs within a very narrow coverage range, between 0.5 and 1 physical monolayer, and only when the annealing temperature exceeds a threshold value of ~900 K (Rh and Pt) or ~500 K (Pd) (1 physical monolayer corresponds to 1.63 x 10@super 15@ atoms/cm@super 2@, sufficient to cover completely all of the exposed W atoms in the W(211) rows and troughs). The reconstruction is almost exclusively (3x1) for Rh and Pt, and (~12x1) for Pd. Scanning tunneling microscopy (STM) investigations of the Rh/W(211) system reveal that the atomic structure of the (3x1) reconstruction is due to very long (up to 1000 Angstroms) double rows of Rh separated by missing rows; the troughs of the W(211) surface presumably are filled with Rh atoms. Similarly, the atomic structure of the Pd/W(211) (~12x1) reconstruction is due to the W(211) surface being covered by the Pd overlayer, except for equally spaced missing rows of overlayer atoms. Furthermore, evidence for two phase coexistence and domain growth (distinct (1x1) and (3x1) regions) is found in STM of Rh/W(211) near one physical monolayer coverage.TPD experiments performed at very high temperatures (up to 2400 K) provide

insight into the adsorption energetics of these metallic overlayers. Our results are discussed in the context of previous experiments: the faceting of W(111) surface into nanoscale three-sided pyramids with (211) facets, induced by metal overlayers.

Surface Science Division Room 308 - Session SS1-WeA

Electromigration and Surface Transport Moderator: T.L. Einstein, University of Maryland

2:00pm SS1-WeA1 Quantifying Surface Electromigration: Si(111) as a Model System@footnote 1@, E.D. Williams, University of Maryland, College Park INVITED

Electromigration induced changes in structure result from a diffusion bias caused by an imposed external electric field. The mechanisms by which the diffusion bias is induced (wind force or direct force) are similar in the surface and the bulk. Thus in temperature regimes where surface diffusion is more readily activated than bulk diffusion, surface electromigration should play an important role in changes in morphology of a currentcarrying structure. Surface electromigration occurs on Si(111) surfaces at elevated temperatures. The signature is the spontaneous evolution of nonequilibrium configurations of the steps with one direction of the current, and the return to equilibrium with the opposite direction of current with respect to the "down-hill" step direction. Quantification of the nature of the surface electromigration force has been performed by STMmeasurement of the shapes and rates of the evolving non-equilibrium morphologies, and by comparison of the rates of decay in the presence and absence of the stabilizing direct current. The basic mechanism of both formation and decay is the motion of individual steps, which occurs with a rate governed by the rate of equilibrium fluctuations of the steps. During formation of non-equilibrium structures, individual fluctuations couple to the external field, yielding single-point step collisions which then "zip" up to form step bunches. The curvature at the "zip" point has been quantified in terms of the competing effects of energetic costs of step bending and the electromigration force. During decay, steps move in a nearly onedimensional mode which has been quantified in terms of the step-step repulsions and the electromigration force. The results are consistent with an effective charge less than 0.01 electron units. The applications of this approach to studying broader problems in electromigration will be discussed. @FootnoteText@ @footnote 1@Supported by the U. of MD NSF-MRSEC

2:40pm SS1-WeA3 Electromigration and Cluster Motion@footnote 1@, O. Pierre-Louis, T.L. Einstein, University of Maryland, College Park

We describe the fluctuations, dynamics, and instabilities of adatom and of vacancy single-layer islands during electromigration, generalizing earlier work on straight steps without driving forces.@footnote 2@ We emphasize the dependence on the mass-transport mechanism: periphery diffusion (PD), terrace diffusion (TD), or evaporation-condensation (EC).@footnote 3@ In particular, we find non-circular steady states and derive the cluster diffusion constant D@sub c@. Analytical calculations using Langevin formalism are corroborated by both Monte Carlo simulations and numerical integration. We determine the cluster drift velocity, which in the 3 limiting cases has the size dependence of cluster-area x D@sub c@. In EC, clusters elongate perpendicular to the drift axis. Differences exist in this novel behavior for atom and vacancy clusters. In PD a morphological instability leads to cluster splitting.@footnote 4@ We show that adatom diffusion across the terrace induces a new morphological instability for vacancy clusters and discuss the threshold. Shape fluctuations and D@sub c@ are studied in our Langevin framework. For weak electromigration the cluster responds isotropically for TD or PD but not EC. Fluctuation behavior close to the instability threshold is characterized analytically and numerically. An electric current can also alter attachment/detachment probabilities; novel consequences on cluster dynamics (drift velocity, shape, etc.) are investigated. We discuss experimental relevance of our results. New phenomena should be observed on metal surfaces, and implications for voids in electric lines are discussed. @FootnoteText@ @footnote 1@Work supported by NSF MRSEC grant DMR 96-32521. @footnote 2@O. Pierre-Louis and C. Misbah, Phys. Rev. Lett. 76, 4761 (1996); Phys. Rev. B 58, xxx (1998). @footnote 3@S. V. Khare and T. L. Einstein, Phys. Rev. B 57, 4782 (1998); 54, 11752 (1996). @footnote 4@W. Wang and Z. Suo, J. Appl. Phys.79, 2394 (1996); M. Schimschak and J. Krug, Phys. Rev. Lett. 80, 1674 (1998).

3:00pm SS1-WeA4 Theory of Surface Electromigration on Metals, P.J. Rous, D.N. Bly, University of Maryland, Baltimore County, US

We describe the application of layer-KKR theory to the calculation of the driving force for adatom electromigration on metallic surfaces. We find

that the dominant component of the force arises from momentum transfer to the adatom from the charge carriers; the so-called wind force. We have computed the direction and magnitude of the driving force for electromigration along typical migration pathways on low Miller index surfaces. Averaging the force felt by an adatom traversing these paths permits the calculation of the effective wind valence Z@sub w@. By comparing Z@sub w@ for impurity and self-electromigration on various substrates we have correlated the magnitude of the driving force with the local carrier density and the adatom transport cross-section. For migration of isolated adatoms, we find that the ballistic model, appropriately modified for the effect of the substrate provides a reasonable qualitative description of the calculated effective valence. @FootnoteText@ This work is supported by the National Science Foundation under Grant No. DMR-9632521

3:20pm SS1-WeA5 Theory of Surface Electromigration on Stepped and Islanded Surfaces., J. Cheng, P.J. Rous, University of Maryland, Baltimore County, US

We have applied multiple scattering theory to explore the variation of the electromigration wind force experienced by an adatom in the vicinity of steps and islands on a metal surface. We find that the electromigration wind force felt by a migrating adatom is strongly perturbed as it approaches a step or island edge. This is a result of multiple scattering of the carriers between the adatom and step/island which alters the local current density. The implications of this inhomogeneity in the electromigration driving force for current-induced changes in surface morphology are discussed. Since the calculated wind valence may be directly related to the surfaceinduced resistivity of an adatom we discuss the how the scattering interactions between steps and adatoms may be manifest in the resistivity of a metallic surface. @FootnoteText@ This work is supported by the National Science Foundation under Grant No. DMR-9632521

3:40pm SS1-WeA6 Surface Electromigration Processes on Gold and Copper Films, *N. Shimoni, O. Biham, O. Millo,* The Hebrew University, Israel Electromigration processes on the surfaces of gold and copper films are studied using scanning tunneling microscopy (STM). We perform time-lapse STM scans under controlled sample temperature conditions, both with and without current stressing. We shall present results regarding the following issues: 1. The evolution of monolayer islands, voids and terraces on the surface of polycrystalline gold films. 2. The appearance and evolution of surface dislocations on flame-annealed gold films. 3. Grain boundary migration, and elongation of surface grains in the direction of the applied current in copper films. Our results will be discussed in context of the various possible surface dynamic processes, including the affect of the subsurface layer on these dynamics. We will also address differences between thermally activated and electromigration induced processes.

4:00pm SS1-WeA7 Molecular Dynamics Studies of Interlayer Mass Transport and Dendritic-to-Compact Morphological Transitions during Submonolayer Growth on Pt(111) Surfaces, V. Chirita, E.P. Münger, J.-E. Sundgren, Linköping University, Sweden; J.E. Greene, University of Illinois, Urbana

We use embedded-atom method molecular dynamics simulations to investigate the kinetics of two processes which are critical in achieving the layer-by-layer growth mode: interlayer mass transport and dendritic-tocompact morphological transitions. The former investigation is carried out by following the dynamics of adatoms, vacancies and adatom-vacancy pairs within hexagonal Pt@sub 19@ clusters on Pt(111) at 1000 K, for simulation times totalling ~ 135 ns. The latter study concentrates on the dynamics of Pt dendrites containing up to 25 atoms on the same surface at the same temperature. The mapping of adatoms motion on top of the clusters shows that prior to incorporation, adatoms are trapped near the cluster edge for $^{\sim}$ 80% of the total simulation time. Cluster configurations with central vacancies are found to be quite stable. Adatom incorporation is observed to occur mainly via the two well known mechanisms of hopping and pushout/exchange with edge atoms. However, our simulations for adatomvacancy pairs within clusters, bring the first direct evidence that both mechanisms can be active in the central region of the cluster, i.e. monovacancies are filled by adatom hopping or via exchanges with one of the atoms adjacent to the vacancy. We carry out minimum energy path calculations to examine the energetics of the two mechanisms. The results show that activation barriers are comparable to the corresponding interlayer mass transport mechanisms observed at the outer edge of the cluster. We have also followed the dynamics of Y-shaped Pt dendrites for simulations times in excess of 100 ns. The results show that, in agreement

with previously proposed models, the dendritic-to-compact morphological transition proceeds via diffusion around branch corners, as well as edge diffusion. Our simulations reveal however, the presence of a new diffusion mechanism, in which the entire corner of a dendritic branch translates to adjacent terrace sites via a concerted motion of the atoms forming the corner. The process has an activation barrier similar to that of two-fold coordinated atoms diffusing around the corner.

4:20pm SS1-WeA8 Edge Barriers and Mass Transport on Metal (100) Surfaces@footnote 1@, W.W. Pai, The University of Tennessee; J.F. Wendelken, Oak Ridge National Laboratory

Since epitaxial growth is subject to kinetic limitations, epitaxial growth morphology is usually thermodynamically unstable. These kinetic limitations, in particular the Schwoebel barrier in homoepitaxial systems, often result in a rough, multilevel morphology which begins during deposition of the first monolayer. Post-deposition equilibration of the resultant morphology occurs through several avenues of mass transport. When the starting condition consists of monolayer height islands following a submonolayer deposition at room temperature, coarsening is observed to result from island diffusion and coalescence on Cu(100) and Ag(100) surfaces, where the island diffusion occurs via rapid edge diffusion.@footnote 2@ When a multilevel system results from higher depositions, islands may still diffuse, but this diffusion is inhibited at downhill step edges due to an edge barrier just as the Schwoebel barrier inhibits downhill transport of adatoms. On the (100) surface, this barrier is found to be very high when the step edge is in the close-packed [110] direction, but very low, or even non-existent, when the edge is oriented in a non-close-packed direction. If a diffusing island encounters an edge with such a low barrier, the island may very quickly descend to the lower level with its atoms being incorporated into the step edge in a manner similar to that which has been reported for Cu(111).@footnote 3@ These low barrier sites, in combination with island diffusion and edge diffusion are found to provide the main pathway for smoothening at room temperature on Cu(100) and Ag(100). This is in contrast to the evaporation-condensation mechanism implied by the line tension driven smoothening at higher temperatures on Cu(100).@footnote 4@ @FootnoteText@ @footnote 1@Research performed at ORNL, which is managed by Lockheed Martin Energy Research Corporation for the U.S. DOE under Contract No. DE-AC05-96OR22464 @footnote 2@Woei Wu Pai, Anna K. Swan, Zhenyu Zhang and J. F. Wendelken, Phys. Rev. Lett.79, 3210 (1997).@footnote 3@M. Giesen, G. Schulze Icking-Konert, and H. Ibach, Phys. Rev. Lett. 80, 552 (1998).@footnote 4@J.-K. Zuo and J.F. Wendelken, Phys. Rev. Lett. 70, 1662 (1993).

4:40pm **SS1-WeA9 Metal Row Growth on a High-Index Silicon Surface**, *H.H. Song*, *K.M. Jones, S.R. Blankenship, J.A. Carlisle, A.A. Baski*, Virginia Commonwealth University

Recent STM studies of high-index silicon surfaces have revealed unique morphologies not found on their low-index counterparts.@footnote 1@ For example, Si(5 5 12) forms a single-domain reconstruction composed of row-like structures, primarily pi-bonded chains. This highly anisotropic surface is expected to provide a unique template for the growth of metal overlayers, particularly in the formation of one-dimensional nanometerscale structures. Our STM studies show that Ag deposited onto Si(5 5 12) and annealed to moderate temperatures does form row-like overlayer features. At coverages as low as 0.05 ML, rows appear on top of the most prominent pi-bonded chains, resulting in a 5.4 nm inter-row spacing. These rows have high aspect ratios (up to 40:1) and a mean length of 20 nm. As the Ag coverage is increased, the overlayer rows grow in length and number until the surface forms a periodic array of such rows at ~0.25 ML. Above this coverage, Ag appears to be incorporated into other structures on the surface and the long-range ordering becomes disrupted. A statistical analysis of the row lengths reveals the expected increase in mean row length as a function of coverage (0.05 to 0.2 ML) and annealing temperature (400 to 550°C). At annealing temperatures above 550°C, however, the deposited Ag causes local faceting of the Si surface, disrupting the ordered arrays of Ag rows. The metal rows must therefore be a metastable arrangement of the surface. @FootnoteText@ @footnote 1@A.A. Baski, S.C. Erwin, L.J. Whitman, Surf. Sci. 392, 69 (1997).

5:00pm SS1-WeA10 One Dimensional Growth Behavior of Xe Atoms on Step Edges of Cu(111), J.-Y. Park, Y. Kuk, Seoul National University, Korea; K. Miyake, H. Shiqekawa, University of Tsukuba, Japan

A rare gas atom adsorbed on graphite or various metal surfaces has been extensively studied as a model two dimensional system because of its weak interaction with the substrate. In this study, we used a low temperature scanning tunneling microscope to understand the interaction of Xe atom with Cu(111) surface in the temperature range of $10K \sim 30K$. Quite different one dimensional wetting behavior was observed at the lower and upper side of Cu surface steps. Xe atoms first adsorb at lower side of steps, but they reveal repulsive interaction among themselves. The Xe adsorbates then modify the Ehrlich-Schwoebel barrier, resulting in the wetting at upper side of steps. A model is proposed to explain the 1D growth behavior. As observed earlier,@footnote 1@ standing waves, caused by reflection of surface state electrons at step edges and impurities, were observed. It was also observed that the surface state energy is shifted in the presence of the Xe overlayer. @FootnoteText@ @footnote 1@M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature 363, 524 (1993).

Surface Science Division Room 309 - Session SS2-WeA

Photochemistry and Deposition

Moderator: C.M. Greenlief, University of Missouri, Columbia

2:00pm SS2-WeA1 Photochemical Routes to Group IV Deposition, G.J. Batinica, J.L. Stepnowski, J.E. Crowell, University of California, San Diego

The fabrication of high-speed electronic devices requires the controlled epitaxial deposition of Si and SiGe thin films. We have explored both thermal and photochemical routes to Si and Ge deposition using disilane (Si@sub 2@H@sub 6@) and digermane (Ge@sub 2@H@sub 6@) as model hydride deposition sources. We have also compared the thermal and photochemical reactivity of Si(100) versus that of Si(111). The deposition reactions have been studied using multiple internal reflection infrared spectroscopy (MIRIRS), temperature programmed desorption (TPD), and Auger electron spectroscopy (AES). Hydrogen and silane (SiH@sub 4@) desorption yields were used to determine the reactivity of disilane on the Si surfaces with and without UV irradiation. Hydrogen and germane desorption yields and relative Ge/Si AES signals were used to determine the reactivity of digermane. UV irradiation during or after dosing of the Si crystal surfaces at 110K greatly enhanced the reactivity of disilane and digermane compared to similar exposures without UV irradiation. Comparison of the reactivity of disilane with Si(100) versus Si(111) show that Si(111) is thermally less reactive than the Si(100) surface. However, both surfaces show similar photo-reactivity to disilane. The photo-induced mechanism of disilane and digermane reactions has been studied using clean, partially deuterated and fully deuterated Si(111) and Si(100) surfaces. Thermally, the reactivity is controlled by the surface dangling bonds; whereas the photo-induced deposition chemistry appears to primarily involve insertion by the photo-generated diradicals, silylene and germylene. The implication of our results on deposition methodologies will be discussed.

2:20pm SS2-WeA2 Electron Induced Deposition of Germanium on Si(100): TPD, XPS, and HREELS Study, J. Lozano, University of Texas, El Paso, U.S.; J.H. Craig, J.H. Campbell, University of Texas, El Paso

Temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS) were used to investigate the effects of an electron beam on Si(100) dosed with digermane at 110 K. At high digermane coverages (>1 ML), three peaks appear on hydrogen TPD traces at 140 K, 575 K, and 740 K. The peak at 140 K corresponds to desorption of hydrogen from molecular overlayers of digermane, as confirmed by the desorption of digermane fragments at 140 K. The TPD features at 575 K and 740 K correspond to hydrogen desorption from surface germanium and from silicon, respectively. The vibrational losses at 820 and 2040 cm@super -1@ in the HREELS data obtained from digermane-covered Si(100) indicate the presence of germanium hydride species on the surface. The formation of the silicon monohydride state is evident by the high-energy broadening of the loss feature at 2040 cm@super -1@. Upon exposure of the highly dosed surface to an electron beam (maximum current density of 9µA/cm@super 2@), the intensity of the low temperature TPD peak at 140 K decreases, while the intensity of the peak at 575 K increases. XPS data show an increase on the relative surface concentration of germanium following electron irradiation of the digermane overlayers. Annealing the surface to 200 K does not decrease the relative concentration of germanium on the electron-irradiated surface. Electron irradiation of digermane/Si(100) at low digermane exposures does not have any detectable effects. These results indicate that the electron beam dissociates the digermane molecular overlayers and deposits germanium on the surface.

2:40pm SS2-WeA3 Photodesorption of Condensed Gases by Lyman-@alpha@, D.A. Bahr, R.A. Baragiola, University of Virginia

We measured the absolute desorption yield of water and carbon dioxide films condensed at low temperatires under irradiation with Lyman-@alpha@ (121.6 nm) photons as a function of sample temperature and irradiation fluence using a double quartz-crystal resonator. We also determined the species desorbed using mass spectrometry. We will discuss the results in terms of basic processes and discuss astrophysical implications.

3:00pm SS2-WeA4 Photodesorption of Positive lons from Oxyanion-Containing Inorganic Crystals, C. Bandis, M.L. Dawes, S.C. Langford, J.T. Dickinson, Washington State University

Surfaces of inorganic, ionic crystals with complex oxyanions can be dramatically altered by UV and electron irradiation. Previous work has shown that such irradiation desorbs XO@sub n@ and O@sub 2@, where X = N, P, C, and possibly S. This electronic decomposition produces cation defect complexes from which intense positive ion emission can be photoinduced. We describe two-beam experiments where either two laser beams or a laser and an electron beam are cofocused. One beam (UV laser or electron) is used to generate defects, and the second beam (laser) is used to photodesorb jons. We report metal and metal-containing jon emission accompanying nanosecond laser pulses at 248 and 1064 nm from alkali nitrates and calcium phosphates. The resulting ion kinetic energies can exceed the photon energy by factors of ten. The effect of time delay between two pulsed beams will also be presented. The critical role of radiation induced chemistry and the ion emission mechanism will be discussed. This work is supported by the Department of Energy under Contract DE-FG06-92ER14252.

3:20pm SS2-WeA5 Direct Observation of Synchrotron-Radiation-Stimulated Decomposition of SiO@sub 2@ Thin Films on Si(111) Surfaces using Scanning Tunneling Microscopy, *T. Miyamae*, *T. Urisu*, *S. Hirano*, Institute for Molecular Science, Japan; *H. Uchida*, *T. Yagi*, Toyohashi University of Technology, Japan; *I. Munro*, Institute for Molecular Science, Japan

Synchrotron radiation (SR) stimulated decomposition of silicon dioxide thin films on Si(111) surfaces were observed by using a ultrahigh vacuum scanning tunneling microscopy (UHV-STM) and Low energy electron diffraction (LEED). SiO@sub 2@ films were shown to be almost removable by SR irradiation. Si(111)-(7 by 7) reconstructed structure were observed by LEED after two hours SR irradiation at surface temperatures as low as 650 C°. In spite of the observation of clear 7 by 7 LEED pattern, the STM images did not show clean and flat surface at this temperature. The clean (7 by 7) reconstructed surface temperature of 700 C°. Analysis of the evolution in the clean region suggests that the desorption mechanism may be different between thermal and SR stimulated desorption processes. The results show that the feasibility of this technique for low-temperature cleaning of silicone surface is demonstrated.

