Surface Science Division Room 606 - Session SS1+EM-MoM

Chemistry on Oxides

Moderator: S.A. Joyce, Pacific Northwest Laboratory

8:20am SS1+EM-MoM1 The Reactions of Maleic Anhydride Over TiO@sub 2@ (001) Single Crystal Surfaces, J.N. Wilson, D.J. Titheridge, H. Idriss, The University of Auckland, New Zealand

The reactions of maleic anhydride have been investigated on the stoichiometric and substoichiometric surfaces of TiO@sub 2@ by Temperature Programmed Desorption (TPD) and Scanning Kinetic Spectroscopy (SKS). SKS technique, showing complementary information to TPD, has been successfully applied to investigate the chemical pathways on this oxide material for the first time. Results from the maleic anhydride TPD and SKS show the desorption of a wide variety of products in several temperature domains. In addition to the decomposition pathway to CO, CO@sub 2@, acetylene, and ethylene, the desorption of coupling reaction products of two molecules of acetylene to vinylacetylene (m/e 52) and of three molecules of acetylene to benzene (m/e 78) is observed. Moreover, the potential desorption of both ends of the molecule, is discussed. The coupling pathways of the reactions of maleic anhydride on the substoichiometric surface were more accentuated.

8:40am SS1+EM-MoM2 S Adsorption on TiO@sub 2@(110) Studied with STM, XPS and LEED, *E.L.D. Hebenstreit*, *W. Hebenstreit*, *U. Diebold*, Tulane University

TiO@sub 2@ surfaces are well-known for their catalytic properties. Since sulfur is known as a catalyst inhibitor, its adsorption behavior on TiO@sub 2@ single crystal surfaces are of great interest. Measurements with a scanning tunneling microscope reveal the existence of two different adsorption sites, depending on the sample temperature during adsorption. Adsorption at room temperature leads to very mobile sulfur atoms sitting on titanium sites of TiO@sub 2@(110). Adsorption at 300°C causes the formation of more stable sulfur chains running along the [1-10] direction with an ordered (3x1) structure at saturation. In the latter case the sulfur atoms are located at the positions of oxygen surface atoms. X-ray-photoelectron-spectroscopy confirms the existence of two chemically different S species.

9:00am SS1+EM-MoM3 Spectroscopic Studies of Sorption Processes at Metal Oxide-Aqueous Solutions Interfaces, G.E. Brown, Jr., T. Kendelewicz, Stanford U.; P. Liu, LBNL; J.R. Bargar, Stanford Synchrotron Radiation Lab.; J.P. Fitts, A.L. Foster, J.D. Ostergren, G.A. Parks, A.H. Templeton, Stanford U.; H.A. Thompson, LANL; S.N. Towle, Intel Corp.; T.P. Trainor, Stanford U.; P. Eng, S. Sutton, Adv. Photon Source INVITED Chemical interactions at metal oxide-aqueous solution interfaces are of great significance in atmospheric and environmental chemistry. They help control many important processes including dissolution and crystal growth of natural solids and the sorption a nd desorption of aqueous metal ions, which can sequester or release heavy metal contaminants in atmospheric and aquatic environments. Metal oxide-water interfaces in natural systems

are extremely complex when viewed at the molecular level because of the many variable that must be accounted for and the difficulty in observing the products of interfacial reactions under in-situ conditions (i.e., with bulk water present). To make this problem more tractable, we have employed a reductionist approach in which interfacial reaction products are examined in simplified model systems under carefully controlled conditions using a combination of classical surface chemistry methods, synchrotron radiationbased surface science methods, and other spectroscopic and scanning force microscopy methods. The resulting information at macroscopic and atomic/molecular scales allows sorption behavior to be correlated with chemical species information, including the structure, composition, and mode of sorption of adsorbates, and, in selected cases, the types of reactive sites on adsorbent surfaces and the effect of aging time. In parallel model system studies, we have also examined the effects of common inorganic ligands, organic ligands, and biofilms on the sorption of metal ions at mineral-water interfaces, and we have used the results as a basis for studies of As and Pb speciation in contaminated soils and mine tailings. These studies have revealed the structure and composition of adsorbates, and for single-crystal adsorbents, have allowed us to place constraints on the stoichiometry of sorption reactions, including the types of reactive sites

to which the adsorbate binds. Selected examples of these studies will be presented.

9:40am SS1+EM-MoM5 Reactions of SeF@sub6@ with Iron and Iron Oxides, S.R. Qiu¹, H.-F. Lai, H.T. Than, C. Amrhein, J.A. Yarmoff, University of California, Riverside

Concentrated levels of selenium in the groundwater of the western US have been found to cause the death and birth-deformation of wildlife. Zero valent iron has been used to immobilize many soluble toxic groundwater contaminants, including selenate (Se@super6+@), by a surface redox reaction in which aqueous contaminants are reduced to less mobile forms. Only limited success has been achieved in the field, however, as the understanding of the reaction mechanism at the liquid/solid interface is incomplete. In this work, the remediation process is modeled by the reaction of SeF@sub6@ with iron and iron oxide surfaces in ultra-high vacuum. Se in SeF@sub6@ is in the same oxidation state as in selenate, and a similar reduction is observed upon reaction with Fe. X-ray photoelectron spectroscopy (XPS) spectra collected following the exposure of a sputter-cleaned Fe foil to SeF@sub6@ show both Se and F on the surface. The Se is found to be directly bonded to Fe, with no bonds to F remaining, indicative of the complete dissociation of SeF@sub6@. The Fto-Se ratio is close to 6 to 1, showing that all of the products remain on the surface. The Fe 2p spectra show the formation of FeF@sub2@ as the major surface species formed. These results suggest that there is a high activation barrier to adsorption, but that once it occurs, the excess energy liberated by the exothermic reaction promotes complete dissociation. To ascertain the role of oxygen, SeF@sub6@ was exposed to both partially and fully oxidized Fe surfaces. Oxygen was found, in all cases, to inhibit the reaction. We are currently investigating this reaction employing clean and oxygen pre-covered single crystal Fe surfaces. Both XPS and scanning tunneling microscopy are being used to understand the chemical reaction mechanism and to ascertain the adsorption sites. The implications of our results on practical remediation methods will be discussed.

10:00am SS1+EM-MoM6 Interactions of HCOOH with Stoichiometric and Defective SrTiO@sub 3@(100) Surfaces, L. Wang, F. Ferris, H. Engelhardt, Pacific Northwest National Laboratories

Interactions of HCOOH with stoichiometric (nearly defect-free) and defective SrTiO@sub 3@(100) surfaces have been studied using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and electronic structure calculations. Two reaction pathways were observed for formaldehyde formation from formic acid on SrTiO@sub 3@(100) surfaces. On stoichiometric surfaces, formaldehyde was produced through bimolecular coupling of two formates. However, on Ar+ sputtered surfaces, formaldehyde formation involves the reduction of surface formate by the oxidation of reduced Ti cations. XPS results show that surface defects on sputtered SrTiO@sub 3@(100) surfaces were reoxidized significantly upon exposure to 30 L HCOOH at 300 K, in contrast to defects on sputtered TiO@sub 2@(110) surfaces where no reduction in defect intensity was observed under the same condition. The fact that surface formate was reduced at 300 K on SrTiO@sub 3@(100) is clearly evident in TPD data where the desorption peak of formaldehyde is shifted to a lower temperature and broadened significantly down to 300 K for Ar+ sputtered SrTiO@sub 3@(100) surfaces as compared with stoichiometric surfaces. Electronic structure calculations have been used to investigate the adsorptive interactions for formate and formaldehyde on the cation sites of both stoichiometric and defective SrTiO@sub 3@(100) surfaces. The results for formate indicate a strong adsorptive interaction consistent with the experimental observations, with significant charge redistribution. Further results will be discussed in terms of potential reaction mechanisms.

10:20am SS1+EM-MoM7 The Structure of the CeO@sub 2@(001) Surface and its Reactions with D@sub 2@O, G.S. Herman, Pacific Northwest National Laboratory; Y.-J. Kim, Taejon National University of Technology, Korea; S.A. Chambers, C.H.F. Peden, Pacific Northwest National Laboratory Angle-resolved mass-spectroscopy of recoiled ions (AR-MSRI) has been used to determine the surface structure of CeO@sub 2@(001). The results indicate that the surface is terminated with 0.5 monolayers of oxygen which gives rise to a zero dipole moment and, thus, a stable surface. The interaction of D@sub 2@O with the CeO@sub 2@(001) surface was studied with temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). It was found with TPD that D@sub 2@O desorption occurs in three states with temperatures of 152, 200, and 275 K which are defined as multilayer D@sub 2@O, weakly bound surface D@sub

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2@O, and hydroxyl recombination, respectively. O 1s XPS measurements for high D@sub 2@O exposures, where multilayer water desorption was observed in the TPD, resulted in emission from only the substrate and surface hydroxyls. This is likely due to a non-wetting behavior of D@sub 2@O on this surface with the formation of nanosized clusters. An analysis of the O1s XPS data indicates that the surface has a hydroxyl coverage of 0.9 monolayers for large water exposures at 85 K. This is consistent with a model in which the polar CeO@sub 2@(001) surface can be stabilized by a reduction of the dipole in the top layer by the formation of full monolayer of hydroxyls. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

10:40am SS1+EM-MoM8 The Correlation Between MgO (100) Surface Morphology and Chemical Reactivity, S.S. Perry, University of Houston, US; S. Imaduddin, O. El-bjeirami, P.B. Merrill, S.M. Lee, H.I. Kim, University of Houston

A critical ingredient of any surface science study is the preparation of the surface so as to present a uniform and homogeneous distribution of surface sites. For metals, the nature of adsorption site is determined by the crystal face exposed and the local coordination of the different metal atoms at the surface. For compound semiconductors and oxide based materials, the situation can be much more complex as the crystal face and coordination now applies to more than one type of element. The preparation of such materials can be further complicated by the possibility of preferential sputtering of one component of the surface. In this study we have used a combination of microscopy, ex-situ processing, ultrahigh vacuum (UHV) processing and UHV surface analysis to correlate the chemical reactivity of a model metal oxide (MgO) with the nature of surface structure and morphology. Atomic force microscopy, low energy electron diffraction, and reflection high energy electron diffraction studies together have allowed the distinction between amorphous and crystalline surfaces as well as the length scale of surface order. Single crystal MgO(100) surfaces have been prepared by a number of procedures including acid etching, high temperature annealing in ambient pressures of oxygen, UHV annealing, and ion bombardment. The compositional changes of the surface region with respect to these procedures have been followed with X-ray photoelectron spectroscopy. Finally, the chemical reactivity of the MgO(100) surface has been studied using temperature programmed desorption, investigating the desorption properties of water, methanol and carbon monoxide. Together, these studies have generated a complete picture of the relationship between microscopic surface morphology and chemical reactivity for this model metal oxide surface and have highlighted several critical aspects involved in the preparation of single crystal metal oxide surfaces for UHV surface science studies.

11:00am SS1+EM-MoM9 Photoconversion of Adsorbed Oxygen States On TiO@sub 2@(110), C.L. Perkins, M.A. Henderson, Pacific Northwest National Laboratory

By means of postirradiation temperature programmed desorption we have investigated further the states of oxygen adsorbed on rutile TiO@sub 2@. Previous work has shown that annealing the (110) surface in vacuum produces isolated bridging oxygen vacancies, and that these vacancies are intimately connected with molecular and dissociative oxygen adsorption channels. We find that at 120 K illumination of the oxygen exposed surface with photons having energies above the band gap (>3.6 eV) results in depletion of the molecular oxygen state observed at 410 K in TPD, in contrast to the remaining oxygen destined for the dissociative channel. An unusual effect of water overlayers on the O/TiO@sub 2@(110) system is explored. For thick overlayers (> 2 ML), it is possible to generate via UV irradiation a previously unobserved oxygen TPD state. Cross sections for the photoconversion of oxygen into this state are measured, and specific mechanisms for the process are proposed.