3:40pm SS2-WeA6 Surface Decomposition Reaction of Trisdimethylaminoantimony on GaSb(100)-(3x1), K. Yong, P.D. Kirsch, J.G. Ekerdt, University of Texas, Austin

Trisdimethylaminoantimony (TDMASb) is a novel Sb-precursor for the deposition of Sb-containing alloys by organometallic vapor phase epitaxy. Deposition using TDMASb can lower the growth temperature and also minimize carbon incorporation in the layers. The decomposition of TDMASb on GaSb(100)-(3x1) was studied using temperature programmed desorption, temperature programmed static secondary ion mass spectroscopy, low energy electron diffraction, and X-ray photoelectron spectroscopy. TDMASb decomposes on the surface at temperatures below 200 K and dimethylamine was desorbed through two reaction pathways. Homolysis of the antimony-nitrogen bond resulted in desorption of the dimethylamine radical at 380 K. Methylmethyleneimine was formed and desorbed from the surface through hydrogen elimination at 480 K. Deposition of Sb from 5 monolayers of TDMASb on GaSb(100) induced the change of surface structure from (3x1) to (1x1). We propose that surface Sb atoms are the reactive sites for the decomposition of TDMASb.

4:00pm SS2-WeA7 Interaction of Ethylene with the Ge(100)-2x1 Surface: Coverage and Time-Dependent Behavior, A.V. Teplyakov, Stanford University; P. Lal, Y. Noah, M.J. Kong, New York University; S.F. Bent, Stanford University

Chemical modification of semiconductor surfaces has been a subject of thorough investigations for decades because of its relevance to the

fabrication of electrical and optical devices. Despite these efforts, very little is known about the chemical properties of germanium surfaces. Here we present studies of the adsorption and thermal chemistry of ethylene on Ge(100)-2x1. Ethylene has been studied in detail on Si(100)-2x1, and provides a good reference system for comparing silicon and germanium reactivity. The results of multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy and temperature programmed desorption (TPD) studies suggest that ethylene chemisorbs on the Ge(100)-(2x1) surface at room temperature. IR spectroscopy gives evidence for only one adsorbate structure on this surface at room temperature. However, TPD measurements show two molecular desorption features, indicating that at least two adsorption configuration can exist. Complex temperature, time-, and coverage dependent behavior of ethylene adsorption on Ge(100)-2x1 will be presented and analyzed.

4:20pm SS2-WeA8 Interaction of Amines with Hydrogen on Al(111), J.N. Russell, Jr., C.S. Kim, Naval Research Laboratory

High quality AIN films, for optoelectronic devices, high power electronics and sensors, are generally produced via MOCVD of NR@sub 3@ and R@sub 3@Al (R = H, CH@sub 3@, or C@sub 2@H@sub 5@). We explored the chemical interaction of ammonia, methylamine, and ethylamine with clean and hydrogenated Al(111) in an UHV environment using temperature programmed desorption and/or infrared reflection absorption spectroscopy. On clean Al(111), the compounds adsorb molecularly and desorb by 200 K. In contrast, on the H-covered surface, a new desorption state (ß) is seen at about 250 K for each reactant. The ß-state coverage of each compound tracks that of H. Infrared spectroscopy shows that NH@sub 3@ preferentially adsorbs via a Lewis acid-base interaction at monohydride sites with the Al-N bond inclined away from the surface normal. While NH@sub 3@ does not dissociate nor exchange H atoms with the H-precovered surface, the alkylamines dissociate. New HD desorption features, at 240 and 270 K, are observed for perdeutero-alkylamines on H/Al(111). In addition, hydrocarbon desorption is observed at about 600 K for the alkylamines when coadsorbed with hydrogen. We discuss the implications of this work on the MOCVD of AIN films.

4:40pm SS2-WeA9 Adsorption and Reaction of Chlorine on Low Index Diamond Single Crystal Surfaces, S. Hadenfeldt, C. Benndorf, University of Hamburg, Germany

The lowering of the substrate temperature achieved by the low pressure diamond deposition from halogenated precursors is believed to involve surface processes, including halogen adsorption, desorption and reaction with H(ad). In this work we studied the adsorption of chlorine on the low index diamond (100), (111) and (110) single crystal surfaces as well as on polycrystalline diamond CVD films in UHV using thermal desorption spectroscopy (TDS), Augerelectron spectroscopy (AES), low energy electron diffraction (LEED) and photoelectron spectroscopy (UPS / XPS). Elemental halogen was dosed by solid state electrolysis of silverchloride at elevated temperatures or direct dosing of chlorine gas through a heated oxide ceramics tube. The single crystals were regularely cleaned by pretreatment in a hydrogen plasma and showed clear reflexes in LEED. The CVD films were studied as received from the CVD process. In AES upon successive halogen dosing a linear increase of the intensity of the halogen Auger signal and a simultaneous decrease in intensity of the 272 eV carbon signal can be seen at first. No LEED overstructures could be observed upon adsorption on either surface. Depending on the sample preparation and history, in general two different desorption behaviours are observed in TDS. From the hydrogen rich, plasma prepared surface chlorine is desorbed continuously with a maximum around 600 K. Around 850 K chlorine is completely removed. On a hydrogen depleted surface, where less halogen adsorbs at a given exposure, two regions of chlorine desorption can be observed. Up to 730 K a steady decrease of chlorine is noted, which levels off, until finally all chlorine is desorbed around 950 K. Halogen uptake of the diamond surface can be increased either by thermally activating the surface or by dosing of atomic hydrogen prior to halogen adsorption.

5:00pm SS2-WeA10 Desorption Kinetics of Hydrogen and Deuterium from Diamond (111)x(1x1) via Helium Atom Scattering, S.A. Safron, J.G. Skofronick, Florida State University; A. Glebov, J.P. Toennies, S. Vollmer, Max Planck Institut fuer Stroemungsforschung, Germany

The rate constants for the isothermal desorption of hydrogen and deuterium from diamond (111)-H(1x1) and -D(1x1) surfaces, respectively, have been measured over the temperature range 990 K to 1080 K by monitoring the helium atom Bragg diffraction beam intensities as a function of time. The rate behavior for both H and D followed first order reaction kinetics and a distinct isotope effect was observed in the

desorption rates. The temperature dependence of the rate constants could be represented by an Arrhenius law. In fitting the data to determine the Arrhenius activation energies, the pre-exponential (or frequency) factors were taken to be the previously reported diamond (111)-(1x1) C-H or C-D stretching mode (S-mode) frequencies, 8.5x10@super13@ s@super-1@ for H and 6.4x10@super13@ s@super-1@ for D. The respective activation energies were then determined to be 2.69 eV (62.0 kcal/mol) and 2.74 eV (63.2 kcal/mol).@footnote1@ @FootnoteText@ @footnote1@ Work supported in part by US DOE grant no. DE-FG02-97ER45635 and NATO grant no. GRC.961145.

Surface Science Division Room 308 - Session SS1+NS-ThM

Growth and Thin Films

Moderator: J.B. Hannon, Sandia National Laboratories

8:20am SS1+NS-ThM1 Peter Mark Memorial Award Address - Morphology of Epitaxial Films during Low Temperature Growth, D.G. Cahill¹, University of Illinois, Urbana-Champaign INVITED

9:00am SS1+NS-ThM3 The Influence of Dislocations on the Intermixing Kinetics of Pd-Au Monolayer Films, O. Schaff, A.K. Schmid, M.C. Bartelt, R.Q. Hwang, Sandia National Laboratories

The kinetics of surface alloying differ dramatically from the bulk counterparts. This is due to the fact that the dominant diffusion mechanisms are fundamentally different on surfaces. In this work, we used classical bulk studies as a guide to construct an effective experimental approach to directly determine such atomic mechanisms controlling intermixing kinetics in two-dimensional samples. On a clean Ru(0001) substrate, we prepared prototypical two-dimensional diffusion couples, consisting of monolayer regions of Au adjacent to monolayer regions of Pd. Between carefully controlled annealing steps, atomic resolution scanningtunneling microscopy was used to image changes in the adlayer structure, and thereby identify and characterize the phenomena leading to the formation of a Pd-Au surface alloy. We report several striking observations: (I) The Pd-Au surface alloy forms only on the Au-rich side of the diffusion couple, reflecting strong asymmetry in the diffusion constants of the two metals across the Pd-Au seam. (II) Diffusion constants, and thus alloying, in this system are strongly anisotropic. Specifically, the rate of interdiffusion at a given Pd-Au boundary, measured from changes in the average position of the alloy interface, depends strongly on the orientation of the boundary with respect to the underlying Ru lattice. We relate these observations to the energetics of exchange of surface atoms with the "gas" of Au and Pd adatoms, as well as to the dynamical properties of the dislocation network present in the Au side of the diffusion couple.

9:20am SS1+NS-ThM4 The Kinetic Nature of Slope Selection during Unstable Growth, *S. van Dijken, L.C. Jorritsma, B. Poelsema,* University of Twente, The Netherlands

At temperatures below 320 K, the Cu(001) transforms into an arrangement of facets upon epitaxial growth, resulting in a pyramidlike surface morphology. The sides of the pyramids all have the same facet orientation, selected by the growth temperature. With increasing growth temperature, [113], [115] and [117] facet faces are obtained.@footnote 1,2@ Up to now, it is not clear whether this slope selection is determined by local equilibrium or by the kinetics of the growth process. We present evidence for the kinetic origin of this phenomenon. At the same temperature various facet orientations can be obtained, depending on the angle of incidence of the impinging adatoms. We will show that the observed slope selection can be explained by the refraction of atoms above the surface. @FootnoteText@ @footnote 1@H.J. Ernst, F.Fabre, R. Folkerts and J. Lapujoulade, Phys. Rev. Lett. 72, 112 (1994) @footnote 2@L.C. Jorritsma, M. Bijnagte, G. Rosenfeld and B. Poelsema, Phys. Rev. Lett. 78, 911 (1997)

9:40am SS1+NS-ThM5 Growth on Cu(100) Using Improved Simulation Algorithm@footnote 1@, J.G. Amar, University of Toledo; M.R. D'Orsogna, T.L. Einstein, University of Maryland, College Park; I. Beichl, National Institute of Standards and Technology; F. Sullivan, Center for Computing Sciences

We have developed a novel Monte Carlo scheme to simulate homoepitaxial growth on (100) surfaces of sc and fcc crystals, using tree and list structures. We have applied it to the specific case of Cu, in both the submonolayer and multilayer growth regimes. Energy barriers were calculated using Effective Medium Theory, and diffusive processes were grouped into 4 classes. The effect of an Ehrlich-Schwoebel barrier was also considered. For the submonolayer regime at 213 K, we find reasonable agreement with experimental results@footnote 2@ for the scaling of the island density as a function of the ratio of diffusion and deposition rates. For multilayer growth at 160 K we find good quantitative and qualitative agreement with experimental results@footnote 3@ for the width as a function of coverage. In particular, the width exponent ß agrees with the

experimentally reported value. At higher temperatures (T=200 K), our simulations underestimate the exponent ß. Presumably a new diffusion channel becomes important. We have tried several single-atom processes, e.g. up-stairs climbing and biased upward and downward funneling, but none improve agreement significantly. The initial surface morphology may also exert an important influence on ß at high coverages. We are currently investigating the effects of different initial growth conditions such as a slightly rough or stepped substrate. @FootnoteText@ @footnote 1@Work partly supported by DoD; MRD and TLE primarily supported by NSF MRSEC grant DMR 96-32521. @footnote 2@A. Swan, Z.P. Shi, J.F. Wendelken, and Z. Zhang, Surface Sci. 391, L1205 (1997). @footnote 3@H.J. Ernst, F. Fabre, R. Folkerts, and J. Lapujoulade, Phys. Rev. Lett. 72, (1994); JVSTA 12, 1809 (1994).

10:00am SS1+NS-ThM6 The Atomistics of Homoepitaxial Growth on bcc(110)-Surfaces, U.K. Koehler, C. Jensen, A. v. Stockhausen, Ruhr-Universitaet Bochum, Germany

Time lapsed STM-movies, which allow a direct observation of the kinetics of growth processes on an atomic level up to 500°C, SPA-LEED and Monte-Carlo simulations are used to study the nucleation and growth behavior of homoepitaxy on the bcc(110)-surface. For Fe on Fe(110) and W on W(110) a strongly anisotropic growth with islands elongated in [001]-direction is found. A very effective Schwoebel-barrier leads to a nearly perfect statistical growth at RT with increasing island anisotropy in upper layers. At higher coverage a complete facetting of the surface is found and analyzed with SPA-LEED. A quantitative analysis of the STM-movies together with a kinetic Monte-Carlo simulation, which includes the full crystallographic symmetry of the bcc(110)surface, is used to extract information on the atomic diffusion behavior governing growth. A variety of growth features like the rugged appearance of the island edges and changes in the island shape with temperature are correctly reproduced in the simulation and can be assigned to the local diffusion energetics at step edges. Especially an anisotropic diffusion, which strongly suppresses diffusion along [001], is needed to reproduce the observed island anisotropies. A comparison of the layer distribution in the simulation with the one found with STM is used to determine the Schwoebel-barrier. Lateral island coarsening and an atom flux across the step edge following a temperature increase after growth is directly observed in STM.

10:20am SS1+NS-ThM7 Probing the Forces Stabilizing Self-Assembled Structures: Dynamics of Vacancy Island Lattices in Ag films on Ru(0001), K. Pohl, M.C. Bartelt, J. de la Figuera, N.C. Bartelt, Sandia National Laboratories; J. Hrbek, Brookhaven National Laboratory; R.Q. Hwang, Sandia National Laboratories INVITED

Nature exhibits processes that rival our most advanced patterning technologies used to create ordered lattices of nanoscale structures. Such self-organized phenomena have the potential to revolutionize materials performance, leading to higher density information storage and high-speed nanoscale electronics. Though many observations of self-organization have been reported, the fundamental mechanisms underlying such behavior remain unclear. The commonly accepted source of such mesoscopic-scale forces is the stress field mediated by the substrate which supports the grown structures. This, however, has not been confirmed, nor have such interactions been directly measured. In our work we have taken the approach of using observations of thermal fluctuations of an ordered array of surface defects to probe the interactions between the defects. In particular, we have used STM to study the array of vacancy lattice islands which forms upon exposure of a monolayer of Ag on Ru(0001) to sulfur. This is an extremely well-defined example of an ordered "mesoscopic" surface structure. At room temperature, each island is observed to vibrate around its equilibrium lattice postion. These vibrations appear to be harmonic and by performing a normal mode (phonon) analysis of the vibrations we can determine the elastic constants of the island array. The magnitude of the interactions is consistent with theories of elastic stepstep interactions in strained films. This work was supported by the Office of Basic Energy Sciences of the U.S. DOE, Division of Materials Science (Contract No. DE-AC04-94AL85000).

11:00am SS1+NS-ThM9 STM Study of Ultrathin NaCl(111) Layers on Aluminum, W. Hebenstreit, J. Redinger, TU Vienna, Austria; R. Podloucky, University Vienna, Austria; M. Schmid, P. Varga, TU Vienna, Austria

Polar surfaces like NaCl(111) are electrostatically unstable and cannot be found as terminating surfaces of crystals. But we can grow NaCl islands with (111) surface orientation on Al(111) and Al(100) single crystals. The (111) structure is revealed by atomically resolved Scanning Tunneling Microscopy (STM). The maxium coverage we could achive was 0.3

monolayer. The islands are triangular shaped, located at the lower side of substrate step edges and in the case of the Al(111) substrate alinged with the closed packed directions of the substrate. The islands consist of two Na layers with one Cl layer in between. We performed ab initio calculations with the FLAPW (full potential lineraized augumented plane waves) method of the electronic structure of a free standing Na-Cl-Na sandwich structure. These calculations reveal that the Na 3s level is filled with half an electron. The sandwich consists of two +0.5 charged Na metallic layers with a -1 charged ionic Cl layer in between, so the whole film ist neutral, free of dipoles, and electrostatically stable. The film is 4.6% laterally contracted and 5.3% expanded in vertical direction with respect to NaCl bulk distances.

11:20am SS1+NS-ThM10 Three-Dimensional SiGe Island Density on Si(001) and Morphology After Si Overgrowth@footnote 1@, J.S. Sullivan, E. Mateeva, H. Evans, D.E. Savage, M.G. Lagally, University of Wisconsin, Madison

Thin films of SiGe deposited on Si(001) can form three-dimensional (3D), coherently strained islands via a modified Stranski-Krastanov growth mode. Single films as well as highly ordered 3D superlattices with specific island sizes and densities may exhibit unique electronic and optoelectronic properties. In order to investigate how common process variables in epitaxial multiple-layer film growth influence 3D island density and morphology, we deposited SiGe films on Si(001) using low-pressure chemical vapor deposition and varied alloy composition, substrate temperature, and deposition rate. Films containing {105} faceted SiGe islands were overgrown with and embedded in Si at various substrate temperatures. Film growth and morphological evolution were monitored with in-situ, real-time reflection high-energy electron diffraction. Atomic force microscopy was performed ex-situ to characterize film morphology, and buried-island morphology was determined with cross-sectional transmission electron microscopy. The 3D island number density exhibits an Arrhenius-type dependence on substrate temperature, a power law relationship with deposition rate, and an inverse proportionality to Ge mole fraction in the alloy. Islands broaden during overgrowth and embedding due to thermally activated mass transport and Si interdiffusion; such that the {105} facets grow outward producing a (001) mesa at the apex. We will discuss our results in the context of simple thermodynamic and kinetic models and describe possible methods of obtaining and maintaining a specific size and size distribution of 3D islands. @FootnoteText@ @footnote 1@Supported by the NSF.

11:40am SS1+NS-ThM11 Effects of Ion Pretreatments on the Nucleation of Silicon on Silicon Dioxide, *C Basa*, University of North Carolina, Chapel Hill; *Y.Z. Hu*, AG Associates Inc.; *M.T. Tinani, E.A. Irene*, University of North Carolina, Chapel Hill

It is well known that the silicon (Si) surface condition is crucial for low temperature Si expitaxy.@footnote 1@ In particular, hydrogen has been implicated as an important factor inhibiting Si nucleation on Si,@footnote 2@ and SiO@sub 2@ surfaces.@footnote 3@ In addition, nuclei densities can change depending upon the preparation of the surface film.@footnote 3@ We previously studied the effects of pretreatments of various forms of hydrogen (molecular and ionic) on nucleation parameters (nuclei density, and incubation time (t@sub inc@)).@footnote 4@ We found that H@sub 2@ pretreatments passivated the surface causing longer t@sub inc@, lower nuclei density, larger nuclei, and rougher final films. H@super +@ pretreatments increased the number of nucleation sites resulting in shorter t@sub inc@, higher nuclei density, smaller nuclei, and smoother final films. However, the mechanism for H@super +@ effects on nucleation was not elucidated in that study. Therefore, the study was extended to include the effects of (1) ion dose and energy, (2) other ions (Ar@super +@, He@super +@, N@super +@) and (3) temperature of the pretreatment on the nucleation of poly-Si on SiO@sub 2@. There are three major results from the surface pretreatment experiments. First, in the range tested, ion dose has more influence on nucleation parameters than ion beam energy. Second, results with different ionic species indicate a physical, rather than chemical mechanism, for creating nucleation sites. Third, high temperature ionic pretreatments damage the surface less than room temperature treatments. @FootnoteText@ @footnote 1@T. Yamazaki, M. Miyata, T. Aoyama, and T. Ito, J. Electrochem. Soc., 139, p. 1175 (1992). @footnote 2@K. Tsubochi and K. Masu, Mat. Res. Soc. Symp. Proc., 315, p. 59 (1993). @footnote 3@J. T. Fitch, J. Electrochem. Soc., 141, p. 1046 (1994). @footnote 4@Y. Z. Hu, C. Y. Zhao, C. Basa, W. X. Gao, and E. A. Irene, Appl. Phys. Lett., 69, p. 485 (1996).