11:20am SS1+EM-MoM10 Reactions of Acetic Acid, Acetaldehyde and Ethanol on the (111) Surface of Uranium Dioxide Single Crystal, S.V. Chong, H. Idriss, The University of Auckland, New Zealand

The reactions of three C2 molecules having different functional group and polarity, have been investigated on the (111) surface of uranium dioxide single crystal, which has been characterised by LEED and AES. The adsorption of acetic acid, the most polar among the three molecules, indicates a higher sticking probability on the oxygen terminated UO@sub 2@(111) surface, followed by ethanol then acetaldehyde. Temperature Programmed Desorption (TPD) for these molecules displays a rich chemistry. Acetic acid-TPD on a stoichiometric surface yields ketene

(dehydration) as the main product, plus acetaldehyde (reduction) as the minor product. While on an electron beam sputtered surface, two additional products were observed - butene and crotonaldehyde. In the case of acetaldehyde, both sputtered and non-sputtered surfaces yield benzene, with ketene as the additional product on the sputtered surface. The reactions of ethanol on a stoichiometric surface give acetaldehyde and ethylene as the only two products with "equal" amount. The comparison of this latter result with those of other metal oxide single crystals indicates a plausible relationship between the dehydrogenation/dehydration selectivity of primary alcohols and the Madelung potential of the cations. In summary, this investigation has shown the ability of UO@sub 2@(111) single crystal to oxidise, reduce, reductively couple, and trimerise organic molecules.

11:40am SS1+EM-MoM11 Surface Reactions on Cr-doped V@sub 2@O@sub 3@, D.S. Toledano, V.E. Henrich, Yale University

Transition-metal oxides are important as gas sensors due to chemisorptioninduced changes in surface conductivity. Conversely, changes in substrate electronic structure may alter surface chemisorption properties. While investigating the effect of metal-insulator transitions in Cr-doped V@sub 2@O@sub 3@ on adsorption, we have observed interesting effects involving surface reduction by CO, as well as differences in adsorption on metallic and insulating substrate phases. (Cr@sub 0.015@V@sub 0.985@)@sub 2@O@sub 3@ exhibits two metal-insulator transitions as a function of temperature; these experiments focus on the insulating phase of single-crystal Cr-V@sub 2@O@sub 3@ using UPS, XPS, LEED and AES. When insulating-phase Cr-V@sub 2@O@sub 3@ (0001) is exposed to CO at 273K, CO appears to adsorb dissociatively up to 10@super 3@ Langmuir. Higher exposures result in a C-containing species, and electron transfer to V cations at energies near E@sub F@; decreased occupation of nonbonding O orbitals is also observed. Heating to 470K desorbs this species, but the surface is further reduced after desorption, with increased charge transfer to V cations. Exposure of a CO-reduced surface to O@sub 2@ does not reoxidize the surface or restore the original electronic structure, but appears to result in adsorbed O@super -@ or (O@sub2@)@super -@ which does not re-enter the lattice unless annealed above 700K. CO adsorption on metallic-phase Cr-V@sub 2@O@sub 3@ differs from that on the insulating phase for intermediate exposures, exhibiting higher initial sticking coefficient and desorption temperature; however, the two phases behave similarly for high CO exposures. Adsorption of H@sub 2@O, SO@sub 2@ and O@sub 2@ on both substrate phases has also been studied. This work was partially funded by NSF grant CTS-96-10140

Surface Science Division Room 607 - Session SS2-MoM

Catalysis on Metals

Moderator: J.W. Niemantsverdriet, Eindhoven University of Technology, The Netherlands

8:20am **SS2-MoM1 The Influence of a Catalytic Surface on the Gas Phase Ignition and Combustion of H2+O2**, *M. Försth*, *F. Gudmundson*, *J. Persson*, *A. Rosén*, Chalmers University of Technology, Sweden

The OH concentration outside a Pt catalyst at 1300K, in a stagnation flow of 90% O@sub 2@ and 10% H@sub 2@, has been studied by Planar Laser Induced Fluorescence, PLIF, and compared to measurements outside a heated glass surface. The total pressure in the system was varied from 0.2 to 120 torr. At low pressure, surface reactions were observed for the Pt surface, but not for the glass. At higher pressure, gas-phase ignition occurred for both systems, but not at the same pressure: ignition occurred at a lower pressure outside the inert glass surface. Computer modeling using CHEMKIN confirmed these results. The difference in gas-phase ignition is also seen in the modelling results, and it is due to the removal of atomic O and H from the gas by adsorption and reaction on the catalytic surface. The catalytic reaction mechanism on the surface plays an important role as it enhances the removal of radicals, compared to a surface where only radical recombination back to reactants is allowed.

8:40am SS2-MoM2 Catalytic Oxidation of Unsaturated C@sub 3@ Hydrocarbons on the Pt (111) Surface, A.M. Gabelnick, A.T. Capitano, D.J. Burnett, University of Michigan; D.A. Fischer, National Institute of Standards and Technology; J.L. Gland, University of Michigan

The catalytic oxidation of unsaturated C3 hydrocarbons (propylene and methylacetylene) has been studied in-situ in oxygen pressures ranging from UHV to 0.01 torr on the Pt(111) surface. Using a combination of kinetic and

spectroscopic in-situ fluorescence yield soft X-ray techniques, we have characterized the oxidation of these hydrocarbons based on absolute carbon coverage and identified oxidation intermediates spectroscopically. The adsorbed intermediates for oxidation of preadsorbed propylene, propylene catalytic oxidation (both propylene and oxygen in the gas phase), and methylacetylene oxidation have been characterized. Despite differences in these intermediates, skeletal oxidation begins at the same temperature, indicating a common rate limiting step in the oxidation process. In the catalytic oxidation of propylene, dehydrogenation of propylene occurs prior to skeletal oxidation, even with both propylene and oxygen in the gas phase. In pressures of oxygen, a monolayer of propylene and methylacetylene completely oxidize by 450 K, with skeletal oxidation of both hydrocarbons beginning near 320 K. Quantitative kinetic studies of methylacetylene oxidation over a range of conditions enabled the determination of both the activation energy and order of the reaction in oxygen. Experiments performed with coadsorbed oxygen confirm that O(a) is the oxidizing agent.

9:00am SS2-MoM3 Thermal Conversion of C@sub 3@ Fragments on Pt(111): Evidence for the Formation of Allylic Intermediates, D. Chrysostomou, C.R. French, J.M. Guevremont, F. Zaera, University of California, Riverside

Platinacyclobutane was selectively formed on Pt(111) via the thermal activation of adsorbed 1,3-diiodopropane, and the mechanism for its conversion to propene was investigated using temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). Thermal desorption of propene from 1,3-diiodopropane occurs at 370 K. The conversion is suggested to involve the formation of a surface bound allylic intermediate. Allyl iodide was used to investigate the further reactivity of that intermediate, and additional experiments were carried out with propyl iodide and propylene as well. Selective deuteration of 1,3diiodopropane was explored as a mean to determine the C'H bonds active in the metallacycle to propene conversion, but the usefulness of this approach was limited by extensive scrambling in platinacyclobutane prior to the formation of propene. Propene itself was identified to exist on the surface in three different configurations depending on the coverage: disigma bonded, pi bonded, and weakly physisorbed. The results from this work provide new insights into the mechanism of hydrocarbon reforming reactions.

9:20am SS2-MoM4 Reactions of Methyl Groups on Sn/Pt(111) Alloys, B.E. Koel, H. He, University of Southern California

Reactions of alkyl intermediates are important in many catalytic hydrocarbon reactions over metal and metal alloy surfaces. Reactions of adsorbed CH@sub 3@ (methyl) groups, formed using a pyrolytic azomethane source to produce incident methyl radicals, on two ordered Sn/Pt(111) surface allows have been studied using HREELS, UPS, TPD, AES and XPS. Chemisorbed CH@sub 3@ species are identified at low doses but longer chain hydrocarbons can be formed at high doses on both Sn/Pt(111) surfaces at 100 K. Chemisorbed methyl groups are characterized by a prominent peak in UPS at 8 eV BE (CH@sub 3@ HOMO) and a strong peak in HREELS at 1240 cm@super -1@ from the @delta@@sub s@(CH@sub 3@) mode. These studies show that alloyed Sn decreases the dehydrogenation rates of akyl groups on Pt(111) surfaces and enables other C-C bond coupling reactions to occur. Alkane and alkene products were desorbed below 200 K in TPD for both Sn/Pt(111) surface alloys. On the (2x2) alloy, only CH species are stable at 300 K, and these react to desorb CH@sub 4@ at 432 K. TPD after methyl dosing on the (@sr@3x@sr@3)R30° alloy at 300 K gave only one very sharp CH@sub 4@ desorption peak at 453 K, and we propose that this arises from decomposition of CH@sub 3@CH species. The chemistry of Pt-Sn alloy surfaces leads to much lower carbon buildup than on Pt surfaces from thermal reactions of alkyl adsorbates.

9:40am SS2-MoM5 Mechanisms and Dynamics in Millisecond Chemical Reactors, *L.D. Schmidt*, University of Minnesota INVITED

It is possible to carry out the partial oxidation of alkanes in reactors with residence times less than 10@super -3@ sec above atmospheric pressure and obtain almost complete conversions with high selectivities to products such as H@sub 2@ and CO, olefins, and oxygenated hydrocarbons. These processes involve extremely large temperature and concentration gradients (10@super 6@ K/sec and 10@super 4@ atm/sec), and at temperatures above 1300K where adsorption lifetimes are typically 10@super -9@ sec. For the oxidation of ethane to ethylene, we can obtain 85% selectivity to ethylene with less than 5% CO and CO@sub 2@, even though at equilibrium CO should be the dominant product. These reactions

occur on a PtSn catalyst surface which consists of ~10 μ m single crystal particles exposing large facets. EDX and XRD of these catalysts show that they consist entirely of intermetallic PtSn compounds with no free Pt phases. This is accomplished by adding large amounts of H@sub 2@ in a ratio of H@sub 2@/O@sub 2@=2. With this feed, the surface reaction forming H@sub 2@O occurs within the first 100 µsec on the first mm of catalyst, while minimizing ethane oxidation. This consumes all O@sub 2@ leaving ethane dehydrogenation which generates as much H@sub 2@ as is fed to the reactor. At 1300K with 10@super -9@ sec adsorption times and very high reactive fluxes, these processes deviate considerably from conventional catalytic reaction conditions, and these processes may involve partially equilibrated internal states of molecules. Implications of nonequilibrium reaction dynamics at extreme these conditions will be considered.

10:20am **SS2-MoM7 In-situ Studies of C-C Hydrogenolysis in Cyclopropane on Platinum using a Combination of Soft X-ray Methods**, *A.T. Capitano*, *A.M. Gabelnick*, University of Michigan; *D.A. Fischer*, National Institute of Standards and Technology; *J.L. Gland*, University of Michigan

In-situ studies fluorescence soft X-ray studies clearly show that a propyl intermediate plays an important role during cyclopropane hydrogenolysis to form propane over the Pt(111) surface. Through a combination of spectroscopic and in-situ catalytic studies, a complete picture of hydrogen induced C-C bond breaking mechanisms during cyclopropane hydrogenolysis has been developed. Molecular cyclopropane is adsorbed in a tilted configuration and desorbs in the 130 K temperature range. Preadsorbed cyclopropane desorbs before reacting with hydrogen, even for pressures as high as 0.02 torr. When both cyclopropane and hydrogen are present in the gas-phase, propane is formed above 300 K. In this temperature range, in-situ soft X-ray studies of the adsorbed species show that a propyl intermediate is formed. The coverage and stoichiometry of this intermediate has been characterized over a range of temperatures and reactant ratios. For large excesses of hydrogen, the average hydrogen stoichiometry of the adsorbed species increases with increasing temperature while the amount of carbon remains constant. Characterization of the dominant intermediate at 300 K with FY-NEXAFS indicates that the hydrogenated intermediate is an adsorbed propyl species. Detailed isothermal kinetic studies were used to establish both the activation energy and prefactor for hydrogenation of this intermediate. During in-situ catalytic studies, an additional C@sub 3@ adsorbed species is observed in the 150 K temperature range. By using FY-NEXAFS, the structure and bonding of this intermediate has been characterized and is consistent with adsorbed cyclopropyl-like. These exciting results have clearly established for the first time under catalytic conditions that C-C bond breaking in cyclopropane proceeds via sequential hydrogen addition.