Surface Science Division Room 309 - Session SS2-ThM

Oxide Surface Chemistry

Moderator: S. Joyce, Battelle Pacific Northwest for USDOE

8:20am SS2-ThM1 Coadsorption Studies with Water: a Small Step Toward Understanding the Surface Chemical and Photochemical Properties of TiO@sub 2@, M.A. Henderson, Pacific Northwest National Laboratory@footnote 1@; W.S. Epling, C.H.F. Peden, Pacific Northwest National Laboratory; U. Diebold, Tulane University INVITED Perhaps the most prevalent surface species on an oxide surface in any environment or application is water. Depending on the conditions this molecule can be present on oxide surfaces as dissociation fragments (hydroxyls), as molecularly adsorbed species, as a thin physisorbed layer or as a bulk solid/liquid interface. The prevalence of water at oxide surfaces may lead one to think that its role in surface chemistry on oxides, such as TiO@sub 2@, is mostly that of a spectator. Although this appears to be the case in the UHV surface chemistry of more strongly bound species such as formate or methanol on TiO@sub 2@(110), water has a significant influence on more weakly bound species. This influence leads to interesting chemistry if defect sites are present. After a brief description of the properties of water on TiO@sub 2@(110), results will be presented for the formation of bicarbonate from coadsorption of water and carbon dioxide at oxygen vacancies, and for the reaction of molecular oxygen with bridging hydroxyl groups at oxygen vacancies. These results provide insights into photochemical oxidation and reduction processes occurring on titanium dioxide.@footnote 2@ @FootnoteText@ @footnote 1@PNNL is a multiprogram national laboratory operated for the U.S. DOE by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.) 2. This work was funded by the DOE office of Basic Energy Sciences, Materials Sciences, and the DOE Environmental Management Science Program.

9:00am SS2-ThM3 HCl Adsorption and Desorption on a Single-Crystal @alpha@-Al@sub 2@O@sub 3@(0001) Surface, C.E. Nelson, J.W. Elam, S.M. George, University of Colorado, Boulder

The adsorption and desorption of HCl on a single-crystal @alpha@-Al@sub 2@O@sub 3@(0001) surface were examined using laser induced thermal desorption (LITD) and temperature programmed desorption (TPD) techniques. @alpha@Al@sub 2@O@sub 3@(0001) models Al@sub 2@O@sub 3@ particles generated by solid rocket motors and HCl interactions with these Al@sub 2@O@sub 3@ particles may affect the stratospheric ozone layer. The initial sticking coefficient for HCl on @alpha@Al@sub 2@O@sub 3@(0001) at 298 K was S~10@super -3@. The HCl sticking coefficient decreased nearly exponentially with HCl coverage and the HCl coverage saturated at @THETA@@sub HCl@=0.10x10@super 15@ molecules/cm@super 2@ after HCl exposures of >10@super 10@ Langmuir. HCl desorption from the @alpha@Al@sub 2@O@sub 3@(0001) surface occurred over a temperature range from 300 K to 650 K. This broad range suggests a distribution of surface sites with different binding energies. HCl desorption results versus HCl coverage prepared by progressively annealing a fully exposed @alpha@Al@sub 2@O@sub 3@(0001) surface confirmed a wide range of binding energies. Additional HCl desorption results versus HCl coverage prepared by varying the HCl exposure revealed that HCl dissociative adsorption randomly fills adsorption sites independent of their adsorption energy. These results also suggest that surface diffusion between the adsorption sites must be negligible. Modeling of the desorption results was consistent with surface site energies that range from 19 to 36 kcal/mole. These adsorption and desorption results predict that HCl will be stable on @alpha@Al@sub 2@O@sub 3@ rocket exhaust particles at stratospheric temperatures and pressures.

9:20am SS2-ThM4 Dissociative Adsorption and Electron Stimulated Desorption of Cl on TiO@sub 2@(110) Studied by STM, AES and ISS, U. Diebold, Tulane University; G. Leonardelli, TU Vienna, Austria; W. Hebenstreit, Tulane University; M. Schmid, P. Varga, TU Vienna, Austria

The catalytic reactivity of a metal oxide can be significantly altered by adsorbed halogen species, but little is known about the adsorption of chlorine on well-characterized model oxide surfaces. We present a combined study of atomically-resolved Scanning Tunneling Microscopy (STM), Auger Electron Spectroscopy (AES) and Ion Scattering Spectroscopy (ISS) of chlorine adsorption on TiO@sub 2@(110). Chlorine was dosed from a calibrated electrolytic AgCl cell at room temperature. STM reveals a dissociative adsorption process. For small doses (@<=@0.01 Cl atoms/unit cell), a large average separation (26 Å) between Cl-Cl pairs indicate that

adsorption energy is transformed into kinetic energy of the Cl atoms. The saturation coverage for an annealed surfaces is 0.3 Cl/unit cell. STM does not show any prefered adsorption at step edges, kink sites or oxygen defect sites. Chlorine atoms can be desorbed from the surface with STM by scanning at sample bias voltages @>=@+4 V. AES measurements are complicated by electron stimulated desorption of the Cl atoms. The desorption cross section is 3 10@super -20@cm@super 2@ for a sputtered surface and >2 10@super -17@ cm@super 2@ for a annealed surface. ISS (He@super +@ ions 1keV, scattering angle 90°) detects Cl only after adsorption on a sputtered surface, while the ISS signal of an annealed surface remains unchanged during adsorption of chlorine.

9:40am SS2-ThM5 Photocatalytic Dehydrogenation of 2-Propanol on TiO@sub 2@(110), D. Brinkley, T. Engel, University of Washington

The use of TiO@sub 2@ as a photocatalyst is not well understood at a fundamental level in environmental remediation. We have investigated the thermal and photocatalytic oxidation of small oxygen containing molecules on TiO@sub 2@ single crystal surfaces using modulated molecular beam techniques. The role of specific surface orientations, defect sites and densities, oxygen sources, surface temperature, and reaction mechanisms on the reaction probability of incident molecules are essential issues that must be understood in order to maximize the efficiency of TiO@sub 2@ as a photocatalyst. For the specific case of 2-propanol on TiO@sub 2@ (110), we found that the total probability for a thermal reaction is less than 0.03 for a single collision of an incident molecule with the surface. The major and minor products in the thermal reaction are propene and acetone respectively. The reaction probability can be increased to 0.15 in the presences of bandgap radiation and molecular oxygen on a sample which has been preannealed in vacuum to create oxygen vacancies. The increase in reactivity is due entirely to the dehydrogenation channel of the reaction. Even a fully oxidized TiO@sub 2@ (110) surface has a reaction probability of 0.08 under the same conditions. The steady state reaction yield for this system is maximized at a temperature of 350 K, with an appreciable reaction rate between 250 K and 600 K. The yield is limited by desorption of acetone below 300 K and by the decrease in the surface coverage of the reactants above 400 K. The low thermal reactivity and the significant photochemical reactivity is attributed to free radical reactions initiated through electron trapping by adsorbed molecular oxygen. Our results suggest that the reaction proceeds primarily through a mechanism in which holes are trapped by undissociated 2-propanol molecules. Studies on TiO@sub 2@ (100) are currently underway and a comparison of the reactivity of this orientation with that of the (110) surface will be presented.

10:00am SS2-ThM6 Photo-stimulated NO Adsorption on Metal Oxides, *E.R. Blomiley*, *E.G. Seebauer*, University of Illinois, Urbana

Coal combustors generate large quantities of NO@sub x@ compounds that face increasingly stringent regulation. Current NO removal technologies depend in part on selective catalytic reduction (SCR) processes that react NO with reductants like CO or NH@sub 3@ at high temperature. The high costs of reheating the flue gas over the catalyst and problems with slip of the reductant past the reactor have stimulated searches for alternative technologies. Here we examine the surface photochemistry underlying one particularly novel alternative: injection of an inexpensive semiconducting metal oxide (like Fe@sub 2@O@sub 3@) in an illuminated flue geometry in order to stimulate photoadsorption. The NO-laden particulates are then removed in an electrostatic precipitator. We have shown in high and lowpressure experiments that while pure iron and titanium oxides are inactive for NO removal, iron oxides supporting adsorbed Cl display significant activity even at room temperature. The presence of such activity is surprising, and appears to result from a complex interaction between the underlying semiconductor, the adsorbed Cl, weakly adsorbed water, and the photogenerated charge carriers. The activity remains surprisingly robust even in the presence of active gaseous species like SO@sub 2@. Temperature-programmed desorption reveals that some of the NO desorbs essentially reversibly, some forms NO@sub 2@, and the remainder desorbs intact while the substrate decomposes by volatilization of iron chlorides. The potential for such reactions to influence tropospheric NO@sub x@ chemistry in urban areas will be discussed.

10:20am SS2-ThM7 The Reaction of H@sub 2@S, S@sub 2@ and SO@sub 2@ with ZnO and Cu/ZnO Surfaces, S. Chaturvedi, J.A. Rodriguez, T. Jirsak, J. Hrbek, M. Kuhn, Brookhaven National Laboratory

The surface chemistry of H@sub 2@S, S@sub 2@ and SO@sub 2@ on polycrystalline ZnO and Cu/ZnO surfaces was investigated using synchrotron-based photoemission and ab initio SCF calculations. At 100 K,

polycrystalline ZnO dissociates H@sub 2@S into HS, and the adsorbed HS species decompose at temperatures between 300 and 400 K leaving S atoms that are bonded to zinc sites of the oxide. By dosing S@sub 2@ to zinc oxide, one can generate a sulfur saturation coverage (0.7 ML) that is larger than that obtained after dosing H@sub 2@S (0.5 ML) and induce the formation of small amounts of SO@sub 3@ species on the surface. Possible reaction pathways for the dissociation of S@sub 2@ on ZnO(0001) and ZnO(1010) terraces were studied using ab initio SCF calculations. At low sulfur coverages, an adsorption complex in which S@sub 2@ is bridge bonded to two adjacent Zn atoms (Zn-S-S-Zn) is probably the precursor state for the dissociation of the molecule. H@sub 2@S and S@sub 2@ mainly react with the zinc sites of the oxide. In contrast, SO@sub 2@ preferentially bonds to oxygen forming a mixture of SO@sub 3@ and SO@sub 4@ at 100 K and pure SO@sub 4@ at 300 K. Results from ab initio SCF calculations indicate that SO@sub 2@ adsorbs on an oxygen site to form SO@sub 3@ which then extracts an oxygen from the ZnO lattice to form SO@sub 4@. The last step in this process has a substantial activation energy, and after dosing SO@sub 2@ to ZnO at 100 K a mixture of SO@sub 3@ and SO@sub 4@ is produced on the surface. Cu two-dimensional islands supported on ZnO show a band structure that is substantially different from that of pure metallic copper. The Cu/ZnO surfaces exhibit a reactivity towards H@sub 2@S and S@sub 2@ that is larger than that of ZnO but smaller than that of metallic copper.

10:40am SS2-ThM8 Methanol Adsorption and Reactivity at U and UO@sub 2@ Surfaces, M.T. Paffett, J.A. Lloyd, Los Alamos National Laboratory

In specific actinide materials storage situations it has been often observed that deleterious hydrocarbon interactions at actinide oxide surfaces have lead to a buildup of potentially explosive gases (usually H@sub 2@) arising from predominately radiolytic effects. Much less emphasis however, has been given to the deleterious consequences of unforeseen catalytic or reactive chemical events, arising from the storage of actinides and actinide oxides in mixed waste (actinides with organic solvents). In this vein we are seeking to unravel some of the fundamental details of reactive surface chemistry at model actinide oxide surfaces. In this study, the interaction of methanol-d (CH@sub 3@OD) with U and UO@sub 2@ surfaces has been studied using x-ray photoelectron spectroscopy (XPS), thermal desorptionmass spectrometry (TDMS), and secondary ion mass spectrometry (SIMS) over the temperature range of 90-500K. Low temperature (90 K) adsorption on uranium resulted in formation of methoxy species along with condensed phase adsorbed methanol. Room temperature (300K) adsorption on uranium produces only methoxy species, uranium carbide and uranium oxide. Heating to 400K completely decomposes the adsorbed methoxy species: 25% desorbing as methane and the remaining methoxide irreversibly converting to uranium oxycarbide (UO@sub 0.7@C@sub 0.3@). Concomitant with these C fragment conversion processes, desorption of hydrogen and deuterium is also seen over a wide temperature regime. Methanol-d adsorption on UO@sub 2@ also produces a methoxy surface species at surfaces temperatures << 150K and submonolayer exposure. Adsorbate decomposition following thermal desorption releases gaseous CH@sub 4@, H@sub 2@, HD, and D@sub 2@. Oxygen derived from the methanol molecule was incorporated into the UO@sub 2@ laver. The reactive adsorption and thermal decomposition of methanol at U and UO@sub 2@ surfaces is compared with that observed at other metal and metal oxide surfaces.

11:00am SS2-ThM9 The Chemistry of CeO@sub 2@(001) and Ce@sub 1x@Zr@sub x@O@sub 2@(001) Studied by Mass-Spectroscopy of Recoiled lons, G.S. Herman, Y. Gao, C.H.F. Peden, Pacific Northwest National Laboratory

Ceria has found considerable use in automotive catalytic converters due to its oxygen storage properties. Ceria can provide oxygen under fuel-rich conditions, to reduce CO and hydrocarbon emissions, and remove oxygen under fuel-lean conditions, to reduce NOx emissions. The addition of zirconium to ceria has been found to improve the oxygen storage properties and increase the stability of the ceria particles. We have used the technique of mass-spectroscopy of recoiled ions (MSRI) to investigate the interaction of O@sub 2@, D@sub 2@, and D@sub 2@O with CeO@sub 2@(001) and Ce@sub 1-x@Zr@sub x@O@sub 2@(001) (x<0.20)films grown by plasma-assisted molecular beam epitaxy. The MSRI technique is extremely surface sensitive, probing the composition in the very topmost atomic layers. By using the temperature programmed mode of MSRI we were able to measure the corresponding signals for @super 18@O@sub 2@, D@sub 2@, and D@sub 2@O to monitor the adsorption,desorption and dissolution of these species. In the temperature range from

300-1000 K, we have found that the O signal increases linearly with temperature for all three molecules. The Ce signal, however, varies considerably over this temperature range depending on the molecular species. The results for the pure ceria and mixed ceria/zirconia films will be compared.

11:20am SS2-ThM10 Reduction of Trace Element Contaminants in Aqueous Solution by Iron and Iron Oxides, S.R. Qiu, H.-F. Lai, J.A. Yarmoff, C. Amrhein, M.J. Roberson, M. Hunt, University of California, Riverside

Irrigation drainage and wastewater often contain elevated levels of trace oxyanions and oxycations, such as selenate, chromate and uranyl, which can be detrimental to humans and wildlife. A potential remediation method is to reduce the contaminants to less mobile forms by reacting the water with zero-valent iron. In this reaction, the iron serves as both an electron source and a catalyst. Most previous studies of this system were limited to the simulation of field work on a macroscopic scale. Consequently, little is known about the basic chemical interactions of these toxic ions at the water-metal interface. Our objective is to determine the microscopic reaction mechanisms by combining surface science methods and bulk chemical studies. Our bulk studies have indicated that the reactions are first-order. For surface studies, iron foil is first prepared in a UHV chamber by sputtering, or iron oxides are prepared by exposure of a hot Fe foil to O2 in UHV. The sample is then transferred to an aqueous solution containing the relevant ions. The pH and amount of dissolved oxygen in the solution are carefully controlled. The reacted surfaces are then characterized in UHV by surface analysis techniques such as x-ray photoelectron spectroscopy (XPS) or scanning tunneling microscopy (STM). We find that films of partially reduced Se, Cr and U are formed by the reaction. The reduction of U is very sensitive to dissolved oxygen, while the reductions of Se and Cr are not. The details of the surface reduction reaction mechanisms will be presented, and the implications of our results on the practical deployment of this remediation method will be discussed.

11:40am SS2-ThM11 Formation of Nitro-PAH on Flyash Particle Surfaces: The Significance of Particle Substrate on PAH Nitration, G.S. Strossman, T.F. Fister, R.W. Odom, Charles Evans & Associates; R.W. Linton, University of North Carolina, Chapel Hill

Polycyclic aromatic hydrocarbons (PAH) are present in the atmosphere in both the gas phase and condensed onto particle surfaces. Coal flyash particles are an important source of condensed PAH since both are byproducts of coal combustion. Many PAHs are hazardous in their own right due to their carcinogenic or mutagenic nature; however another factor to be considered is the transformation of PAH into potentially more harmful analogues during their exposure to the atmosphere. One example is the formation of nitro-PAH after exposure of the parent PAH to atmospheric NO@sub 2@. A full understanding of these reactions requires determining how the near surface composition of flyash particles can affect the rate of nitration of adsorbed PAH. The PAH studied in this work was benzo[a]pyrene (BaP). BaP was chosen for its reactivity and because its size (5 rings) makes it likely to exist in the atmosphere primarily in the condensed phase. Submonolayer coverages of BaP on four different flyashes were exposed to NO@sub 2@ in both dry air and with different levels of relative humidity. The samples were analyzed by TOF-SIMS, a technique that can both obtain surface elemental information and detect low levels of organic molecular species on single particles in the 3-10 @micron@ range. The results show a distinct relationship between the particle compositions and the formation of nitro-BaP, both macroscopically and among individual particles within a single flyash sample. Furthermore, for two Class C (calcium-rich) flyashes, the role played by the substrate is distinctly different between dry air and humid air exposures, while for a class F flyash (high Al, Si and Fe, low Ca) no such difference is observed.

Surface Science Division Room 308 - Session SS1-ThA

Surface Diffusion

Moderator: G.L. Kellogg, Sandia National Laboratories

2:00pm SS1-ThA1 A Novel Real-time Technique for Monitoring Adatom Surface Diffusion and Island Nucleation, *P.M. DeLuca*, *S.A. Barnett*, Northwestern University

The surface diffusion coefficient of Ga adatoms, along with twodimensional (2D) island nucleation and coarsening were measured in realtime on vicinal GaAs(001) 2x4 surfaces using specular ion current measurements (SICM). In this new technique, 3 keV Ar ions were incident upon the surface at a glancing angle (typically 1° to 3°), and the specularly scattered ion current measured. Since specular scattering requires a locally-flat surface, surface defects cause a decrease in the scattered ion current, providing a measure of average adatom and/or step-edge density. The time dependence of the Ga adatom population was measured during and after the deposition of 0.1 monolayers of Ga on vicinal GaAs(001)2x4. The scattered ion current dropped with an exponential dependence upon opening the Ga shutter and increased exponentially upon closing the shutter, in good agreement with a simple model for adatom diffusion across terraces to step edges. Diffusion coefficients, D, were obtained using the measured adatom lifetimes,@tau@, and the 70Å terrace width, x, (the miscut was 2.3 ° towards (1 1 0)) in the expression D=x2/@pi@ 2 @tau@, yielding D=(8.89x10-10 cm@super 2@/sec) exp (0.74/kT) for an As@sub 4@ ambient over the temperature range 450 to 570°C. For larger Ga coverages and/or lower substrate temperatures, deviations from simple exponentials and much longer time constants were observed, suggesting that 2D islands had nucleated. The island nucleation and coarsening behaviors will be described.

2:20pm SS1-ThA2 Direct Measurement of Adsorbed Si Dimer Dynamics on Siloga) I M. Cominalli B. S. Sugrtantrukar, Sandia National Laboratories

Si(001), J.M. Carpinelli, B.S. Swartzentruber, Sandia National Laboratories Silicon atom deposition onto a clean, well-ordered Si(001) crystal surface results in the formation of adsorbed dimers. This presentation details the use of atom-tracking scanning tunneling microscopy to determine the detailed energetics of such species in a variety of local environments at elevated temperatures (~ 100°C). Dimer diffusion along a buckled A-type step edge is found to be weakly asymmetric, indicating that the adsorbed dimer does not strongly perturb the underlying substrate bonding. A dimer adsorbed onto the middle of a terrace is attracted at only a single lattice site to a 2+1 defect in an adjacent diffusion channel, pinpointing the probable location of subsurface contamination responsible for defect formation. Additionally, a linear dependence between the activation barrier for diffusion and perpendicularly applied electric field magnitude is measured. These results provide valuable insight into the bonding and interaction of dimers with surface features prevalent during homoepitaxial growth. The quantitative measure of lattice-site specific energy parameters not only serves as input to realistic simulations, but also enables the validation and refinement of such calculations. 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.

2:40pm SS1-ThA3 Ion-Induced Surface Diffusion of Ge on Si(111), E.G. Seebauer, R. Ditchfield, University of Illinois, Urbana

In thin film deposition, bombardment of the surface with low-energy (10-100 eV) ions during growth has been shown to improve film quality in a variety of applications. In many cases, the improvement is attributed to enhancements in surface diffusion of the depositing species. However, such effects have never been quantified in a direct way, and the mechanisms for energy transfer from the ions to the mobile atoms remain unclear. Here we report for the first time the direct quantification of ioninfluenced surface diffusion, using Ge on Si(111) as the adsorption system and second harmonic microscopy as the measurement probe. The effects are significant and fall into two regimes of temperature. Below about 700 C, the activation energy E@sub diff@ remains unaffected, but the preexponential factor D@sub o@ increases. The increase varies as the square root of ion energy and mass (going from He to Ar to Xe), culminating in a factor of 10 increase for Xe near 60 eV. Simulations by molecular dynamics reproduce this effect nearly quantitatively, and point to an increase in the average jump length due to billard-ball-like collisions as the governing mechanism. At higher temperatures, both E@sub diff@ and D@sub o@

decrease dramatically, again according to a square-root energy and mass dependence. E@sub diff@ falls by 75%, while D@sub o@ falls by 8 orders of magnitude. Molecular dynamics simulations again reproduce the effects, and point to ion-mediated changes in the number of mobile adatoms as the governing mechanism. In both temperature regimes, the effects set in only above a threshold energy of about 15 eV.