10:40am SS2-MoM8 Direct Evidence of Surface Intermediates from the Reactions of C@sub 3@ Hydrocarbons on Cu(100), *H. Celio, K.C. Smith, J.M. White,* University of Texas, Austin

Using reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD), we have characterized important intermediates of the thermal and electron-induced surface chemistry of C3 hydrocarbons on Cu(100). The molecules that have been studied include allyl bromide, allyl chloride, propene, and cyclopropane. We find that the allyl halides dissociate to form pi-bonded allyl groups and halogen atomns at a wide temperature range (110-350 K). Furthermore, we observed an exceptionally facile carbon-carbon coupling between allyl bromide and pibonded allyl groups that lead to the formation of 1,5-hexadiene at 110 K. Conversely, allyl chloride principally forms pi-bonded allyl groups, which remained inert in the presence of allyl chloride molecules on the second layer. The implications of the dissimilar surface reactions of these allyl halides are discussed in terms of an Eley-Rideal rather than a diffusionlimited reaction. Electron irradiation (<50 eV) of weakly adsorbed cyclopropane lead to the formation of metallacyclobutane and cyclopropyl groups at 100 K. The thermal chemistry of the latter products yield propene but not pi-bonded allyl groups. The results of the allyl halides and cyclopropane are also compared and discussed for Ag(111).

11:00am SS2-MoM9 Carbon-Carbon Coupling from Formaldehyde Reaction on Mo(110), *K.T. Queeney*, Harvard University; *C.R. Arumainayagam*, Wellesley College; *C.M. Friend*, Harvard University

Formaldehyde (CH@sub 2@O) reaction on Mo(110) was studied with temperature programmed reaction and infrared reflectance absorbance spectroscopy. We present preliminary results which demonstrate the evolution of gas-phase ethylene from the formaldehyde reaction, to the best of our knowledge the first example of carbon-carbon bond formation

on clean Mo(110). This reaction is proposed to proceed via an ethylene dialkoxide intermediate, analogous to that formed during reaction of ethylene glycol on Mo(110). Other reactions include hydrogenation of CH@sub 2@O to form a methoxy intermediate which subsequently undergoes C-O bond scission to evolve gas-phase methyl radicals at ~600 K.

11:20am SS2-MoM10 Adsorption of Propylene Oxide on Pt(111) Surfaces and its Reactions with Gaseous and Adsorbed H Atoms, A. Dinger, C. Lutterloh, J. Biener, J. Küppers, Universität Bayreuth, Germany

The adsorption of propylene oxide (PO) on Pt(111) surfaces and its reactions with gaseous and adsorbed H atoms, respectively, was studied with TDS and HREELS methods. Monolayer PO desorbs near 180 K, while multilayer PO desorbs at 130 K. Approximately 50% of the monolayer PO molecules dissociate leading to the desorption of CO and H@sub 2@. The decomposition of PO is initiated by a cleavage of the C-O-C ring. Gas phase H atoms react with PO monolayers on Pt(111) to n-propanol, i-propanol, and acetone with the latter as a minor product and about equal amounts of the alcohols. On the other hand, the reaction between PO and coadsorbed hydrogen leads to the selective formation of acetone.

11:40am SS2-MoM11 Interaction of Atomic Hydrogen and Deuterium with the Ir(111)-p(1x1)-H, Ir(111)-p(1x1)-D, and Ir(111)-p(1x2)-O Surfaces, C.J. Hagedorn, M.J. Weiss, W.H. Weinberg, University of California, Santa Barbara

The interaction of gas phase atomic hydrogen and deuterium with chemically modified Ir(111)-p(1x1)-D, Ir(111)-p(1x1)-H, and Ir(111)-p(1x2)-O surfaces at cryogenic temperatures has been studied using thermal desorption mass spectrometry and high-resolution electron energy loss spectroscopy. Although the Ir(111)-p(1x2)-O surface at a temperature of 90 K is passivated with respect to exposure to gas phase H@sub 2@ and D@sub 2@, the interaction of gas phase atomic H and D with this surface at 90 K results in the subsequent desorption of water in thermal desorption spectra. These results suggest that the dissociative chemisorption of molecular hydrogen on Ir(111) is precluded by the presence of the (1x2)-O oxygen overlayer, whereas energetically "hot" gas phase atomic hydrogen reacts readily with this oxygen modified surface. Moreover, a strong isotope effect has been observed in the interaction of gas phase atomic H and D with deuterium and hydrogen modified surfaces. The abstraction cross section for atomic D interacting with the Ir(111)-p(1x1)-H surface to form HD is approximately a factor of two greater than that for atomic H interacting with the Ir(111)-p(1x1)-D surface. This difference between the abstraction cross sections can be explained qualitatively by considering the differences associated with the expected zero point energy of the transition state for the abstraction reaction and the differences associated with the zero point energy between H and D adatoms.

Surface Science Division Room 612 - Session SS3-MoM

Water-Surface Interactions

Moderator: E.M. Stuve, University of Washington

8:20am SS3-MoM1 Surface Chemistry of Organic Aerosols, G.B. Ellison, University of Colorado, Boulder INVITED

Organic aerosols are believed to be important cloud condensation nuclei in the earth's atmosphere. We suggest a chemical model for the composition, structure, and atmospheric processing of these organic aerosols. This model is stimulated by recent field measurements showing that organic compounds are a significant component of atmospheric aerosols. The proposed model organic aerosol is an "inverted micelle" consisting of an aqueous core that is encapsulated in an inert, hydrophobic organic monolayer. We propose a chemical mechanism by which the organic surface layer will be processed by reactions with atmospheric radicals. Surface reactions of the hydrocarbon film with atmospheric species such as OH, Cl, O3, and NO3 will transform the organic film. The net result is the transformation of an inert hydrophobic film to a reactive hydrophilic layer.

9:00am SS3-MoM3 Water Adsorption Structures on Flat and Stepped Ru(0001)-Surfaces, W. Hoffmann, C. Benndorf, University of Hamburg, Germany

We investigated the structural influence of vicinal Ru(0001) surfaces to water adsorption and desorption kinetics. Flat Ru(0001) surfaces show a unique behavior in the difference of H@sub2@O and D@sub2@O desorption spectra - referred to as the isotope effect. In accordance with other authors we observed on Ru(0001) three desorption peaks for

H@sub2@O denoted as C, A@sub2@ and A@sub1@ (C, 155 K / A@sub2@, 190 K / A@sub1@, 212 K). The isotope effect for D@sub2@O on Ru(0001) is characterized by a missing A@sub1@ peak. Isothermal desorption measurements were performed using @Delta@@phi@, in order to determine the different kinetics for H@sub2@O and D@sub2@O. Neither for D@sub2@O nor for H@sub2@O the desorption of the A@sub2@-state can be described by 1st order kinetics. Especially for the A@sub2@ peak of H@sub2@O we observed an initial range of 1st order kinetics followed by a strong deviation, which could be described by Avrami kinetics or lateral interactions.@footnote 1@ Stepped Ru surfaces were used for comparison and @Delta@@phi@ measurements were complemented by ARUPS measurements of H@sub2@O and D@sub2@O adsorption. Further we performed LEED structure calculations of the clean stepped hcp(0001)-surfaces using a spherical wave model approach and single scattering theory.@footnote 2@ In experiments the vicinal Ru(0001) surfaces show a triplet spot splitting due to the alternating step width with different atomic arrangements at the steps, in agreement with our calculations. Regarding the adsorption phenomena on low indexed stepped surfaces, the diffraction pattern do not show ordered structures of water molecules. Higher indexed surfaces allow to built ordered water super structures as observed for flat Ru(0001) surfaces.@footnote 3@ @FootnoteText@ @footnote 1@ W. Hoffmann, C. Benndorf, Surface Sci. 377-379 (1997) 681-686. @footnote 2@ W.P. Ellis and R.L. Schwoebel, Surface Sci. 11 (1968) 82-98. @footnote 3@ D. L. Doering and T. E. Madey, Surface Sci. 123 (1982) 305-337.

9:20am SS3-MoM4 Kinetics of Water Uptake on a Hydrophobic Surface Studied by UHV-TPD, *T.R. Linderoth*, *P. Löfgren*, Chalmers University of Technology, Sweden; *V.P. Zhdanov*, Boreskov Institute of Catalysis, Russia; *B. Kasemo*, Chalmers University of Technology, Sweden

Thin water (ice) films are currently receiving much attention. The motivations are both intrinsic scientific interest and their importance in areas such as astrophysics, biology and atmospheric chemistry. As a model of water adsorption on a very hydrophobic surface, we have investigated the uptake of water onto an octane (C@sub 8@H@sub 18@) covered Pt(111) surface and compared the results with previous studies on hydrophilic clean Pt(111). Our adsorption experiments were executed at substrate temperatures (T) in the range 100-120 K. A water-doser provided precise control of dosage flux (F) and exposure time (t). The adsorbed amount of water (@theta@) was determined by thermal desorption spectroscopy (TDS). In contrast to the case of hydrophilic metal substrates, we find that the apparent sticking (condensation) coefficient is well below unity for adsorption on the octane film (typically <<1 ML is adsorbed for exposures up to 10 ML). Furthermore, the adsorbed amount of water at a given exposure is strongly dependent on dosage flux and substrate temperature, being larger for higher F or lower T. Qualitatively, these findings can be understood if the binding of a single water molecule to the octane surface is so weak that adsorbed, diffusing water molecules can redesorb before they manage to nucleate with other adsorbed molecules or incorporate into already stable water islands. A quantitative treatment of the corresponding kinetic equations yields: @theta@(t)~F@sup 3@exp[(3E@sub d@-2E@sub a@)/k@sub B@T]t@sup 2@ (E@sub d@/E@sub a@ are activation energies for desorption/surface diffusion of water molecules). The experimental data agree well with the predicted time and temperature dependences: We find that @theta@~t@sup 2.3@ and from the Ahrrenius analysis 3E@sub d@-2E@sub a@=0.20 eV is obtained. The observed flux-dependence of @theta@~F@sup 0.6@ is not in agreement with the model, however. Further investigations of the system are currently being undertaken.

9:40am SS3-MoM5 Soft-Landed Ion Study of a Liquid-Liquid-Solid Interface, J.P. Cowin, K. Wu, M.J. Iedema, Pacific Northwest National Laboratory

Ion beams with energies of about 1 eV allow one to gently land, without damage, molecular ions important to aqueous/organic liquid chemistry. We have used these soft-landed ions to probe the transfer of hydronium ions from non-aqueous to organic media. Molecular beam epitaxy is used to create aqueous/organic interfaces with monolayer precision, and the motion of the ions is detected with a non-contact work function probe, in UHV environments. Amorphous vapor- deposited films become true liquids above their glass temperatures (135 for water, 85 K for methyl cyclohexane (MCH)). We find hydrating the hydronium strongly effects its ability to enter the organic phase. We also see strong non-linear electric field effects. When a "dry" 30 monolayer MCH film is ramped at 0.2 K/s, we find that the ions traverse a film at about 97 K, under their self-induced field on order of 6 volts/(10.2 nm). We then added water with the ions on top of the MCH

film. The temperature for ion transport shifts linearly with added water to 100 K at 0.4 monolayer, and is constant at @DELTA@T of 3K from 0.4 to 1.0 monolayer. This is consistent with an increase of ion size due a large hydration "sphere" (or pancake) being dragged through the organic film. Above 1 monolayer of added water the temperature shifts as much as 15 K, and is consistent with the expected @DELTA@G difference for transferring a solvated ions from this nano-aqueous environment to the organic phase. At electric fields from 0.01 to 0.1 V/angstrom, we see considerable deviations from simple viscosity-based ion transport models.