3:00pm SS1-ThA4 Schwoebel Barriers on Stepped Pt(111)@footnote 1@, P.J. Feibelman, Sandia National Laboratories

The ab-initio Schwoebel barrier calculated for downward self-diffusion across A-type steps on Pt(111) is E@super S@(A) ~ 0.02 eV. This is too small to be consistent with the notion that lowering E@super S@(A) is how O promotes layer-by-layer epitaxy on Pt(111). Geometric arguments explain why E@super S@(B), the Schwoebel barrier at B-type steps, is more than an order of magnitude larger than E@super S@(A), a result in conflict with the observation of three-dimensional Pt islands on Pt(111) bounded by A-type steps. The first-principles downward-transport barriers are vindicated by new observations of Pt growth morphology, in which the CO background has been greatly reduced. @FootnoteText@ @footnote 1@ Work supported by the U. S. Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company for the U. S. Department of Energy.

3:20pm SS1-ThA5 Diffusion and Island Formation of Water Molecules on Ice Ih Surfaces, E.R. Batista, H. Jonsson, University of Washington INVITED We present theoretical calculations of the deposition, adsorption, diffusion, and island formation of water admolecules on the basal face of ice Ih. The calculations are based on both pairwise additive interaction potentials as well as a polarizable model. The sticking coefficient is found to be near unity for vapor deposition, but drops to 0.9 for incident energy of 1.5 eV and 60 degree angle of incidence. At low coverage, an admolecule prefers to sit at non-crystallographic sites (i.e. not fitting into the ice lattice) with a large binding energy. Since ice Ih is proton disordered, there is a range of binding energies, and for some local environments the binding energy is on the order of (and even larger than) the cohesive energy. The proton disorder also results in a range of activation energies for diffusion. After mapping out a large number of diffusion barriers using the Nudged Elastic Band method, a kinetic Monte Carlo calculation of the diffusion at 140 K was performed. At short time, the mean squared displacement has anomalous scaling with time as is common for diffusion on random lattices. From the long time scaling a diffusion barrier is obtained which is not inconsistent with recent upper bound found by Brown and George. The simulated diffusion is also reasonably consistent with earli! er estimates of the diffusion leng th by Mason. Paths and energy barriers for the formation of small islands have also been studied. It is found that islands up to and including pentamer are non-crystallographic, but the hexamer is crystallographic. The dominant activation energy barrier to the formation of the hexamer is the admolecule diffusion barrier.

4:00pm **SS1-ThA7 H and O promoted Self-Diffusion of Pt(110)**, *S. Horch*, *S. Helveg*, *I. Stensgaard*, *E. Laegsgaard*, *F. Besenbacher*, Aarhus University, Denmark

The surface self-diffusion of Pt adatoms on the Pt(110)-(1x2) surface is studied using variable-temperature Scanning Tunneling Microscopy. Exposing the surface to Hydrogen or Oxygen leads to an enhancement of the mobility of the adsorbed Pt adatoms. Atomically resolved STM movies provided the first experimental evidence that in the case of H this is due to the existence of H-Pt ad-dimer skyhooks diffusing several orders of magnitude faster than normal Pt adatoms. These movies allow us to analyse the lifetime distribution of these ad-dimers which gives a surprisingly high binding energy of about 0.8 eV. Nevertheless, only a small fraction of all Pt adatoms form these ad-dimers at the same time. A tentative model will be presented to explain these findings and compare them to the case of O.

4:20pm SS1-ThA8 Adsorption of N on Fe(100): Diffusion and Adatom-Adatom Interactions Studied with Scanning Tunneling Microscopy, *M.O. Pedersen*, *L. Österlund*, *E. Laegsgaard*, *I. Stensgaard*, *F. Besenbacher*, University of Aarhus, Denmark

The dynamics and adsorbate-adsorbate interactions of N adatoms on a Fe(100) surface have been studied using variable temperature Scanning Tunneling Microscopy (STM). By recording a sequence of STM images as a film, we can track the individual N atoms at low coverage, and study their mobility. From these STM films, the diffusion constant of the N atoms can be derived, and by varying the sample temperature from 299 K to 323 K, a

diffusion barrier of 0.92 eV \pm 0.04 eV and a prefactor of D@sub 0@ = 2.4 10@super -3@ cm@super 2@/s are found. This value of the diffusion barrier is in good agreement with the diffusion barrier calculated using Density Functional Theory.@footnote 1@ From the STM images, the N adatom pair correlation function can also be deduced, from which an ensemble interaction potential can be found. Measuring the ensemble interaction potential at two different coverages (0.034 ML and 0.10 ML), allows us to quantify the entropic contributions and thus find the direct pair interaction potential between the N atoms. As expected, the nearest neighbour interaction is found to be strongly repulsive, whereas the next nearest neighbour interaction is attractive. From the STM images, the N atoms are found to adsorb in the four-fold hollow site, confirming previous LEED experiments. Due to the attractive interactions between the N adatoms, island nucleation is observed, even at sub-monolayer coverage. @FootnoteText@ @footnote 1@J.J. Mortensen, L.B. Hansen and J.K. Norskov, private communication

4:40pm SS1-ThA9 Novel Diffusion Channel Parallel to Steps: CO on Pt(111), X.D. Xiao, J.-W. Ma, M.M.T. Loy, The Hong Kong University of Science and Technology, China

Surface diffusion parallel to steps for CO on Pt(111) has been studied by an optical diffraction technique. With a large accessible dynamic range for diffusion coefficient measurement from 10@super -12@ to 10@super -8@ cm@super 2@/sec, we could cover a wide range of temperatures from 120 to 320 K, within which non-Arrhenius processes can be unambiguously identified. For steps along [110] direction (B-type steps in the present experiment) with a density of one-step/30-atoms, it was found that diffusion at low temperatures are controlled by terrace diffusion and at high temperatures controlled by diffusion along step edges. At 0.3 ML CO coverage, the terrace diffusion was measured with an activation energy of 4.2 kcal/mol and a prefactor of 6x10@super -7@ cm@super 2@/sec. The diffusion along step edges was measured with an activation energy of 10.9 kcal/mol and a prefactor of 0.2 cm@super 2@/sec. It is this large prefactor that compensates the respect high activation barrier for step edge diffusion to take control at high temperatures. As we change the step direction to along [112], a novel diffusion channel was observed. Now, with the same step density as in the previous case, the diffusion is enhanced by a factor of ~10 over the entire temperature range as compared to the terrace diffusion. At 0.3 ML CO coverage, this new channel is characterized by a simple Arrhenius behavior with E@sub D@=3.2 kcal/mol and D@sub o@=5x10@super -7@ cm@super 2@/sec. At 0.5 ML CO coverage, the diffusion is dominated by this new channel only at low temperatures but still by along step edge diffusion at high temperatures. Discussion on how the new channel is formed will be presented.

5:00pm **SS1-ThA10 Potassium Surface Diffusion by Optical Techniques**, *W. Zhao*, *M. Asscher*, The Hebrew University, Israel

Coverage grating-optical second-harmonic diffraction method has been used to measure the diffusion of pure potassium and coadsorbed with CO on Re (001) surface in the potassium coverage range of 0.6-1 ML. The activation energy (E@sub d@) and the preexponential factor (D@sub 0@) for diffusion in both show a clear compensation effect. For the pure potassium case, E@sub d@ and D@sub 0@ change quadratically with the coverage, having a minimum in the potassium coverage of 0.75 ML. The activation energies for diffusion are determined to be 5.0±0.2, 3.9±0.7, 3.6±0.2, and 5.0±1.0 kcal/mol, the preexponentials are 5.6x10@super -3±0.3@, 3.5x10@super -4±1.1@, 5.8x10@super -4±0.3@, and 3.7x10@super -1±1.9@ cm@super 2@/s corresponding to potassium coverages of 0.93, 0.84, 0.73, and 0.59, respectively. The results are discussed in terms of electrostatic dipole-dipole repulsive interactions among neighboring adsorbates. In the coadsorption case, it is found that CO hinders potassium surface diffusion significantly, with the effective activation energy for 0.8 ML K rising to 15 kcal/mol for CO average coverage of 0.06 ML. The attractive interaction and complex formation (observed by TPD) of CO-K are proposed as the main reasons for the increasing E@sub d@.

Surface Science Division Room 309 - Session SS2-ThA

Oxide Growth and Structure

Moderator: W. Hebenstreit, Tulane University

2:00pm SS2-ThA1 Structural and Pt Adsorption Properties of Ultrathin Al@sub 2@O@sub 3@(001) Films on Al(111), Mo(110), and Ru(001)@footnote 1@, D.R. Jennison, C. Verdozzi*, P.A. Schultz, M.P. Sears, Sandia National Laboratories

Using first-principles LDA calculations, we explore Al@sub 2@O@sub 3@ ultrathin films on a variety of metallic substrates. A general principle of interface structure is proposed, which then affects the film-surface termination (i.e., Al or O) and the degree of surface polarity. Several film thicknesses are compared. In the thinnest films, we find a favored phase not observed in bulk crystals, having only four-fold coordinated Al-ions. For all studied substrate materials, this indicates that a structural transformation could occur during film growth, as the film bulk and interfacial energies compete. Large differences, ~50%, are found in the adhesion of a metallic overlayer (Pt) with two vs. three O-layer thicknesses. This is due to greater surface polarity in the latter, which in turn is related to decreased stability of the thinnest film phase. Diffusion barriers are presented for isolated Pt adatoms and predictions made of hop length and symmetry. Huge coverage dependences (five-fold) in the adsorption energy of Pt occur between 1/3 and 1 ML, the binding being ionic when the Pt atoms are isolated (Pt@super +1@ or greater), but image-polarization driven at 2/3 ML and higher coverages. Our results agree with experimental ISS and HREELS data on the thinnest films.@footnote 2@ @FootnoteText@*Current address: Univ. of Edinburgh, Edinburgh EH9 3JX, UK. @footnote1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE under Contract DE-AC04-94AL85000. @footnote 2@J. Libuda, et al., Surf. Sci. 318 (1994)

2:20pm SS2-ThA2 Interaction and Growth of Rh on Hydroxylated Alumina Model Substrates, J. Libuda, S. Stempel, M. Heemeier, M. Frank, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; A. Sandell, Lund University, Sweden; S. Andersson, P.A. Brühwiler, N. M@aa@rtensson, Uppsala University, Sweden; M. Bäumer, H.-J. Freund, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

In contrast to simple model surfaces, alumina supports employed in technical catalysis exhibit a variety of complex surface structures. In particular, depending on preparation, their surface can be covered to a large extend by hydroxyl groups, affecting the chemical behaviour not only with respect to adsorption of gases but also the interaction with the catalytically active metal component. In order to study the dependence of metal growth and metal oxide interaction on the surface properties of an alumina support, we have established a hydroxylation procedure based on Al deposition and subsequent water exposure, which is applied to a well ordered Al@sub 2@O@sub 3@ film grown on NiAl(110). The hydroxylated surface is characterized with respect to morphologic (Scanning Tunneling Microscopy (STM) and Spot-Profile Analysis-LEED (SPA-LEED)) and electronic properties (High Resolution Photoelectron Spectroscopy (PES)). Upon Al deposition, uniformly distributed small metallic aggregates are formed, which can be transformed to larger two-dimensional patches and three-dimensional islands by annealing. The small aggregates can be completely oxidized by water exposure. Following this treatment, characteristic features in the Al 2p and O 1s regions are observed. The growth of Rh on the modified surface has been investigated by STM and SPA-LEED and compared to previous results for the non-modified alumina support. In contrast to the non-modified support, no decoration of characteristic one-dimensional oxide defect structures is found. Instead, the formation of a high density layer of uniformly distributed aggregates is observed. The dissappearance of the characteristic O 1s and Al 2p features upon metal exposure points to a direct chemical interaction between the surface hydroxyl groups and the Rh deposided.

2:40pm SS2-ThA3 Growth of Ultrathin ß-MnO@sub 2@ on TiO@sub 2@(110) by Oxygen-Plasma-Assisted Molecular Beam Epitaxy, S.A. Chambers, Y. Liang, Pacific Northwest National Laboratory

We have used oxygen-plasma-assisted MBE to grow epitaxial rutile films of pyrolusite (@beta@-MnO@sub 2@) on TiO@sub 2@(110) for thicknesses of 1 to 6 bilayers (BL). We define a BL to be a layer of Mn and lattice O and an adjacent layer of bridging O within the rutile structure. The resulting surfaces have been characterized in-situ by RHEED, LEED, XPS, XPD, and AFM. Well-ordered, pseudomorphic overlayers form for substrate

temperatures between 400C and 500C. Mn-Ti intermixing occurs over the time scale of film growth for substrate temperatures in excess of 500C. Films grown at 400-500C exhibit classic Stranski-Krastanov growth whereas those grown at higher temperatures are atomically flat. 1-BL films grown at 450C form a well-ordered surface cation layer of Mn on the rutile structure with at most 10% indiffusion to the second cation layer. Thicker films rapidly disorder due to the simultaneous formation of pyrolusite and ramsdellite (@gamma@-MnO@sub 2@), which is orthorhombic and not lattice matched to TiO@sub 2@(110). However, thin films of rutile pyrolusite are preferentially stabilized by the TiO@sub 2@ substrate. @FootnoteText@ Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research - Environmental Management Science Program.

3:00pm SS2-ThA4 Ordered Cerium Oxide Thin Films Grown on Ru(0001) and Ni(111)@footnote 1@, D.R. Mullins, P.V. Radulovic, S.H. Overbury, Oak Ridge National Laboratory

Ultrathin oxide films grown on single crystal metal substrates are advantageous for studying the adsorption and reaction of gases on oxide surfaces. Ultrathin films have a high surface area relative to their bulk volume. Their composition can be controlled during growth. They can be grown as nearly single crystals, can be readily removed and replenished in situ and they don't suffer from sample charging when using electron or ion probes. Cerium oxide thin films between 1 - 10 ML thick have been grown in situ on the Ru(0001) and Ni(111) surfaces. Well ordered films were grown by dosing metallic Ce in an oxygen ambient of 10@super -8@ -10@super -7@ torr while the substrate was at 700K. Fully oxidized films could be grown by using a higher oxygen pressure while substoichiometric films were grown by reducing the oxygen pressure. The relative amounts of Ce@super +3@ and Ce@super +4@ were determined by soft x-ray photoelectron spectroscopy. Ion scattering spectroscopy (ISS) and LEED indicate that the cerium oxide films have the same symmetry as the substrate on which they are grown, i. e. six-fold on Ru(0001) and three-fold on Ni(111). The principal azimuths of the oxide films are aligned parallel to the principal azimuths of the substrates. The lattice constant of the cerium oxide is nominally the same as cubic CeO@sub 2@. Angle resolved ISS indicated that the fully oxidized films were predominantly terminated by an oxygen layer, whereas the substoichiometric films had a significant amount of cerium in the top layer. The structure and composition of the films grown on Ru(0001) were stable at temperatures up to 1000K. The films grown on Ni(111) lost oxygen upon annealing to 1000K. @FootnoteText@ @footnote 1@ Research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. under contract number DE-AC05-96OR22464.

3:20pm SS2-ThA5 Evolution of Surface Morphology and Growth Modes for Epitaxial alpha-Fe@sub 2@O@sub 3@ on alpha-Al@sub 2@O@sub 3@, I. Yi, A. Chambers, Pacific Northwest National Laboratory

We have investigated how the surface morphology of epitaxial alpha-Fe@sub 2@O@sub 3@ evolves with film thickness on alpha-Al@sub 2@O@sub 3@ as a function of growth rate and surface orientation. The lattice mismatch of this materials system is 5.7%. The growth technique used was oxygen-plasma-assisted molecular beam epitaxy. Film surfaces were characterized as a function of thickness in situ using reflection highenergy electron diffraction, low-energy electron diffraction, x-ray photoelectron spectroscopy and diffraction, and non-contact atomic force microscopy. Island formation is observed upon relaxation of the Fe@sub 2@O@sub 3@ film to its bulk lattice spacing. Relaxation begins at coverages of only ~1 full monolayer. Furthermore, the shape and size distributions of the islands are critically dependent on growth rate during the early stages of film growth. Sparsely populated, high-aspect-ratio islands form at higher growth rates, whereas more densely populated islands with lower aspect ratios form at lower growth rates. The former surface morphology is found to be a very poor template for further epitaxy, and gives rise to poorly ordered material, whereas subsequent epitaxy on the latter morphology produces very well ordered films and surfaces. The low-aspect-ratio islands formed at the initial stages of film growth coalesce within the first 50 Å. With a reduced number of islands, the surface becomes smoother. With additional growth, the surface morphology is greatly improved and the island-to-island height variation is reduced to few Ångstroms.@footnote 1@ @FootnoteText@ @footnote 1@Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research Environmental Management Science Program.

3:40pm SS2-ThA6 The Nature, Growth and Stability of Vanadium Oxides on Pd(111), F.P. Leisenberger, M.G. Ramsey, S.L. Surnev, F.P. Netzer, Karl-Franzens-Universität Graz, Austria

The study of metal - oxide interfaces is at the cutting edge of present day surface science. This particular study is inspired by the fact that the vanadium oxide - palladium phase boundary is an important system in practical heterogeneous catalysis. In this work high resolution XPS and NEXAFS have been used to characterise the growth and stability of vanadium oxide on a Pd(111) single crystal surface as a model system. The vanadium oxides have been prepared by reactive evaporation of vanadium in p@sub O2@ = 2 x 10@super -7@ mbar at 250°C from submonolayer to 15 ML coverages. The oxide morphology has been gauged by the C 1s XPS following the adsorption of CO as a probe molecule for the bare palladium sites. The stoichiometry of the oxide phase varies as a function of coverage, V@sub 2@O@sub 5@ / VO@sub 2@ - like at low coverages to V@sub 2@O@sub 3@ for the thicker oxide layers as indicated by the characteristic NEXAFS fingerprints at both the V 2p and O 1s edges. The thermal stability of the oxides is dependent on the coverage: the decomposition onset temperatures range from 300°C for submonolayer coverage to @>=@600°C for 15 ML. The V 2p XPS data indicate that the oxides disproportionate into higher and lower oxidation state phases. For nominal oxide coverage of 1 ML two different LEED patterns are observed on annealing between 250°C to 350°C. The surface formed below 300°C has a complex pattern and allows the uptake of CO, while on heating to 300 -350°C a simple p(2x2) structure evolves, on which CO cannot be accommodated. This behaviour suggests that initially ordered oxide island structures are formed with bare palladium in between. At the higher temperature (300 - 350°C) a more homogeneous passive surface layer evolves.

4:00pm SS2-ThA7 Photoemission Study of Ultra-thin NiO(111) Films Grown on Au(111), B.R. King, M. Howard, P.S. Robbert, H. Geisler, C.A. Ventrice, Jr., University of New Orleans; D.A. Hite, P.T. Sprunger, CAMD/Louisiana State University

Only a few systems are known where the polar surface of an ionic metaloxide crystal can be grown without the introduction of surface impurities. One example of a stable polar surface is the growth of NiO(111) on Au(111) by evaporation of Ni in an O@sub 2@ atmosphere at ~300 °C.@footnote 1@ STM analysis of this surface has shown that the NiO(111) surface consists of a p(2x2) array of four-atom tripods with several missing-atom point defects on the surface as well as regions of bare Au.@footnote 1@ Angle-resolved photoelectron spectroscopy and x-ray absorption measurements have been performed to better understand the growth morphology and the resulting electronic structure of this system. Significant changes in the Au-5d photoemission intensity features are observed after the growth or the NiO which indicates that the Au regions observed with STM result from segregation, not NiO three-dimensional island growth into the Au substrate. The photoemission results also show a 1 eV shift in the Ni-3d emission to lower binding energy when compared to previously published results for single-crystal NiO(100).@footnote 2@ Since Ni deficient NiO results in a p-type substrate, this shift and the observation of missing-atom point defects with STM provide evidence that the (111) surface is Ni terminated. Analysis of structural changes in the Ni coordination upon oxidation is currently being performed by comparison of x-ray absorption features of Ni/Au(111) and NiO(111)/Au(111) systems. @FootnoteText@ @footnote 1@C. A. Ventrice, Jr., et al., Phys. Rev. B 49, 5773 (1994). @footnote 2@S. Hüffner et al., Z. Phys. B 83, 185 (1991).