10:00am SS3-MoM6 The Molecular Volcano: Release of Trapped Volatile Gases by Amorphous Solid Water, *K.P. Stevenson*, *Z. Dohnálek*, *G.A. Kimmel*, *R.S. Smith*, *B.D. Kay*, Pacific Northwest National Laboratory

The trapping and release of volatile gases by amorphous solid water (ASW) has important astrophysical implications, predominately for the adsorption of gases on icy planetary surfaces and the outgassing behavior of cometary bodies. A previous study involving ASW and CCl@sub 4@ introduced the concept of the molecular volcano,@footnote 1@ wherein the abrupt release of trapped CCI@sub 4@ was driven by the amorphous to crystalline ice phase transition. The mechanism for the release of gas was postulated to be the formation of connected pathways in the ASW film during the nucleation and growth of the crystalline ice. We have investigated the mechanisms for trapping and release of volatile gases by ASW using temperature programmed desorption (TPD) from N@sub 2@, O@sub 2@, and Ar adsorbed underneath thin ASW films. The TPD of physisorbed N@sub 2@ monolayers from the ASW surfaces was used to probe the crystalline ice surface fractions and surface area changes during crystallization of the ASW films. The isothermal desorption and TPD of N@sub 2@, O@sub 2@, and Ar deposited beneath thin ASW overlayers results in the desorption of the trapped gas at the onset of crystallization in the ASW. During crystallization, the trapped gas escapes in concert with a cracking of the ASW film as observed by a significant change in film surface area. For thicker ASW overlayers (~600 BL), the gas release is delayed until after the ASW film has crystallized. A comparison with the isothermal desorption of pure ASW films, reveals that the amorphous to crystalline ice phase transition kinetics are independent of the trapped gas in the ASW films. @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, PRL, 79, (1997) 909.

10:20am SS3-MoM7 The Effect of Water on the Nitric Acid Pressure Dependence of the Reaction Between Gas Phase Nitric Acid and NaCl Surfaces.@footnote 1@, J.C. Hemminger, S. Ghosal, University of California, Irvine

The reactions of oxides of nitrogen with sea salt particles, that liberate halogenated compounds into the gas phase, may play an important role in the chemistry of the marine troposphere. Recent laboratory measurements have shown that the reactive sticking coefficient of HNO@sub 3@ on NaCl particles exhibits a significant dependence on the HNO@sub 3@ pressure. when the measurements are carried out under conditions of steady state reaction. This pressure dependence has been rationalized in terms of a two-site Langmuir model for dissociative adsorption of the HNO@sub 3@. However, our XPS experiments show that the dissociative adsorption of HNO@sub 3@(g) on NaCl to form NaNO@sub 3@(s) and HCl(g) follows single-site Langmuir adsorption behavior. We also used XPS to show that the amount of "strongly adsorbed water" on the surfaces of NaCl particles strongly depends on the particle size. Particles of 1-10 micron diameter show large quantities of adsorbed water that remain on the sample up to temperatures of 200 degrees C. Particles in the size range of 500 micron diameter have less, but still easily measurable, amounts of strongly adsorbed water. We present a model for the HNO@sub 3@ pressure dependence of the reactive sticking coefficient of HNO@sub 3@ on NaCl under steady state reaction conditions. The origin of the pressure dependence in the model is the competition between site blocking on the surface by the build-up of the NaNO@sub 3@ reaction product and the water induced 3-d recrystallization of the NaNO@sub 3@ that frees up reactive sites for further reaction. @FootnoteText@ @footnote 1@ This work was supported by the National Science Foundation Grant ATM-9707285.

10:40am SS3-MoM8 Giant Cl@super-@ and F@super-@ Enhancements in Electron-Stimulated Desorption of CF@sub2@Cl@sub2@ Coadsorbed with Water or Ammonia Ices: Implications for Atmospheric Ozone Depletion, *T.E. Madey*, *Q.-B. Lu*, Rutgers, The State University of New Jersey

Dissociative electron attachment to form Cl@super-@ and F@super-@ can be an important process for the destruction of ozone-depleting chlorofluorocarbons (CFCs) in the upper atmosphere, because of their extremely large electron attachment cross sections. We have observed giant Cl@super-@ and F@super-@ enhancements by several orders of magnitude in electron-stimulated desorption of a fractional monolayer of CF@sub2@Cl@sub2@ coadsorbed with water ice and ammonia ice on a Ru(0001) surface at ~25 K, respectively. The yields of negative ions are measured by an electron-stimulated-desorption ion angular distribution (ESDIAD) detector with time-of-flight capability. The enhancement of Cl@super-@ is much stronger than that of F@super-@, and the enhancements for both ion species by NH@sub3@ coadsorbate are stronger than by H@sub2@O. Moreover, all magnitudes of enhancement increase strongly with decreasing CF@sub2@Cl@sub2@ concentration; for 0.3 ML CF@sub2@Cl@sub2@, the largest Cl@super-@ enhancements are ~3x10@super4@ for NH@sub3@ and ~10@super2@ for H@sub2@O. In contrast, the enhancements are much smaller for CF@sub2@Cl@sub2@ coadsorption with rare-gas atoms or nonpolar molecules. Whereas the primary electron beam energy is 250 eV, the giant negative-ion enhancements are attributed to dissociation of CF@sub2@Cl@sub2@ by capture of low-energy secondary electrons self-trapped (solvated) in polar water or ammonia clusters. This process may be an important sink for chlorofluorocarbons (CFCs) in the atmosphere, where low-energy electrons created by cosmic ray ionization can be trapped in clouds. Cl@super-@ ions produced may be directly or indirectly converted to Cl atoms, which then destroy ozone.