4:20pm SS2-ThA8 The Effects of High Temperature Annealing on the Surface Reconstruction of NiO(111), *M.A. Schofield*, *A.K. Hicks*, *M. Gajdardziska-Josifovska*, University of Wisconsin, Milwaukee

NiO is an ionically bonded solid with a rocksalt structure. In the crystallographic direction, NiO consists of alternating close-packed planes of nickel and oxygen. The bulk terminated (111) surface, therefore, is a polar surface with theoretically predicted infinite surface energy. Consequently, adsorption of charged species at the surface or a considerable rearrangement of the atomic ordering is expected to occur to stabilize the surface. While microscopic faceting into neutral planes has been the accepted model for polar oxide surfaces, recent theoretical and experimental studies have reported a 2x2 reconstruction as a stabilize known as octapolar, or nanofaceting structure) is the smallest possible scaling of the faceting model. In the present work we report two new reconstructions of annealed NiO(111) surfaces which cannot be readily explained by nanofaceting. Electron transparent single-crystal NiO samples were prepared for study of the (111) surface in plan view by transmission

electron microscopy (TEM) and diffraction (TED) techniques. Annealing experiments were performed under high vacuum and atmospheric conditions over a wide range of temperatures and times. Under high vacuum annealing conditions a preferential desorption of oxygen from the sample surface resulted in the formation of epitaxial nickel islands. Conversely, for annealing experiments performed under atmospheric conditions, the NiO(111) samples exhibited surface reconstructions. Two reconstructions were observed and identified as having (@sr@3x@sr@3)R30° and (2@sr@3x2@sr@3)R30° surface periodicities from TED patterns obtained after annealing above 800°C in air. Both reconstructions were stable in air even after prolonged exposure of several weeks to atmospheric conditions.

4:40pm SS2-ThA9 Morphology of MgO (111) Surfaces: Artifacts Associated with the Faceting of Polar Oxide Surfaces into Neutral Surfaces, R.A. Plass, J. Feller, M. Gajdardziska-Josifovska, University of Wisconsin, Milwaukee

We have found using optical, atomic force, scanning and transmission electron microscopies that the polar ionic MgO (111) surface does not facet into neutral (100) type planes upon high temperature annealing, as has been commonly believed, rather it appears to be stabilized by surface reconstructions containing cyclic ozone. The triangular pyramidal pits which Henrich@footnote 1@ associated with this presumed faceting turn out to be artifacts of the acid etch used in the sample preparation process. We have determined that the pits have walls sloped at $10.8^{\circ} \pm 2.8^{\circ}$ with respect to the (111) surface, not the 54.7° expected for faceting to (100) type planes. The pit edges were confirmed by transmission electron microscopy to be along the three equivalent type directions. The morphology of this surface before and after annealing as well as transmission electron diffraction data and proposed atomic structures of three native surface reconstructions seen after annealing will be discussed. @FootnoteText@ @footnote 1@V.E. Henrich, Surf. Sci., 57 (1976) 385

5:00pm SS2-ThA10 Surface Phonons and Surface Phase Transitions in KTaO@sub3@ (001), J.A. Li, E.A. Akhadov, T.W. Trelenberg, S.A. Safron, J.G. Skofronick, Florida State University; L.A. Boatner, Oak Ridge National Laboratory

Phase transitions of the (001) surface of KTaO@sub3@, prepared by cleaving a single crystal sample in situ, have been investigated by highresolution Helium Atom Scattering (HAS). Angular distribution measurements of the diffractive scattering show that thermal cycling of the sample from room temperature to low temperatures (@<=@140 K) and back to @>=@220 K induces the (1x1) surface found after cleaving at ~300 K to reconstruct to a (2x1) surface. The reconstruction appears to occur much more rapidly, minutes vs. days, when the temperature is cycled to above ~250 K. The (2x1) phase appears to be stable until ~365 K at which point the surface reverts partially to the (1x1) structure. A time-of-flight technique was employed to measure the helium atom-single phonon creation/annihilation scattering events in order to examine the surface phonon dispersion of this surface. Experiments were carried out over the temperature range of 80 to 220 K. For bulk KTaO@sub3@ considerable softening near the Brillouin zone center of the transverse optical phonon branch had been reported as the temperature was reduced. For the surface, the observed softening in the surface phonon branches is not as great, but it appears to become more pronounced as the temperature is raised from 80 to 220 K. The implications of the temperature behavior of the surface lattice dynamics and the surface phase transitions are discussed.@footnote1@ @FootnoteText@ @footnote1@ Work supported in part by US DOE grant No. DE-FG02- 97ER45635.

Surface Science Division Room Hall A - Session SS-ThP

Surface Science Division Poster Session

SS-ThP1 Photon-Induced Localization and Correlation Effects in Optically Absorbing Materials, *D.E. Aspnes*, North Carolina State University; *L. Mantese*, University of Texas, Austin; *K.A. Bell*, North Carolina State University; *U. Rossow*, Technical University of Ilmenau, Germany

Surface-optical data that contain structures related to energy derivatives of bulk critical points show that photons themselves modify the optical properties of the material being measured, and therefore, that the standard picture of optical absorption must be revised. Using a simple model that retains correlations discarded in the random phase approximation yet can be solved analytically to first order in timedependent perturbation theory, we show that (1) the final electron and hole states are localized near the surface by the finite penetration depth of the photons but (2) these final-state packets also evolve by propagation with their respective group velocities. More important, since the energy of a wave function is the expectation value of the Hamiltonian, for finite packets the surface contribution to the energy and lifetime is also finite, thereby providing a natural explanation to derivative structures and to apparent differences in nominally bulk critical point energies and broadening parameters with surface preparation. Further, we show that (3) broadening must be described by a sinc function as in standard filter theory, instead of the traditional phenomenological broadening parameter. The implications are extensive. For example, these results show that (4) slab calculations of surface electronic properties, where limited spatial extent is an unwelcome consequence of limited computing power, may actually provide a more accurate representation of surface optical spectra than hypothetical calculations that take the entire bulk into account.

SS-ThP2 Study of Aluminum Deposition on GaN (0001)@footnote 1@, H. Cruguel, Y. Yang, S.H. Xu, G.J. Lapeyre, Montana State University; J.F. Schetzina, North Carolina State University

GaN has attracted much attention because of its great importance in fabricating light emitting diodes (LED), detectors and laser devices which operate in the green, blue and ultraviolet range. The vapor (in situ) deposition of Al on wurzite n-GaN(0001) clean surface is investigated with high-resolution photoemission. The samples grown at North Carolina State University were successfully clean by several techniques and measured at the Wisconsin Synchrotron Radiation Center (SRC). We have measured both Al 2p and Ga 3d photoemission level for different coverage of Al on GaN. With the Voigt line fitting of Al 2p we found two components, in addition to the metallic component, for all the deposition. The behavior is attributed to the formation of both AlGa@sub x@N@sub 1-x@ and AlN compounds on the GaN surface. The explanation is in agreement with the line fitting of Ga 3d level which also shows three components (bulk GaN, AlGa@sub x@N@sub 1-x@ and metallic). When we anneal the sample after the Al deposition the metallic peak disappears but the intensity of the two other components of the AI line and the components in the Ga line associate with AlGa@sub x@N@sub 1-x@ are still increasing. This means that the reaction still occurs and that the thickness of the two compounds increases. In addition we have deposited Mg on the sample to determine which compound is nearest the surface. We found that a metallic peak is only observed in Al 2p spectra. The results suggest that the sequence of materials is AIN on top, following by AlGa@sub x@N@sub 1-x@ and then GaN. The interpretation of the data will be presented. @FootnoteText@ @Footnote 1@ Research supported by ONR/DEPSCOR grant, SRC supported by NSF.

SS-ThP3 Adsorption Site of Mg on GaN(0001) from Photoelectron Holography Imaging, S.H. Xu, H. Cruguel, Y. Yang, Montana State University; J.F. Scheitzina, North Carolina State University; G.J. Lapeyre, Montana State University

The adsorption sites of Mg on GaN(0001) with and without predosed atomic hydrogen have been determined by the small-cone photoelectron holographic imaging(PHI) technique.@footnote 1@ The experiments were performed at the Iowa/Montana State University beamline at Synchrotron Radiation Center(SRC) in Madison. The diffraction data is directly inverted without the need for models to observe the local site of the Mg emitter. The GaN samples were grown with the MOCVD method. In the analysis chamber the samples were cleaned by several heatings at about 850 °C, and the sample showed a good 1x1 LEED net. After dosing with atomic

hydrogen followed by deposition of 0.5 ML Mg, the 1x1 LEED net is still observed but with a higher background. A set of 82 emission spectra by photon energy scans at the constant initial energy(CIS) of the Mg 2p level were measured. The angles for the set of CIS span a grid over one-sixth of the emission hemisphere(the surface irreducible symmetry element). The PHI images show that the adsorption sites in each case is different. With H interlayer, Mg adsorbs in a three fold site with an atom directly below the Mg emitter, usually called the T4 site. The adsorption height is about 1.4 Å above the Ga adlayer. Without the H interlayer, Mg likes to replace the Ga atoms in adlayer. The observations suggested that the H interlayer plays a key role in preventing Mg from diffusion into GaN bulk by not interchanging with the Ga atoms. This work is supported by ONR/DEPSCOR grant, SRC supported by NSF. @FootnoteText@ @footnote 1@Huasheng Wu and G. J. Lapeyre, Phys. Rev. B 51, 14549(1995)

SS-ThP4 Time-Resolved RHEED Studies of Ge(111)-c(2x8) <-> (1x1) Phase Transition, X.L. Zeng, B. Lin, H. Elsayed-Ali, Old Dominion University

The dynamic behavior of Ge(111)-c(2x8) <-> (1x1) phase transition was investigated by time-resolved reflection high-energy electron diffraction which employs a 100 ps electron pulse as a RHEED probe synchronized with 100 ps 1.06 μ m laser pulse to produce a transient surface temperature rise. By recording the RHEED intensities of (0,1/2) and (0,1) spots, the transient process of the reconstruction phase transition was monitored. First, our static RHEED study shows that Ge(111)-c(2x8) reconstruction state starts to disorder at the vicinity of 500K and are converted to a highly disordered adatom arrangement at 573K. Second, the time-resolved RHEED measurements are carried out by biasing the Ge(111) sample at 500K and using IR laser to produce a transient surface temperature jump as high as 130K. Under these conditions the Ge(111)-c(2x8) reconstructed adatom arrangement remains ordered up to 630K for a time duration of 400 ps, which is well above the characteristic temperature of 573K for the Ge(111)-c(2x8) <-> (1x1) phase transition.

SS-ThP5 Correlation Effects and Origin of the Phase Transition in Pb/Ge(111), A. Mascaraque, Universidad Autonoma Madrid, Spain; J. Avila, M.C. Asensio, LURE and CSIC, France; E.G. Michel, Universidad Autonoma Madrid, Spain

The @sr@3 x @sr@3-Pb/Ge(111) structure undergoes a phase transition to a @sr@3 x @sr@3 phase at low temperature (LT),@footnote 1@ which has been interpreted as the stabilization of a charge-densitywave.@footnote 1@ The role of correlation effects and Fermi surface (FS) nesting as driving forces of the transition has been considered.@footnote 1,2@ We report an investigation on the electronic structure and Fermi surface of Pb/Ge(111) along the phase transition using angle-resolved photoemission. Pb/Ge(111) exhibits a prominent Pb p@sub z@ dispersing surface state at RT, that splits in two dispersing bands at LT. We monitored in detail the intensity at the Fermi energy, both at room temperature (RT) and LT, in different points of the surface Brillouin zone. While there is an overall intensity decrease at LT, the effect is more pronounced at 1/2@GAMMA@K, suggesting that the LT phase is indeed metallic. The role of correlation effects and FS nesting was also tested by measuring the dispersion of the surface features both at LT and RT. The evidences found support that nesting is not the driving force of the transition. However, the modifications observed in the LT electronic structure indicate a significant gain in electronic energy along the phase transition. These findings will be discussed in view of existing theoretical models. @FootnoteText@ @footnote 1@J.M. Carpinelli et al., Nature 381, 398 (1996). @footnote 2@A. Goldoni et al, Phys.Rev. B 55, 4109 (1997).

SS-ThP6 Adatom Pairing or Dimer Formation for Si on Ge(001)?, H.J.W. Zandvliet, E. Zoethout, University of Twente, The Netherlands; W. Wulfhekel, University of Twente, The Netherlands, Netherlands; G. Rosenfeld, B. Poelsema, University of Twente, The Netherlands

The early stages of room temperature growth of Si on Ge(001) have been studied with Scanning Tunneling Microscopy. The smallest observed entity is a cluster containing two Si atoms. The two atom clusters residing on top of the substrate dimer rows are dimers. These on top dimers exhibit a rotational mode and diffuse preferential along the substrate rows with activation barriers of 0.7 eV and 0.86 eV, respectively. Using dual bias imaging we show that the two-atom clusters that are positioned in trough positions are ordinary dimers too rather than adatom paired units. These "trough" dimers occasionally hop to an on top position and vice versa providing a pathway for diffusion across the substrate dimer rows.

SS-ThP7 Step Fluctuations on Vicinal Si(113), K. Sudoh, T. Yoshinobu, H. Iwasaki, Osaka University, Japan; E.D. Williams, University of Maryland The properties of steps play an important role in the description of dynamics of processes such as faceting and crystal growth. The vicinal surfaces of Si(113) are a model system for studying the evolution of steps into stable facets involving step-step attractions.@footnote 1@ In this paper, we investigate quantitatively the fluctuation properties of steps relevant to step coalescence using scanning tunneling microscopy (STM) on a Si(113) surface miscut along a low symmetry azimuth. In local thermal equilibrium at 710 °C, which is near the faceting transition temperature, coexistence of single, double, triple, and quadruple steps has been observed. To determine the dependence of the step stiffness on step height, we have measured the step-correlation function@footnote 2@ for the steps with different heights from STM images. This result shows that the step stiffness is proportional to the step height. This behavior can be qualitatively understood in terms of a terrace-step-kink (TSK) model which includes a short range step-step attraction. Performing Monte Carlo calculations, we have found that the linear dependence of the step stiffness on step height is expected only near the faceting temperature where unbinding of steps becomes facile. The high resolution STM images of the edge of triple and quadruple-steps evidently reveal significant unbinding of steps, in agreement with the prediction. @FootnoteText@ @footnote 1@S. Song and S. G. J. Mochrie, Phys. Rev. B51, 10068 (1995) @footnote 2@N. C. Bartelt, T. L. Einstein, and E. D. Williams, Surf. Sci. 273, 308 (1992)

SS-ThP8 Control of Atomic Step Arrangements on a Patterned Si(111) Substrate Through Molecular-Beam Epitaxy, *H. Omi, T. Ogino,* NTT, Basic Research Labs, Japan

Atomic steps on a surface have great potential to act as templates for nanostructure formation. Therefore, control of step arrangement is critical for positioning these nanostructures on a wafer-scale. In our previous study,@footnote 1@ we have focussed on step motions on a patterned Si(111) surface during high temperature annealing and found that regular atomic step bands are formed on the surface. In this presentation, we show that atomic step arrangement can also be designed by step-flow growth on a patterned Si(111) surface using molecular-beam epitaxy. We used a Si(111) wafer, miscut by 1.5 ° to the direction, 7 ° rotated from the [1 1 -2] direction, on which periodic mesa and trench patterns were fabricated by standard Si process. These patterns are aligned along the direction, 7 ° rotated from the [1 1 -2]. The pattern sizes are 1 - 10 μm wide and 1 um deep. By the introduction of such boundaries on the Si(111) surface, step-flow speed can be changed. This is because, concentration of adsorbed atoms on the restricted surface will be modulated by the presence of boundaries. In fact, we obtained particular step patterns related to the step-flow speed modulation. On a surface of 1 μ m wide mesa, for instance, steps become curved and projected towards the [-1 -1 2] direction by high temperature annealing before the Si deposition. These steps evolve into arrowhead-like shape with increasing Si layer thickness. These step arrowheads point towards the [1 1 -2] direction at an arrow angle of 60°, and therefore suggest that they are composed of [-1 -1 2] type steps. The above results demonstrate that the orientation of steps on a Si(111) surface can be regulated by introducing boundary conditions into the step-flow growth. The step-flow growth on a patterned substrate offers the possibility to design step arrangements on a wafer scale. @FootnoteText@ @footnote 1@ T. Ogino, H. Hibino, and Y. Homma, Appl. Surf. Sci. 117/118, 642 (1997).

SS-ThP9 The Atomistics of Silicide Formation on Si(111) and Si(113) Studied with High Temperature STM, V. Dorna, P. Kohstall, U.K. Koehler, Ruhr-Universitaet Bochum, Germany

Basic steps of the nucleation of iron silicide on Si(111) and Si(113) during gas phase deposition (CVD) were investigated by high temperature STM directly during growth up to 650°C. The formation of ordered silicides above 300°C is directly observed in form of STM-"movies". When solely iron is deposited via Fe(CO)@sub 5@ as a gaseous source, silicon from the substrate reacts to form the silicide. On Si(111) always three different types of islands nucleate even in the very first stage. The dominating @gamma@-silicide type is surrounded by holes in the silicon substrate. In a quantitative analysis the stochiometry of the silicide nuclei was found to be temperature dependent, whereas the sticking behavior of the precursor gas is not activated. At higher temperatures the fraction of a second island-type increases, which shows an only weakly ordered surface periodicity pointing to an @alpha@-silicide. A reversible transition between both phases can be forced by a surplus of Si or Fe. The third island type is implanted into the substrate surface. When Fe and Si using Si@sub

2@H@sub 6@ are co-deposited, a gas composition for a stochiometric silicide growth is found which is in agreement with separately determined sticking coefficients on the substrate. With increasing coverage all different phases transform into @gamma@-silicide, but no layer by layer growth could be archived on Si(111). On Si(113), on the other hand, the 3D-growth seems to be suppressed in the case of the co-depositon, which may be a chance to achieve layer by layer growth.

SS-ThP10 Reconstructions of Ag on High-Index Silicon Surfaces, S.R. Blankenship, H.H. Song, A.A. Baski, J.A. Carlisle, Virginia Commonwealth University

Si(5 5 12), a recently discovered, stable high-index surface of silicon, may offer a superior template for the growth of 1D metallic structures. This surface predominately consists of long pi-bonded Si rows. We are using Reflection High-Energy Electron Diffraction (RHEED) to determine the surface phase diagram of Ag on this surface, and the related surface of Si(337). Each of these surfaces exhibit a very sharp (2x1) reconstruction after flashing to ~1250°C. The growth of Ag on these surfaces is split into two distinct regimes. For growth at low coverages (@THETA@0.4 ML) and temperatures (450°C

SS-ThP11 Structure Determination of Si(111)/Sb-(@sr@3x@sr@3)R30@degree@ using Photoelectron Diffraction Direct Methods, M. Martin, LURE, Centre Universitaire Paris Sud and ICMM, France; H. Ascolani, Centro Atomico Bariloche, Argentina, Argentine; N. Franco, J. Avila, M.C. Asensio, LURE, Centre Universitaire Paris Sud and ICMM, France

The determination of the local adsorption structure of absorbed atoms and molecules on single-crystal substrates is a key prerequisite for understanding the electronic and chemical properties of surfaces. Most of the fragments or molecular adsorbates generally present a well defined local order, although, do not form the long-range ordered structures required for conventional LEED studies. One technique applicable to such problems is Photoelectron Diffraction, where the intensity of a core level peak is recorded as a function of the kinetic energy or the emission angle. The spectra measured in this way show intensity modulations which can be strictly correlated with the local structural environment of the atomic emitter. Recently, new direct methods based on energy scan mode have been developed relying on the high scattering factor for 180° backscattering, at low energies. This "backscattering searching" approach requires the measurement of scanned energy spectra at several angles along the high symmetry direction. In the present communication, we report the results of different direct methods for the Si(111)-Sb (@sr@3x@sr@3) structure. The limitations and advantages of each method are analized and the results are contrasted with the final structure obtained by a full multiple scattering trial-and-error analysis.

SS-ThP12 Photoelectron Diffraction Intensity Calculation by Using Tensor LEED Theory, S. Omori, Y. Nihei, University of Tokyo, Japan

Low-energy photoelectron diffraction (PED) by using synchrotron radiation (SR) has become more and more important for determining surface structures. In particular, PED has the advantage that surfaces having no two-dimensional translation symmetry such as initial-stage adsorption systems can be analyzed provided that the atomic arrangements around photoelectron emitters are symmetric. Since low-energy PED is extremely sensitive to surface structures, multiple structural parameters are usually to be determined by fitting experiment and theory. However, since multiple-scattering effects are important at low photoelectron energies, the structural analysis might be very time-consuming. In this study, we tried to incorporate the tensor LEED (TLEED) theory, a powerful perturbative approach to LEED intensity calculation,@footnote 1@ into the PED formalism and to develop a high-speed trial-and-error method for the structure determination with PED. Since scattering processes that occur in solid surfaces are almost the same for PED and LEED, the formulation of tensor PED is straight-forward. The change in the transition matrix of an atom brought about by its displacement can be calculated by the same method as in TLEED. Once the quantities related to the reference structure, namely the amplitudes of spherical waves incoming to and outgoing from the displaced atom are calculated in the process of multiple-scattering cluster (MSC) calculation for the reference structure and are stored in a hard disk, it is easy to evaluate the changes in the diffraction wave field for many trial structures. We demonstrate the efficiency and accuracy of this method. @FootnoteText@ @footnote 1@P. J. Rous et al., Phys. Rev. Lett. 57 (1986) 2951.

SS-ThP13 The Surface Structure Determination of @alpha@-Fe@sub 2@O@sub 3@(0001) by Low-Energy X-Ray Photoelectron Diffraction, S. Thevuthasan, Y.J. Kim, S.A. Chambers, Pacific Northwest National Laboratory; J. Morais, R. Denecke, C.S. Fadley, Lawrence Berkeley National Laboratory; P. Liu, T. Kendelewicz, D.E. Brown Jr., Stanford University

The structure and composition of oxide surfaces strongly influence the chemical and mechanical properities of these materials. As such, there is a growing interest of determining surface termination, reconstruction and relaxation on these surfaces. Recent theoretical work by Wasserman et. al [1] have shown that hematite(@alpha@-Fe@sub 2@O@sub 3@(0001)) surface has a single Fe layer termination with relaxations in the first four planes of -49%, -3%, -41%, and 21% of the bulk values respectively. We recently performed x-ray photoelectron diffraction measurements at Advanced Light Source on a clean, epitaxially grown Fe@sub 2@O@sub 3@(0001)/Al@sub 2@O@sub 3@(0001). A photon energy of 400 eV (Fe 3p E@sub kin@ = 344 eV) was used to collect several Fe 3p azimuthal scans at different take off angles. The experimental data were compared to the theoretical simulations using single and multiple scattering calculations with trial geometries. R-factors were calculated and minimized to obtain the optimum geometry. The surface appears to be Fe-terminated and the first four layer spacing are -41%, +18%, -8%, and 47% of the associated bulk values, respectively. @FootnoteText@ Work supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences and Biological and Environmental Research Environmental Management ScienceProgram

SS-ThP15 Barrier-Height Imaging of Defects on the Si(001) 2x1 Surface, S. Kurokawa, A. Sakai, Kyoto University, Japan

The C-type defect on the Si(001) 2x1 surface is known to be an active site in Fermi level pinning and also in the initial oxidation of Si(001). In spite of its practical importance, the atomic structure of this defect has not completely understood yet. Controversies also exist on the tunneling barrier height at the C defect. Hamers and Köhler@footnote 1@ found that the barrier height decreases around the defect but increases just above the defect site. On the other hand, Ukraintsev et al.@footnote 2@ reported no such changes in the barrier height at and around the C defect. We have performed the STM barrier-height imaging on clean and oxygen-adsorbed Si(001) 2x1 surfaces and investigated the barrier height at various surface defects. We find that the apparent barrier height at the C defect closely follows the STM corrugation profile: the barrier height increases at the defect site under positive sample bias, but shows no depression around the defect. Our finding is consistent with the relation between barrier-height and STM images but not in agreement with Hamers and Köhler.@footnote 1@ Upon exposure to 1L of oxygen, preliminary barrier-height measurements show that the apparent barrier height at the C defect site appears to be reduced. The effects of oxygen adsorption on other surface defects will also be presented. @FootnoteText@ @footnote 1@R. J. Hamers and U. K. Köhler, J.Vac.Sci.Technol. A7, 2854 (1989). @footnote 2@V. A. Ukraintsev, Z. Dohnalek, and J. T. Yates. Jr., Surf. Sci. 388, 132 (1997).

SS-ThP16 Disappearance of Element-Specific Kikuchi Bands from Fluoride Surfaces, S. Omori, Y. Nihei, University of Tokyo, Japan

We will discuss X-ray photoelectron diffraction (XPED) from fluoride surfaces with different crystal structures, namely SrF@sub 2@ (fluorite structure) and MgF@sub 2@ (rutile structure). Scanned-angle XPED patterns of substrate emission over a large solid angle consist of strong forward-scattering peaks along high-density crystal axes, surrounded by first-order interference fringes, and Kikuchi bands along the projections of low-index crystal planes. In contrast to Kikuchi electron diffraction, Kikuchi bands in XPED patterns originate from a specific element in a sample. It has been shown that such element-specific Kikuchi bands have the following characteristics;@footnote 1@ (1) There is a site-specific extinction rule, in addition to the ordinary one that the Fourier coefficients of the crystal potential are zero. (2) The intensity of Kikuchi bands strongly depend both on those coefficients and on photoelectron-emitter sites. (3) Dark Kikuchi bands of depressed int! !! ensity can occur if photoelectron emitters satisfy a certain condition. In this presentation, we mainly concentrate on such element-specific Kikuchi-band effects. It was found that a set of (111) bands disappear in the Mg 2s pattern for MgF@sub 2@ and in the F1s pattern for SrF@sub 2@, although they were clearly observed in the pattern for the other element of each sample. We show that these element-specific effects on the extinction of Kikuchi bands occur by different mechanisms and that such apparently complex intensity properties can be well understood on the basis of three principles described above and can be well reproduced by multiple-scattering cluster

(MSC) calculations. @FootnoteText@ @footnote 1@ S. Omori et al., Jpn. J. Appl. Phys. 36 (1997) L1689.

SS-ThP17 Anisotropic Electron Scattering from Point Defects on Graphite at Low Temperature, K.F. Kelly, Rice University; J.G. Kushmerick, H.P. Rust, The Pennsylvania State University; N.J. Halas, Rice University; P.S. Weiss, The Pennsylvania State University

A low temperature ultrahigh vacuum scanning tunneling microscope was used to image threefold symmetric electron scattering from point defects in the graphite surface. Such defects were theoretically predicted,@footnote 1@ but had only previously been observed with C@sub 60@-functionalized tips at room temperature.@footnote 2@ Cryogenic temperatures sharpen the Fermi distribution enabling the observation of electron scattering. The energy dependence of the scattering was mapped by spectroscopic imaging and acquiring complete current-voltage curves at specific positions with respect to the scattering center. @FootnoteText@ @footnote 1@H. A. Mizes and J. S. Foster, Science 244, 559 (1989). @footnote 2@K. F. Kelly, D. Sarkar, G. D. Hale, N. J. Halas, Science 273, 1371 (1996).

SS-ThP18 Vacancy Creation as the Rate Limiting Step in Halogen Etching of Si(100)-2x1, K. Nakayama, University of Minnesota; C.M. Aldao, Universidad Nacional de Mar del Plata-CONICET, Argentina; J.H. Weaver, University of Minnesota

We have studied the etching on Si(100)-2x1 using scanning tunneling microscopy. Surfaces exposed to Cl@sub 2@ or Br@sub 2@ are etched at elevated temperature via the thermal activation reaction 2SiX(a) <--> SiX@sub 2@(a) + Si(a), where SiX@sub 2@(a) is a volatile molecule, Si(a) is a bystander Si atom, and X = Cl or Br. Formation of SiX@sub 2@(a) breaks the dimer @sigma@-bond and leaves the destabilized bystander with two dangling bonds. Conventional wisdom would indicate that SiX@sub 2@ desorption is the rate-limiting step. Instead, we show that the rate limiting step occurs when the bystander breaks away and moves onto the terrace. Thus, the de-excitation pathway to 2SiX(a) is eliminated. This increases the overall probability for SiX@sub 2@ desorption. We show that the rate of etching increases with halogen concentration until ~0.8 ML. It is reduced at higher coverage as the adsorbates block the escape of the bystander onto the terrace. We discuss the consequences and examine the post-etch surface morphology.

SS-ThP19 Growth of Ultrathin Mn Films on W(110), M. Bode, M. Hennefarth, M. Getzlaff, R. Wiesendanger, University of Hamburg, Germany

At room temperature bulk Manganese (Mn) exhibits complicated cubic structures with large unit cells. Simple crystallographic structures like fcc @gamma@- and the bcc @delta@-Mn are high temperature phases. However, it is well known that thin solid films can be stabilized on appropriate substrates in crystalline symmetries and lattice constants that are far from those of the corresponding bulk material. We have studied the growth of Mn on W(110)-substrates by means of STM and LEED. With our home-build MBE-STM@footnote 1@ we obtained growth sequences of particular microscopic locations. Up to a coverage of 0.5ML the nucleation of first monolayer islands which are elongated along the [110]-direction could be observed. The nucleation of second monolayer patches occurs before the completion of the first ML. We found that up to a total coverage of 2 monolayers Mn grows pseudomorphically on W(110), i.e. in the bcc @delta@-phase and strained by approximately 10%, as indicated by the absence of satellite spots in the LEED-pattern. If the total amount of deposited material exceeds 2ML we observed the evolution of rectangular islands with a minimum height of 5ML. This coincides with an increasing diffuse background in the LEED-pattern. Further deposition leads to a very rough surface morphology. @FootnoteText@ @footnote 1@ Ch. Witt, U. Mick, M. Bode, and R. Wiesendanger, Rev. Sci. Instrum. 68, 1455 (1997).

SS-ThP20 Electronic States and Structural Characterization in Single-Crystal Fe-Ni-O Alloy Thin Films Grown by Molecular Beam Epitaxy, *C.L. Chang*, Tamkang University, Taiwan; *G. Chern*, Chung-Cheng University, Taiwan; *C.L. Chen*, *H.H. Hsieh*, *W.F. Pong*, Tamkang University, Taiwan; *T.C. Leung*, Chung-Cheng University, Taiwan

Stimulated by the recent success of the research on epitaxial Fe@sub 3@O@sub 4@ and NiO thin films on MgO(001), we extend our study to the growth of a series of alloy Fe-Ni-O thin films with various Fe/Ni concentration ratio by molecular beam epitaxy. Total of 9 samples, around 500 Å thick, are fabricated including Fe@sub 3@O@sub 4@, NiO and Fe@sub x@Ni@sub 1-x@O@sub y@ (x=0.15, 0.3, 0.35, 0.56, 0.65, 0.71). These films are expected to show a structural crossover from spinel

to rocksalt structure and to show an associated change on valance states of Fe and Ni ions while x varies from 0 to 1. After analyzed by in-situ reflection high energy electron diffraction (RHEED), ex-situ x-ray diffraction, and x-ray absorption spectroscopy (XAS). It is observed that the crystal structure of all the alloy Fe@sub x@Ni@sub 1-x@O@sub y@ films resembles that of the spinel Fe@sub 3@O@sub 4@. The lattice spacing along the perpendicular direction as a function of x shows a minimum at x=0.5 instead of a linear variation indicating that the structures are different from a bulk ferrite Fe@sub 2@NiO@sub 4@-like phase. The distribution of the cations in Fe@sub x@Ni@sub 1-x@O@sub y@ system was studied by Fe and Ni L@sub 2,3@ XAS edge shapes, which are sensitive to the structural symmetry of the sites of the absorbing atoms. The results are qualitatively consistent with the x-ray observations. For x0.5 the excessive Ni ions occupy the Fe@super 3+@ sites of tetrahedral and octahedral symmetry up to the x value 0.71. The mechanism of forming the metastable phase and its implication on the magnetic properties of these Fe-Ni-O films will also be discussed. This work is supported by National Science Council of R. O. C. under grands NSC87-2613-M-032-001 and NSC87-2112-M-194-009

SS-ThP21 Field Desorption of Gallium from Liquid Metal Ion Source Studied by Back Scattered Electron Scanning Electron Microscopy, H. *Kimata*, Y. *Kondo*, ERATO, Japan Science and Tech. Corp., Japan; K. *Takayanagi*, Tokyo Institute of Technology, Japan

Field desorption of gallium metal from a home-made liquid metal ion source (LMIS) was studied in a scanning electron microscope (SEM). The LMIS has a needle and a reservoir filled with the liquid gallium and a filament. The needle apex is electrochemically sharpened, and the temperature of the LMIS was controlled. We found that the back scattered electron scanning electron microscopy (BSE-SEM) can give images of the needle apex during operation, the emission current being monitored simultaneously. The Taylor-cone and the change of the cone angle depending on the extraction voltage was observed by BSE-SEM. In case that the needle was grooved enough to supply liquid gallium towards the apex.@footnote 1@ the emission current vs. extraction voltage relations were found to fit well with the previous experimental results and theoretical predictions qualitatively. Rarely, the emission did not occur at the apex but the side of the needle, when the supply was limited by poor grooving on the needle. The critical voltage Vc was found to decrease linearly as the temperature T of the ion source increased from 200 to 450(°C). The Vc vs. T relations were analyzed to estimate temperature dependence of the surface tension of the liquid gallium, using the tip radius measured in SEM. The surface tension change like (0.8) - (3x10@super -4@)T, in accordance with the value given in a literature, (0.721) -(1.0x10@super -4@)T. Thus, BSE-SEM is useful to study the dynamics of LMIS. The present techniques are applied for testing a commercial LMIS because of large sample space in a SEM. @FootnoteText@ @footnote 1@A. Wagner and T. M. Hall, J. Vac. Sci. Technol. 16, 1871 (1980).

SS-ThP22 Stoichiometric Phase Transition and Facetting of Low Index Fe@sub 3@Si Surfaces, J. Schardt, W. Weiss, W. Meier, University of Erlangen-Nuernberg, Germany; C. Polop, P.L. de Andres, Universidad Autonoma de Madrid, Spain; U. Starke, K. Heinz, University of Erlangen-Nuernberg, Germany

In binary compounds segregation of one of the constituents is a frequently observed phenomenon. The respective changes of the stoichiometry are often not restricted to the topmost surface region. In this line, two phases of different stoichiometry can be stabilized on the (100), (110) and (111) surfaces of Fe@sub 3@Si bulk samples. On each surface the two phases can be reversibly transformed into each other by extended annealing cycles. The stability regions of each phase and the phase transition temperatures were determined using the stoichiometric information obtained from Auger electron spectroscopy (AES) and structural fingerprints gained from spot intensity spectra, I(E)-curves, of the lowenergy electron diffraction (LEED) pattern. These I(E)-curves were used for quantitative LEED structure analyses of each phase. In the low temperature regime (400° C) for all surfaces a D0@sub 3@ crystal structure can be confirmed. However, for preparation temperatures of around 600° C a restructuring of the surface region is observed. Segregation leads to a Si enrichment of the surface. This is accompanied by a structural transition to a CsCl crystal structure within the region accessible to the low-energy electrons. In addition, using LEED facetting of the (100) and (111) surfaces is observed with facets in (110) orientation which obviously is the energetically most stable plane of Fe@sub 3@Si.

SS-ThP23 Local Composition and Electronic and Optical Properties of Cr Oxide-Based Thin Films, J. Smith, D.A. Bonnell, The University of Pennsylvania, US; P. Carcia, R.H. French, E.I. Dupont de Nemours; X.F. Lin, The University of Pennsylvania

Oxynitride thin films are increasingly used to optimize resolution in optical lithography. Recently, a series of complex Cr-O-C-N films have been developed that allow simultaneous precise control over optical transmission, reflection, and phase shift. Subtle variations in optical properties appear to be related to small differences in O:C:N bond ratios across 100 nm films. To understand the mechanisms by which variations in anion coordination affect properties, the electronic structure near the Fermi level and local electrical conductivity measured by tunneling spectroscopy was related to optical properties in the end member compositions. Results from CrOx, CrCx, and CrNx this films, where x varies from 0.1 to 0.7, will be discussed in terms of the relationship between electronic and optical density and the consequence to optical properties.

SS-ThP24 Formation of a Bilayer Ordered Surface Alloy of Mn Thin Films, W. Kim, Seoul National University, Republic of Korea; J. Seo, Chodang University, Republic of Korea; J.-S. Kim, Sook-Myung Women's University, Republic of Korea; S.-J. Oh, Seoul National University, Republic of Korea We report a new type of surface alloy,the formation of a bilayer ordered

surface alloy of Mn thin films deposited on some transition metal (100) surfaces, from the results of Low-energy electron diffraction(LEED) I/V analyses. For Mn on Ag(100), very sharp and bright c(2x2) LEED pattern is observed with norminal 1 monolayer Mn deposited, and the experimental I/V curve is well fitted only by a model, a bilayer ordered surface alloy structure with little corrugation of Mn atom. Sudden disappearance of c(2x2) pattern is, however, observed on light annealing at 400K. By analyses on atomic compositions of each layer using averaged t-matrix approximation(ATA), we find out that vanishment of LEED superstructure is due to the segregation of Ag atoms. For the case of Mn on Pd(100), we achieve more improved fitting of the experimental I/V curves by employing a bilayer ordered surface alloy instead of the single layer ordered alloy model which was tried in the previous study of Tian et. al.@footnote 1@ However, unlike the Mn atoms deposited on Ag(100) surface, the topmost Mn atoms in this system are severely buckled out from the surface and its amount of corrugation is comparable to that of Mn/Cu(100) system. Thermodynamic property is also different: More clear c(2x2) LEED pattern is obtained after annealing. Mn 3s core level spectra of both systems show exchange splittings similar with that of bulk Mn, so magnetic effect on surface alloving is important in common with two cases. The distinctive characteristics of these two systems belonging to the same class of surface alloy, can be understood qualitatively, considering the differences in surface free energy and atomic size effect between Ag and Pd. @FootnoteText@ @footnote 1@ D. Tian, R.F. Lin, F. Jona, P.M. Marcus, Solid State Commun. Vol. 74, 1017(1990)

SS-ThP25 Surface Reconstruction and Charge Density Wave on ß-(BEDT-TTF)@sub 2@PF@sub 6@ Studied by Scanning Tunneling Microscopy, M. Ishida, K. Miyake, K. Hata, University of Tsukuba, Japan; T. Mori, Tokyo Institute of Technology, Japan; H. Shigekawa, University of Tsukuba, Japan ß-(BEDT-TTF)@sub 2@PF@sub 6@ is one of the quasi-one-dimensional organic conductors and is known to show metal-insulator transition at ~297 K with Charge Density Wave(CDW). STM/AFM study on this crystal revealed the characteristic properties of the molecular crystal surface for the first time. On the PF@sub 6@ surface, superstructure was formed by missing alternate molecular rows of PF@sub 6@. This is the first observation of the surface reconstruction of molecular crystal including a dractic change in the molecular arrangement.@footnote 1@ On the other hand, BEDT-TTF terminated surface induced molecular rearrangement with charge redistribution resulting in the symmetry breaking; formation of the twofold periodicity in the direction perpendicular to the one-dimensional conductive axis. The origin of these structures could be explained comprehensively by the compensation mechanism of the incomplete charge transfer on the polar surface.@footnote 2@ Furthermore, STM measurement was performed from 80K to room temperature to observe the CDW phase directly. In the low temperature range up to 280 K, it was difficult to observe detailed surface structure because of low conductivity owing to the CDW gap. In the temperature range from 280 K, however, long range modulations were observed and we concluded that the modulations reflect the CDW phase. @FootnoteText@ @footnote 1@M. Ishida, K. Hata, T. Mori, and H. Shigekawa, Phys. Rev. B 55, 6773 (1997). @footnote 2@M. Tsukada and T. Hoshino, J. Phys. Soc. Jpn. 51, 2562 (1982).

SS-ThP26 Structure of the Five-Fold Surface of Al@sub 70@Pd@sub 21@Mn@sub 9@, J. Ledieu, A. Munz, T. Parker, R. McGrath, University of Liverpool, United Kingdom; R.D. Diehl, Pennsylvania State University; D.W. Delaney, T.A. Lograsso, Iowa State University

Quasicrystals are bi- or tri-metallic alloys with long range orientational order and no short range translational order. Coatings of quasicrystals have low coefficients of friction and high resistance to wear,@footnote 1@ and hence the surface structure is of obvious interest. We have investigated the five-fold surface of the Al@sub 70@Pd@sub 21@Mn@sub 9@ quasicrystal using STM, LEED and AES. Surfaces annealed to 875 K showed excellent five-fold symmetric LEED patterns, and STM revealed disordered clumps of cluster-like protrusions 25±2 Å in diameter, similar to those observed for surfaces cleaved in vacuum.@footnote 2@ Higher resolution images showed these clusters were themselves composed of 2.5 Å diameter protrusions. Surfaces annealed to 1100 K showed sharp LEED patterns and atomically flat surfaces, in agreement with previous work.@footnote 3@ The data quality have allowed us to go beyond the previous analysis@footnote 3@ to examine structural features of the surface in detail. The most striking features are groups of protrusions forming fivefold star-shaped patterns. Threshold and pattern analysis of the images shows that the surface can be generated by tiling with pentagons using parallelograms to take up frustration. The parallelograms contain defects in the form of large protrusions, and gradients of the defect peaks were found to match angles present in the stereographic projection of the icosahedral group m35. Ratios of distances between the defect peaks and ratios of sequential step heights were found to equal the golden mean @tau@. Further analysis and adsorption experiments are being undertaken. @FootnoteText@ @footnote 1@S. L. Chang, W. B. Chin, C. M. Zhang, C. J. Jenks and P. A. Thiel, Surf. Sci. 337 (1995) 135; S. S. Kang, J. M. Dubois and V. J. Stebut, J. Mater. Res. 8 (1993) 2471. @footnote 2@Ph. Ebert, M. Feuerbacher, N. Tamura, M. Wollgarten, K. Urban, Phys. Rev. Lett. 77 (1996) 3827. @footnote 3@T. M. Schaub, D. E. Buergler, H. -J. Guentherodt, J. -B. Suck, Phys. Rev. Lett. 73 (1994) 1255.

SS-ThP27 Quantum-Size Effects on the Pattern Formation of Monatomic-Layer-High Metal Islands at Surfaces, K. Jin, University of Tennessee, Knoxville; G.D. Mahan, Univ. of Tennessee, Knoxville & Oak Ridge National Lab; H. Metiu, University of California, Santa Barbara; Z. Zhang, Oak Ridge National Laboratory

The quantum-size effects are shown to play a crucial role in defining pattern formation of metal island on surface.@footnote 1@ The energy in elongated needle-like growth is found to oscillate with the width of the needle, clearly demonstrating the existence of preferred needle widths. The energy of the square or rectangular islands varies periodically with the side length, predicting stability variations of the islands with different sizes. This work is supported by University of Tennessee, by Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract number DE-AC05-96OR22464 @FootnoteText@ @footnote 1@ K.-J. Jin, G. D. Mahan, H. Metiu, and Z. Y. Zhang, Phys. Rev. Lett. 80, 1026 (1998).

SS-ThP28 Finite-size Scaling Behavior of the Tracer Surface Diffusion Coefficient near a Second-order Phase Transition, *F. Nieto*, Universidad Nacional de San Luis, Argentina; *A.A. Tarasenko*, National Academy of Science of Ukraine, Ukraine; *C. Uebing*, Max-Planck-Institut fuer Eisenforschung, Germany

We investigate the finite-size scaling behavior of the tracer surface diffusion coefficient in the vicinity of a second order phase transition. For this purpose, we use a lattice gas model of repulsively interacting particles on a square lattice. For all lattice sizes L studied, the measured tracer surface diffusion coefficient, D@sub t@, is a smooth function, having an inflexion point at critical temperature. Its derivative, dD@sub t@/d(1/k@sub B@T), exhibits a cusp-like maximum which is (a) sharply pronounced and (b) converged to T@sub c@ for large lattice sizes. We have analyzed the finite-size behavior of D@sub t@ and obtained its critical exponent @sigma@=0.665±0.003.

SS-ThP29 Computer Simulation of the Au(111) @sr@3 x 22 Surface Reconstruction, *T.M. Trimble*, University of Maryland; *R.C. Cammarata*, Johns Hopkins University; *E.D. Williams*, University of Maryland; *K. Sieradzki*, Arizona State University

A computer simulation study of the Au(111) $@sq@3 \times 22$ surface reconstruction will be discussed. This reconstruction can be described as involving a uniaxial in-plane contraction of the top monolayer corresponding to a surface strain of about 4%, and has been observed to be the stable surface structure at low temperatures. The driving force for this reconstruction has been identified as the difference in the surface stress f and the surface free energy @gamma@ of the 1x1 surface, while the opposing force is owing to the free energy cost associated with the top monolayer losing atomic registry with underlying lattice. A simple continuum analysis gave the following stability criterion: a (111) fcc metal surface will undergo a reconstruction involving contraction of the top monolayer if the ratio (f - @gamma@)/µb exceeds a certain critical value of order 0.1, where μ is the shear modulus and b is the nearest neighbor distance. This criterion was tested with computer simulations that were conducted using the Johnson analytical embedded atom method (EAM) potential. Since the standard Johnson potential for Au leads to the result that the 1x1 surface is stable to reconstruction, modifications were made in values of some Johnson EAM input paramters in order to stabilize the reconstruction. It was found that although the resulting values of f and @gamma@ were somewhat lower than those obtained from first principles calculations, the driving force (f - @gamma@) obtained by the simulation and the first principle calculations were very close. Furthermore, the critical value of the stability parameter (f - @gamma@)/µb, inferred from results obtained from simulations of reconstructions with different surface strains, was found to be very close to that predicted by the continuum analysis. This work was supported by NSF through the University of Maryland MRSEC.

SS-ThP30 LEED Study of the Relaxation of Cu(211), *Th. Seyller*, *R.D. Diehl*, Pennsylvania State University; *F. Jona*, State University of New York, Stony Brook

A low-energy electron diffraction study of the vicinal Cu(211) surface has been carried out at 300 K. The experiments were carried out at normal incidence to the (211) planes and the calculations were carried out using the CHANGE program@footnote 1@ which is capable of calculating intensities for surface structures which have small interlayer spacings. The results indicate a large (15 percent) contraction of the top layer Cu atoms and essentially bulk spacings for deeper layers. The large contraction of the top layer agrees very well with a first principles calculation for Cu(211).@footnote 2@ However, the first-principles calculation as well as earlier embedded-atom model calculations@footnote 3@ predict large relaxations of the deeper layers as well. These discrepancies will be discussed in light of structure determinations for other vicinal surfaces. @FootnoteText@ @footnote 1@D. Jepsen, in "Determination of Surface Structure by LEED" edited by P.M. Marcus and F. Jona, Plenum Press 1984, p.17. @footnote 2@C.Y. Wei, Steven P. Lewis, E.J. Mele and Andrew M. Rappe, Phys. Rev. B 57 (1998) 10062. @footnote 3@S. Durukanoglu, A. Kara and T. S. Rahman, Phys. Rev. B 55 (1997) 13894.

SS-ThP31 Interlayer Diffusion Near Ledge Contacts: Comparison of Systems with Positive and Negative Schwoebel-Ehrlich Barriers, V. Shah, L. Yang, Iowa State University; T.L. Einstein, University of Maryland

We present molecular statics studies on the diffusion mechanisms near steps on fcc (111) surfaces. We use the Molecular Dynamics/Monte Carlo-Corrected Effective Medium (MD/MC-CEM) interatomic potential, which has been applied to the study of the Schwoebel-Ehrlich (SE) barriers for single atom diffusion towards a single descending step on Ag, Cu, Au, Pd, Ni, and Pt [Y. Li and A. E. DePristo, Surf. Sci. 351, 189 (1996)]. Among these six transition metals, the MD/MC-CEM potential predicts that Cu and Pd, respectively, have the highest (137 meV) and lowest (-4 meV) SE barriers for interlayer diffusion, via the exchange mechanism at the B-type step. In the present study, we focus on the change in the SE barrier for single- and multi-atom diffusion at descending step edge contacts for two model systems that have positive (Cu) and slightly negative (Pd) SE barriers for atomic diffusion at a single step. We also track the potential surface as an atom approaches corners while diffusing along island edges and as it diffuses away from the step edge on an island plateau. Our results on the behavior of mass transport near ledge contacts will be discussed in the light of recent experimental observations [M. Giesen et al., Phys. Rev. Lett. 80, 552 (1998)]. Two of us (VS and LY) would like to thank members of the Department of Chemistry and the surface physics group at the University of Maryland for their hospitality during our visit there. TLE was supported by NSF-MRSEC at U. of Md.

SS-ThP32 Scanning Tunneling Spectroscopy and X-ray Photoemission Spectroscopy Studies of Thin Films of WO3 and In2O3, *S. Santucci, L. Lozzi, L. Odorisio, M. Passacantando, C. Cantalini,* Università dell'Aquila, Italy

p-n junction between p-Si and n-type semiconductor oxides like WO3 and In2O3 have been fabricated by thermal evaporation in high vacuum of pure powders onto p-doped Si(100) and submitted to anneal at different temperatures up to 450°C at different times. The rectifying properties of

the films have been studied by using the Scanning Tunneling Spectroscopy (STS) technique in air and using Cr-Au contacts on the etched surface of silicon and on the deposited films respectively. I-V characteristics have been measured for the films in the presence of NOx gas carried in a flux of dry air. The surface morphology of the deposited films with different annealing temperatures have been studied by Atomic Force Microscopy (AFM) where we have observed a regular rearrangement of the surface with a globular aspect for the In2O3 deposits whereas for WO3 films it showed a more flat and regular surface. X-ray Photoelectron spectroscopy (XPS) has been employed to study the composition of the deposited films and an ion beam depth profile technique to study the interface formation with the silicon substrate. n-type behavior of the films which is due to the oxygen deficiency has been observed by studying the valence band spectra of the films. A comparison with the Density Of States obtained by calculating the (dI/dV)/(I/V) of the I(V) curves detected by the STS technique has been also performed.

SS-ThP33 Atomic Force Microscopy Examination of the Evolution of the Surface Morphology of Bi@sub 4@Ti@sub 3@O@sub 12@ Grown by Molecular Beam Epitaxy, G.W. Brown, M.E. Hawley, Los Alamos National

Laboratory; C.D. Theis, J. Yeh, D.G. Schlom, Pennsylvania State University Bi@sub 4@Ti@sub 3@O@sub 12@ is a candidate material for use in electro-optic devices and non-volatile ferroelectric-based memories. In these applications, obtaining the desired electronic or optical properties depends on the ability to deposit very smooth films. We have examined the molecular beam epitaxial nucleation and growth of these films on SrTiO@sub 3@ with ex-situ atomic force microscopy (AFM) to observe the thickness dependence of the surface morphology. From the AFM data we obtain the direct, real space surface morphology, the RMS surface roughness as a function of thickness, the amount of material present in the growing layers, and the height difference correlation function of the surface. Bi@sub 4@Ti@sub 3@O@sub 12@ growth begins with the nucleation of a layer that is 1/4 unit cell thick followed by growth of 1/2 unit cell thick layers. A transition to multilayer island (3-dimensional) growth occurs somewhere between deposition of 25 % of the second layer and the completion of the third layer. This implies that the film grows in a Stranski-Krastonov mode with a critical thickness between 0.325 and 1.250 monolayers. After 3-dimensional growth begins, the surface morphology can be described with the dynamic scaling hypothesis (DSH).@footnote 1,2@ The DSH scaling exponents, extracted from the AFM images, are compared to other thin film growth systems and should provide checks for future models or simulations of Bi@sub 4@Ti@sub 3@O@sub 12@ growth. We observe an interesting thickness dependence of one of the scaling exponents which may be related to the stress relief involved in the S-K growth mode. Possible models for the stress relief will be discussed. Finally, results of deposition on substrates providing different lattice mismatches will be shown and implications for the growth of thicker, smooth films will be discussed. @FootnoteText@ @footnote 1@F. Family and T. Viscek, J. Phys. A: Math. Gen. 18, L75 (1985). @footnote 2@J. Lapujoulade, Surf. Sci. Rep. 20, 191 (1994).

SS-ThP34 AES-LEED Study of the Growth Mode of Ag on Au (111),(311) and (554) Single Crystal Surfaces, V.F.S. Rooryck, C. Buess-Herman, Universite Libre de Bruxelles, Belgium; G.A. Attard, University of Wales, United Kingdom; F.A.B. Reniers, Universite Libre de Bruxelles, Belgium

The growth mode of silver onto gold substrates has been the subject of many controversies. The energetics and lattice misfit between gold and silver seems to favor a layer-by-layer mode, confirmed by some studies, while others reported a Stransky-Krastanov mode. The deposition method (electrodeposition, UHV deposition), the analysis technique and the surface structure could be responsible for these different results. We have undertaken a LEED-AES study of the deposition of thermally evaporated silver onto gold single crystal surfaces. The Au (111), (311) and (554), with different atomic roughness were investigated. The deposition mode was determined from the intensity versus time evolution of the Auger lines of gold (69 eV) and silver (351-356 eV). The Gallon model was used to fit the experimental data to theoretical simulations. The most recent values of IMFP and AL were introduced in the model. Following the results, the Stransky-Krastanov growth occurs, but 2 or 3 layers are deposited before the island growth begins. The evolution of the surface structure during silver deposition was simultaneously followed by LEED. We showed that the reconstruction of thermodynamically equilibrated pure gold surfaces was progressively removed by silver adsorption, apparently starting at half a monolayer coverage. The possibility of the formation of an interfacial alloy is investigated, and a comparison is made with the results that we obtained for the electrodeposition of silver on the same gold surfaces.

Surface Science Division Room 308 - Session SS1-FrM

Surface Structure and Strain

Moderator: R.Q. Hwang, Sandia National Laboratories

8:20am SS1-FrM1 Ultrathin Metal Films on W(111) and W(211): Nanoscale Faceting, Structure, Electronic Properties, and Reactivity@footnote 1@, T.E. Madey, Rutgers, The State University of New Jersey INVITED The W(111) surface is morphologically unstable when covered by monolayer films of certain metals (including Pt, Pd, Rh, Au), and develops nanoscale 3-sided pyramidal facets with mainly [112] faces upon annealing. In the present work, we focus on the structure, electronic properties and reactivity of planar and faceted W(111) and W(211) covered by ultrathin films of metals (0 - 8 ML, mainly Pt, Pd, Rh) and non-metals (S, O). The measurements include UHV-STM, soft XPS (SXPS) using synchrotron radiation, Auger spectroscopy, LEED, and thermal desorption spectroscopy. The observed formation of 3-sided pyramids with both [110] and [112] facets, as induced by 1 ML of overlayer metal, is predicted also by recent first-principles calculations of surface energetics. The faceting is caused by an increased anisotropy in surface free energy that occurs for the filmcovered surfaces. The adsorption of S induces a different reconstruction with nanoscale texturing of the surface. At coverages above 1 ML, SXPS data indicate that interfacial alloys are formed upon annealing films of Pt and Pd, but not Au. These findings are discussed in terms of structural and electronic properties of bimetallic systems. The relevance to the surface chemistry of a structure-sensitive reaction (acetylene cyclization to benzene over Pd/W) is also discussed. @FootnoteText@ @footnote 1@Supported in part by US DOE, Office of Basic Energy Sciences @footnote 2@Collaborators include C.-H. Nien, J.J. Kolodziej, K. Pelhos, I. Abdelrehim, H.-S. Tao, R. Barnes (Rutgers); J. Keister, J.E. Rowe (NC State); J. Eng, J.G. Chen (EXXON); C-T. Chan (HKUST)

9:00am **SS1-FrM3 Determination of Thin Film Interface Structure by the Quantum Size Effect in Electron Reflectivity**, *M.S. Altman*, *W.F. Chung*, Hong Kong University of Science and Technology, Hong Kong; *H.C. Poon*, *S.Y. Tong*, University of Hong Kong, Hong Kong

It has long been recognized that it is very difficult to obtain detailed structural information of buried interfaces. The quantum size effect (QSE) in electron reflectivity offers some interesting insight into this and other structural features of thin films. The QSE has been understood qualitatively in the past to be an interference phenomenon between the electron waves which are reflected from the surface of a thin film and from the interface between film and substrate. The prominent QSE interference peaks which occur at very low energies are sensitive indicators of film thickness. We have examined the QSE in electron reflectivity from Ag films on the W(110) surface using the low energy electron microscope (LEEM) as an electron interferometer. This approach allows the reflected intensity from regions of different film thickness to be distinguished with atomic precision. Fundamental disagreement was found between the unique experimental data provided by LEEM and the predictions of the simple free electron model which has been invoked in the past to explain the QSE. A quantum mechanical Kronig-Penney model is presented as the first step towards a better understanding of the QSE. An analysis of the QSE peak positions by dynamical theory, aided by R-factors, also provides an accurate determination of the Ag-W interface spacing as a function of the Ag film thickness.

9:20am **SS1-FrM4 Interaction of Dislocations on Strained Metal Films**, *J. de la Figuera*, *K. Pohl, A.K. Schmid, N.C. Bartelt, R.Q. Hwang*, Sandia National Laboratories

Misfit dislocations appear in thin film growth to relieve the mismatch between substrate and film. A general family of dislocation networks has been found on substrates with triangular symmetry such as Pt(111), Ru(0001) and Au(111). A common uncertainty in understanding the observed surface structures is the stacking sequence followed by each adlayer, information that is relatively simple to extract for single layer films but requires more detailed information in multilayer films. Another recurrent question is the role played by the substrate in the network structure and periodicity, as some networks are attributed to ``long range elastic effects'' on one hand,@footnote 1@ but in other cases can be explained disregarding those effects.@footnote 2@ Cu on Ru(0001) presents a variety of different networks as a function of film thickness,@footnote 3@ and can be considered a testbed for the study of

misfit dislocations on a triangular substrate. But even in this case, most of the studies have not dealt in detail with the stacking sequence in the first few layers (other than by assuming that the dislocations observed are present at the interface between the substrate and the Ru film). We will discuss how one can use STM to unambiguously determine the stacking sequences in films thicker than one monolayer. We then proceed to determine the range of dislocation interactions. On the basis of these measurements it is possible to compare the model of long ranged dislocation interactions due to Ru substrate relaxations versus local exponentially decaying interactions between dislocations due to 2-D distortions within the Cu film. @FootnoteText@ @footnote 1@S. Narasimhan and D. Vanderbilt, Phys. Rev. Lett. 69, 1564 (1992). @footnote 2@J. C. Hamilton and S. M. Foiles, Phys. Rev. Lett. 75, 882 (1995). @footnote 3@C. Günther et al, Phys. Rev. Lett. 74, 754 (1995).

9:40am SS1-FrM5 Low Energy Electron Microscope Measurements of Oxygen-Induced Strain Relief on Si(001), J.B. Hannon, B.S. Swartzentruber, G.L. Kellogg, Sandia National Laboratories

Real-time observations of step configurations on Si(001) with the low energy electron microscope (LEEM) show a continuous and irreversible change in the populations of the (1x2) and (2x1) domains (i.e., the ratio of adjacent terrace widths) upon exposure to oxygen at elevated temperatures. In the initial configuration, populations of the two domains differ significantly due to an external strain field. Exposure of the surface to ~10@super-8@ Torr oxygen at temperatures between 750-850 C causes the domains to become approximately equal in area. Based on previous LEED and STM measurements,@footnote 1,2@ we conclude that the progression towards equal domain populations results from the removal of the external strain. During equilibration, the potential in which the step moves is determined from the step velocity. The measured exponential time dependence of the equilibration rate is consistent with step motion in the presence of the step-interaction potential proposed by Alerhand et al.@footnote 3@ This agreement implies that strain relief takes place on a time scale of a few seconds. We propose that the mechanism of strain relief is an oxygen-induced change in the shear threshold of Si due to dissolution of oxygen into the bulk. The ability to modify the elastic properties of materials with common adsorbates such as oxygen is important in heteroepitaxy where strain is known to play a key role in defining the properties of the epitaxial film. 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@F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. 61, 2469 (1988). @footnote 2@B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, JVST A8, 210 (1990). @footnote 3@O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. 61, 1973 (1988).

10:00am SS1-FrM6 The Strain Effect on Ge-covered Si(001) Surface, F.-K. Men, C.-R. Hsu, National Chung Cheng University, Republic of China

By loading the free end of a cantilevered bar, we have studied the effect of strain on the Ge-covered Si(001) surface. On this surface, strain produces a reversible change in the relative population of the 2xn and nx2 domains. This change is driven by the relaxation of the energy associated with a longrange strain field extending into the bulk due to the anisotropy of the intrinsic stress tensor of the two reconstructed domains. The dependence of the surface stress anisotropy, defined as the difference of the components of the surface stress tensor parallel and perpendicular to the dimer bond, on the Ge overlayer thickness has been studied. By varying the separation between two neighboring dimer vacancy lines (DVL's) we have investigated the DVL-DVL interaction. Based on a linear-dipole-force model for the step-step interaction and the theory of long-range elastic relaxation of orientationally inequivalent domains, we have estimated the DVL formation energy and the DVL-DVL interaction strength. We have also studied the change in the relative population of the two orthogonal domains as a function of time at different temperatures. Results on the kinetics of the step migration will be presented.

10:20am **SS1-FrM7 Spontaneous Domain Formation on Ge(001)**, H.J.W. Zandvliet, University of Twente, The Netherlands; B.S. Swartzentruber, Sandia National Laboratories; E. Zoethout, G. Rosenfeld, B. Poelsema, University of Twente, The Netherlands

Scanning tunneling microscopy measurements of Ge(001) reveal the presence of an ordered domain pattern consisting of c(4x2) and (2x1) domains arranged in stripes with a width of several dimer row spacings, oriented along the dimer rows. We suggest that the existence of a soft domain wall between the domains combined with a difference in the stress

component along the dimer bond for the (2x1) and c(4x2) domains, respectively, can produce such an ordered domain phase. We have observed fluctuations of the domain walls indicating that the system is in thermal equilibrium. A simple model based on strain relaxation explains the observed size of the domain pattern.

10:40am SS1-FrM8 New Results for Analytical Approximants of Terrace-Width Distributions on Vicinal Surfaces, and Some Consequences@footnote 1@, T.L. Einstein, O. Pierre-Louis, University of Maryland, College Park; B. Joós, University of Ottawa, Canada

Quantitative measurement of the equilibrium terrace width distribution P(L) of vicinal surfaces has proved a powerful and convenient way to investigate the interactions between steps. Most analyses have relied on simple analytic results based on the Gruber-Mullins approximation: one "active" step wandering between two fixed straight steps separated by twice the average step spacing . For non-interacting, free-fermion (FF)-like steps, P(L) corresponds to the ground-state density of a confined fermion, going like sin@super 2@(@pi@L/2), while for significant repulsions decaying as A/L@super 2@, this density is a Gaussian.@footnote 2@ For both cases, P(L) vs. L/ can be written as a "universal function." Rather complicated analytic expressions can be written for FF@footnote 3@ and for a special value of A. For FF, H. Ibach concocted a simple but excellent approximation for P(L) involving a power law and a gaussian decay.@footnote 4@ This expression turns out to be the celebrated "Wigner surmise" for the distribution of energies in gaussian unitary ensembles, long known to correspond to free fermions. Based on this recognition and results from random-matrix theory, we present a general universal expression that has just one fitting parameter, the power, from which A can be easily estimated. We provide calibrations at the values of A for which exact solutions exist. We use these results to clarify recent controversies@footnote 5@ about how to extract A from P(L). We also discuss what can be learned from the third moment of P(L) and from the covariance of adjacent terrace widths. @FootnoteText@ @footnote 1@Work supported by NSF MRSEC grant DMR 96-32521. @footnote 2@N. C. Bartelt, T. L. Einstein, and E. D. Williams, Surface Sci. 240, L591 (1990). @footnote 3@B. Joós, T. L. Einstein, and N. C. Bartelt, Phys. Rev. B 43, 8143 (1991). @footnote 4@H. Ibach, private communcation; M. Giesen, Surface Sci. 370, 55 (1997). @footnote 5@L. Masson, L. Barbier, J. Cousty, and B. Salanon, Surface Sci. 317, L1115 (1994); L. Barbier, L. Masson, J. Cousty, and B. Salanon, Surface Sci. 345, 197 (1996); T. Ihle, C. Misbah, and O. Pierre-Louis, Phys. Rev. B 58, xxx (1998).

11:00am SS1-FrM9 Enantiospecific Adsorption of Chiral Hydrocarbons on Naturally Chiral Pt and Cu Surfaces, *T.D. Power, D.S. Sholl,* Carnegie Mellon University

Many stepped metal surfaces exhibit chiral step structures which can, in principle, affect the properties of adsorbed chiral molecules@footnote 1@. These highly characterizable systems may be useful for isolating the fundamental mechanisms of enantiospecific reactions in chirally active heterogeneous catalysts. We have used Monte Carlo simulations to examine the energetic and entropic contributions to the free energy of adsorption of several chiral hydrocarbons adsorbed on naturally chiral Pt and Cu surfaces. By simulating both enantiomeric forms of the adsorbates, we are able to directly probe the enantiospecific nature of the adsorbate/surface interactions. These simulations have allowed us to explore the roles of adsorbate size and surface step spacing. Our results indicate that many examples of enantiospecific adsorption exist in which the energy shifts between enantiomers should be readily detectable using standard experimental tools such as Temperature Programmed Desorption. @FootnoteText@ @footnote 1@ C. F. McFadden, P. S. Cremer, and A. J. Gellman, Langmuir, 12 (1996) 2483.

11:20am **SS1-FrM10 Xe Adsorption Sites on Metal Surfaces**, *M. Caragiu*, *Th. Seyller*, *R.D. Diehl*, Pennsylvania State University; *P. Kaukasoina*, *M. Lindroos*, Tampere University of Technology, Finland

Based on an adsorbate-substrate potential which consists of the attractive van der Waals interaction and a repulsive interaction due to wave function overlap, the equilibrium site for physisorbed noble gases would be expected to be a high-coordination site. The presumption which arose from this expectation, that physisorbed atoms prefer high-coordination sites, has been a great hindrance to the development of physisorption potentials since it has delayed experiments to measure the adsorption geometries of physisorbed atoms. Several years ago, a top-site geometry was proposed for Xe/Pt(111) based on He-atom diffraction intensities from an incommensurate phase, although this assignment was disputed by a later SPLEED study. Nevertheless, a density-functional theory cluster calculation

suggested that a preference for top sites in this case may arise from the hybridization of the Xe 5p electrons with the Pt 6d states. Recently it has been shown that Xe on Ru(0001) adsorbs in the top-site geometry in the (@sr@3x@sr@3)R30° phase. If hybridization with substrate d-states is the origin for top-site adsorption, then Xe would not be expected to occupy the top sites on Cu surfaces where the d-states are several eV below the Fermi energy. We present the findings of LEED I(E) studies of Cu(111)-(@sr@3x@sr@3)R30° and Pt(111)-(@sr@3x@sr@3)R30° which were carried out to test this hypothesis and to resolve the disagreement on the adsorption site for Xe on Pt(111). These LEED studies indicate that Xe occupies the top site in both cases. Since it is unlikely that Xe atoms hybridize appreciably with the deep d-levels in Cu(111), we propose a new model for Xe adsorption on metal surfaces in which the hybridization occurs between the occupied part of the excited Xe 6s resonance (which extends below the substrate Fermi energy) and the unoccupied substrate orbitals near the Fermi level.

11:40am **SS1-FrM11 A NIXSW Study of the InP(001)-(4x2) and InP(001)-(1x1)-CI Surfaces**, A.A. Davis, C.J. Fisher, **R.G. Jones**, University of Nottingham, United Kingdom; G. Scragg, J. Ludeke, D.P. Woodruff, University of Warwick, United Kingdom; B.C.C. Cowie, Daresbury Laboratory, United Kingdom

The Normal Incidence X-ray Standing Wave (NIXSW) technique has been used to study the reconstructed, indium terminated InP(001)-(4x2) surface and the InP(001)-(1x1)-Cl chemisorbed surface, using the (002), (20-2) and (113) Bragg reflections. Auger electrons and photoelectrons from the In, P and Cl were used to monitor the X-ray absorption profiles. The reconstructed, indium terminated surface was found to contain In dimers orientated in the direction of the four times periodicity, which is in contrary to earlier studies, but in agreement with the findings of Sung et al.@footnote 1@ The chemisorbed chlorine surface had chlorine bonded to the top layer In atoms with the In-Cl bond probably extending along the [110] substrate direction. The inadvisability of using low energy Auger peaks, and the effects of non-dipole photoemission in XSW determinations, are also discussed. @FootnoteText@ @footnote 1@M. M. Sung et al; Surface Sci. 322(1995)116

Surface Science Division Room 309 - Session SS2-FrM

Water and Ice Interfaces

Moderator: B. Mason, North Carolina State University

8:20am SS2-FrM1 Dielectric Response and Ionization of Water Adlayers in High Electric Fields: Calculations and Experiments, *T.D. Pinkerton, D.L. Scovell, V. Medvedev, E.M. Stuve*, University of Washington

Water/metal interfaces typically support high surface electric fields on the order of 1-3 V/Å (100-300 MV/cm) - fields strong enough to make or break chemical bonds. While the surface electric field depends upon electrode potential and the nature of both electrode and electrolyte, the response of the electric field to these parameters and its subsequent influence in electrochemical processes remain unknown. Controlled high surface electric fields can be obtained on sharp field emitter tips in vacuum through potentials of 1-5 kV applied to tips of radius 100-1000 Å. The response of both thin and thick water layers adsorbed on these tips thereby allows the influence of electric field to be probed directly. Theoretical and experimental results show the transition of the location of the field from the water/vacuum interface for thin water layers to the metal/water interface for water layers above 500 Å thickness. Ionization at the water/vacuum interface represents UHV adsorbed water, whereas ionization at the metal/water interface represents an electrochemical response. The field required for onset of ionization increases linearly with adlayer thickness, in agreement with calculations. With increasing field strength water ionizes to form H@sub 3@O@super +@, OH@super -@, and H@sub 2@O@super +@. These results demonstrate the electrochemical response of water as a function of field and have implications in basic electrochemistry, nanolithography, and the design of tips for field emitter arrays.

8:40am SS2-FrM2 Crystallization Kinetics of Amorphous Solid Water: The Effect of Underlying Substrate, *Z. Dohnálek*, *G.A. Kimmel*, *K.P. Stevenson*, *R.S. Smith*, *B.D. Kay*, Pacific Northwest National Laboratory

Thermally induced crystallization of ultra-thin amorphous solid water (ASW) films grown from a directed H@sub 2@O(g) beam is investigated. The temperature programmed desorption (TPD) spectra of N@sub 2@(g)

physisorbed on ASW and crystalline ice (CI) surfaces exhibit striking differences in their lineshapes. The spectroscopic sensitivity of the N@sub 2@(g) TPD provides a unique opportunity to study the ASW crystallization with high sensitivity at temperatures well below H@sub 2@O desorption. The ASW crystallization kinetics are followed isothermally on Pt(111) and CI substrates as a function of temperature and ASW film thickness. The crystallization kinetics are strongly substrate dependent. On Pt(111), the data is consistent with the 3-dimensional crystallization model with the nucleation occurring in the bulk of the ASW film as shown previously.@footnote 1@ In contrast, on the CI substrate we observe that the CI surface serves as a 2-dimensional nucleation center and the crystallization proceeds from the ASW/CI interface towards the ASW surface. The activation barrier of the crystallization process on the CI substrate is significantly lowered as compared to the Pt(111) due to the presence of the crystalline template. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830. @footnote 1@ R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay, Surf. Sci. 367 (1996) L13.

9:00am SS2-FrM3 A Study of Amorphous Solid Water (ASW) Morphology using N@sub 2@ Gas Adsorption and Thermal Desorption, K.P. Stevenson, Z. Dohnálek, G.A. Kimmel, R.S. Smith, B.D. Kay, Pacific Northwest National Laboratory

We have probed the morphology of amorphous solid water (ASW) thin films grown below 140 K using N@sub 2@ gas adsorption and temperature programmed desorption (TPD). Surprisingly, we find that ASW films grown with increasing angles of incidence from a directed vapor source show 20-100 fold increase in the uptake of N@sub 2@ gas at 26 K. The integrated N@sub 2@ TPD signals obtained from subsequent thermal desorption experiments reflect significant increases in the available surface area and porosity of ASW films with increasing incident angle. In comparison, ASW films grown by ambient H@sub 2@O backfilling of the experimental apparatus show integrated N@sub 2@ signals most comparable with ASW films grown at oblique angles of incidence. This observation has important implications for those studying ASW in laboratory settings, since the angle of incidence as an experimental control variable has not been widely appreciated in the preparation of ASW thin films. Further, we have investigated the affects of growth temperature, film thickness, and annealing on ASW morphology. The available ASW film surface area is observed to decrease with increasing growth temperature until 80 K where it becomes relatively constant thereafter. For a given incident angle, a roughly linear increase with increasing film thickness is observed for ASW films grown at 22 K. ASW films annealed above 120 K show a significant collapse of the micropore structure consistent with previously published accounts. These results have important implications for understanding the chemical and physical properties of ASW found in astrophysical media such as comets, planetary satellites, and interstellar grains. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

9:20am SS2-FrM4 Origin of Non-Zero-Order H@sub2@O Desorption Kinetics from Crystalline Ice Multilayers on Ru(001), F.E. Livingston, J.A. Smith, S.M. George, University of Colorado, Boulder

Recent studies have reported non-zero-order kinetics for H@sub2@O desorption from crystalline ice multilayers on Ru(001). To understand the origin of the non-zero-order kinetics, D@sub2@O desorption from ultrathin crystalline D@sub2@O ice multilayers on Ru(001) was measured using a combination of laser-induced thermal desorption (LITD) spatial probing and isothermal desorption flux analysis. The ice multilayers were grown on Ru(001) using either backfill D@sub2@O vapor deposition or multichannel capillary array dosing methods. The ice multilayers grown via backfill vapor deposition were smooth and highly uniform. The LITD and isothermal desorption flux studies demonstrated that D@sub2@O desorption from these uniform ice multilayers exactly followed zero-order kinetics. Slight deviations from zero-order desorption kinetics were observed only at low D@sub2@O coverages of @<=@5 BL D@sub2@O. In contrast, the ice films prepared using capillary array dosing were spatially non-uniform and exhibited a decreasing multilayer coverage versus distance from the center of the substrate. This initial non-uniform D@sub2@O coverage distribution had a dramatic impact on the isothermal desorption flux measurements and produced non-zero-order desorption kinetics. The deviations from zero-order kinetics were directly related to changes in the ice film surface area as the non-uniform initial multilayer coverage is completely desorbed at various positions on the Ru(001) substrate at different times. The previous reports of non-zero-order

kinetics on Ru(001) are assigned to a non-uniform initial D@sub2@O multilayer coverage distribution.

9:40am SS2-FrM5 Low Energy Dynamics through the Verwey Transition : Water Adsorbed on Fe@sub 3@O@sub 4@(100)/MgO(100), C.J. Hirschmugl, M. Takasaki, M. Collins, University of Wisconsin, Milwaukee; C.H.F. Peden, S.A. Chambers, Pacific Northwest National Laboratory

The far- and mid-infrared broadband absorptions and discrete vibrations have been studied for water adsorbed on an epitaxial 2000 Å Fe@sub 3@O@sub 4@(100) film using infrared synchrotron radiation. Water on Fe@sub 3@O@sub 4@ represents an ideal example both practically and fundamentally, as Fe@sub 3@O@sub 4@ is a prominent subsurface mineral (magnetite), and the material exhibits an interesting electronic transition. Specifically, the substrate undergoes a metal-semiconductor (Verwey) transition at 120 K (ten-thousand-fold change in conductivity from approximately 10@super 2@ [ohm-cm]@super -1@ to approximately .01 [ohm-cm]@super -1@), while water adsorbed on the surface is stable in vacuum until above 350 K. The frequency-dependent conductivity in normal-incidence reflectance measurements follows a Drude behavior above the transition, and is non-Drude below the transition. Hence, the infrared response of this system, both above and below the transition, provides a comparison of the water-substrate interaction in the metallic and semiconducting states. The present infrared studies employ synchrotron radiation, which can extend traditional IRAS measurements to below 400 cm@super -1@ with noise levels of approximately .01% attainable in 100 seconds measuring time. In addition, these measurements are complemented by TPD and concurrent resistivity measurements. Notably, three distinct cation adsorption sites are available on the reconstructed Fe@sub 3@O@sub 4@(100) surface: a tetrahedrally bonded Fe@super 2+@; a tetrahedrally bonded Fe@super 3+@; and an octahedrally bonded Fe@super 3+@. Molecularly adsorbed water is shown to sequentially fill these sites. In addition, adsorbed multilayers of water reveal large anti-absorption resonances in the infrared spectra for the molecular vibrations and the substrate phonons.

10:00am SS2-FrM6 Surface Restructuring of Magnesium Oxide at the Interface with Water, *J. Jupille,* CNRS, France; *P. Nael, D. Abriou,* Laboratoire CNRS/Saint-Gobain, France; *H. Arribart,* Saint-Gobain Recherche, France

Interactions of water with oxide surfaces are among the most common chemical reactions since they can be observed at any time in the surrounding medium. Nevertheless, despite their apparent simplicity, they often lack microscopic description. A well known example is the adsorption of water on magnesium oxide. Cleaved MgO samples, which show mostly flat (100) terraces, undergo dramatic rearrangements upon exposures to surrounding atmosphere. Their surfaces are becoming very rough, so that flat (100) terraces are no longer visible. These changes in morphology are usually suspected to arise from the reaction with water molecules present in the ambient air. However, according to theory, water is not expected to dissociate on the dense (100) faces of MgO, but only on sites of lower coordination numbers. To demonstrate that water adsorption induces a restructuring of the MgO(100) surfaces, the behaviour of cleaved MgO surfaces which have been brought in contact with water have been examined by atomic force microscopy. It has been observed that pits are directions. Moreover, rearrangements along similar formed along directions have been seen by exposing cleaved MgO surfaces either to the ambient air or to moist nitrogen. Consistently with calculations relative to hydroxylated MgO surfaces, the orientation of the pits suggests that the driving force for the restructuring is the change in surface energy upon water adsorption.

10:20am SS2-FrM7 Interaction of Water and Dimethyl Sulfoxide with Gold Surfaces, A.A. Gewirth, N. Ikemiya, S.K. Si, University of Illinois, Urbana

We discuss recent results examining the initial stages of water and dimethyl sulfoxide adsorbtion on Au surfaces. We show that water first adsorbs on Au at low temperature as a planar, amorphous, monolayer-high film. The subsequent growth of water clusters occurs atop this film, but not on the bare metal surface. The growth and structure of dimethyl sulfoxide on Au surfaces is surface-structure dependent with more highly corrugated faces providing localized electron density yielding ordered arrays. Results obtained at room temperature from bulk liquid dimethyl sulfoxide are in close correspondance with low temperature UHV measurements.

10:40am SS2-FrM8 Coadsorption of Water and Hydrogen on Pt(110), P. Blowers, N. Chen, R. Masel, University of Illinois, Urbana

In previous papers, various investigators have discovered a new species when hydrogen and water coadsorb on various faces of platinum. However, the exact nature of the species is still in dispute. In this paper we combine high quality HREELS spectra with abinitio calculations to try to identify the species. The EELS spectrum of coadsorbed water an hydrogen shows peaks at 1180 and 3340 cm-1 which are not seen with water or hydrogen alone. The peaks shift with deuteration in a way expected for compound formation between water and hydrogen. Abinitio methods at the MP2/6-31G* level are used to identify the species. We have not found any (H2O)nH clusters, radical species or negative ions with vibrations near 1180 cm-1 However, cationic species e.g. [H3O]+, [H5O2]+, [H7O3]+ give vibrations in the right range. A detailed comparison of theory and experiment suggests that a number of hydrated ions form during the coadsorption process, with [H5O2]+, and [H7O3]+ being the most important.

11:00am SS2-FrM9 Equilibrium Water Structures at Well-Defined Organic Surfaces, D.L. Allara, T.J. Boland, Pennsylvania State University

We report combined in-situ infrared vibrational spectroscopic and coverage measurements, from submonolayer to near condensation, of equilibrium water adsorption at well-defined organic surfaces synthesized by molecular self-assembly. The adsorption isotherm data were used to develop thermodyamic parameters of the adsorbed films while the IR data give information on the water structures. The IR spectra were interpreted quantitatively by using modeling based on electromagnetic theory and the known optical function spectra of various phases of water. The results reveal a range of water structures from ice-like to clathrate-like and liquidlike depending on the water chemical potential, the chemical functionality of the surface and on the presence of dilute inorganic salts dissolved in the near water films. In the case of hydrophobic methyl-terminated surfaces. the water adopts a liquid-like structure from submonolayer to nearcondensation coverages in surprising contradiction to the traditional view of ordered water at hydrophobic surfaces. In contrast, for polar surfaces such as CO2H, the water adopts a strongly H-bonded structure up to the condensation point. The incorporation of dissolved salts at the interfaces serves to broaden the range of water structures observed.

11:20am SS2-FrM10 Effect of Boron on the Surface Chemistry of Single Crystal Ni@sub 3@(Al,Ti), B. Zhou, J. Wang, Y.W. Chung, Northwestern University

Previous work demonstrated that water dissociates into atomic hydrogen on Ni@sub 3@(Al,Ti)(100). There is clear evidence that this dissociation reaction results in the reduced ductility of many polycrystalline aluminumbased alloys in a moist environment. Ductility measurements further show that boron addition to these alloys increases ductility. Therefore, it is reasonable to expect that boron may affect the production of atomic hydrogen from water vapor dissociation and its surface mobility. To explore the effect of boron, we first dosed the surface of clean Ni@sub 3@(Al,Ti)(100) with controlled amounts of boron, using a specially designed low-energy boron ion source, followed by low-temperature exposure to D@sub 2@O and temperature-programmed desorption. The state of the surface was determined by x-ray photoemission. These studies show that addition of boron reduces the production of atomic hydrogen. The significance of this observation in explaining the beneficial effect of boron will be discussed.

11:40am SS2-FrM11 Interactions of 50-2500 eV Electrons with Ice, C.D. Wilson, C.A. Dukes, R.A. Baragiola, University of Virginia

We investigate the interactions of 50-2500 eV electrons with vapor deposited ice by means of Electron Energy Loss Spectroscopy (EELS), Auger Electron Spectroscopy (AES), and Secondary Electron Emission (SEE). The EELS data is used to measure low lying excitations and to ascertain the production of radicals in the near surface region. This is done by observing the appearance of energy loss features in the band gap region as a function of irradiation fluence. We will discuss electrostatic charging and chemical alterations during irradiation and relate the results to astronomical problems.

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