11:00am SS3-MoM9 Cation Trapping Effects on HCl Diffusion in Ice Measured Using a New Laser Resonant Desorption Depth-Profiling Technique, F.E. Livingston, S.M. George, University of Colorado, Boulder

HCl diffusion in ice is important for an understanding of heterogeneous atmospheric chemistry on ice particles and may influence the interpretation of ice core data. The diffusion of alkali metals in ice is also relevant for the evaluation of ice core samples and alkali cations may interact strongly with coadsorbates in ice. Novel laser resonant desorption depth-profiling techniques were used to measure HCl and Na diffusion in ice. The diffusion was monitored using a Q-switched Er:YAG laser to depthprofile the ice multilayer. The Er:YAG laser emits infrared light at 2.94 microns. This light can be resonantly absorbed by the O-H stretching vibration of H@sub2@O and thermalized to induce resonant desorption. HCl diffusion was monitored in ice multilayers containing a thin HCl interlayer. The HCl spatial coverages at various diffusion times and temperatures were used to extract the diffusion coefficients. The measured HCl diffusion coefficients ranged from D=(3.8±2.8)x10@super-13@ cm@super2@/s at T=169 K to D=(2.0±1.5)x10@super-10@ cm@super2@/s at T=197 K. Arrhenius analysis yielded diffusion kinetic parameters kcal/mol of $E = 14.6 \pm 1.6$ and D@subo@=(2.9±2.0)x10@super6@ cm@super2@/s. Na was also observed to diffuse in the ice multilayers. In addition, coadsorbed Na decreased the HCl diffusion rate by a factor of ~5-85 for Na/Cl ratios ranging from 0.05-0.5. The Na-induced decrease in the HCl diffusion rate may be attributed to cation trapping manifested by NaCl formation in the ice.

11:20am SS3-MoM10 The Effect of Porosity on the Crystallization of Amorphous Solid Water, Z. Dohnálek, G.A. Kimmel, K.P. Stevenson, R.S. Smith, B.D. Kay, Pacific Northwest National Laboratory

The annealing and crystallization of amorphous solid water (ASW) is important to understand the properties of ice in extraterrestrial environments. Here we show a dramatic effect of the initial porosity of the ASW films on their crystallization kinetics. The porosity of the films was varied by changing the incident angle of the H@sub 2@O molecules during the deposition.@footnote 1@ The crystallization kinetics were followed using the temperature programmed desorption (TPD) of N@sub 2@(g) monolayers from the ASW film surface. Despite the fact that the films densify upon annealing, before any crystallization takes place, a strong dependence of the crystallization kinetics on the initial porosity exists. The crystallization of dense ASW films (grown at zero angle of incidence) proceeds via classical bulk nucleation and 3-dimensional growth. In the case of porous films (grown at high angles of incidence) the crystallization half time is reduced by more than an order of magnitude and the apparent activation energy decreases to a value that corresponds to the growth of

the crystalline phase in the absence of nucleation. We propose that the lowering of the activation energy is due to seeding of the porous films that is likely to occur during the densification. This conclusion is supported by detailed Monte Carlo simulations of the effect of seeding on the crystallization kinetics. @FootnoteText@ * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830. @footnote 1@ K. P. Stevenson, G. A. Kimmel, Z. Dohnálek, R. S. Smith, and B. D. Kay, Science 283 (1999) 1505.

Surface Science Division Room 606 - Session SS1+EM-MoA

Metals on Oxides

Moderator: U. Diebold, Tulane University

2:00pm SS1+EM-MoA1 Nucleation and Growth of Copper Islands on TiO@sub2@(110): Evidence for Self-limited Island Sizes, D.A. Chen, University of South Carolina; M.C. Bartelt, R.Q. Hwang, K.F. McCarty, Sandia National Laboratories

Metal-oxide interfaces play an important role in a variety of technological applications, including those involving the design of electronic devices, sensors and heterogeneous catalysts. In order to develop a fundamental understanding of these metal-oxide interfaces, we have studied the formation of Cu islands on TiO@sub2@(110)-(1x1) in ultrahigh vacuum using scanning tunneling microscopy for Cu coverages up to 1.25 ML. The formation of 3D islands at all the coverages reflects the relatively high mobility of Cu atoms on TiO@sub2@ at room temperature and the weak interactions between Cu and TiO@sub2@. Surprisingly, the island diameter remains almost constant for all coverages. Furthermore, the Cu islands exhibit self-limiting growth at low coverages (0.5 ML), the average island size scales with coverage, but this increase in island size is primarily due to an increase in height not diameter. Although larger islands can be formed by annealing, the average size of the islands is independent of coverage for any given annealing temperature. We propose two general schemes that could lead to the observed self-limiting growth. The first is that the attachment rate of adatoms drops as the island size increases. The second is that the rate at which adatoms reach existing islands drops as the islands grow. We will discuss physical scenarios under which each of these effects may be dominant. This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported in part by the USDOE-OBES-Division of Materials Sciences.

2:20pm SS1+EM-MoA2 Influence of Surface Reactions on Morphology: Ag Nanoclusters on TiO@sub 2@(110), X. Lai, T.P. St. Clair, D.W. Goodman, Texas A&M University

The effects of in situ O@sub 2@ exposure on TiO@sub 2@(110)-supported Ag nanoclusters were investigated using x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). An oxygen-induced cluster ripening was observed by STM after exposing Ag/TiO@sub 2@(110) to 10.00 Torr O@sub 2@ in an elevated-pressure reactor. A bimodal size distribution of Ag clusters was evident after a 10 minute O@sub 2@ exposure at room temperature. Time-dependent studies of the ripening process indicated that the majority of the ripening occurred within the first hour of exposure. The cluster density also increased 5-15%, indicating that redispersion simultaneously occurred with ripening. For comparison, a reduced, roughened TiO@sub 2@(110) and a fully oxidized TiO@sub 2@(110) were prepared and used as Ag supports. Propylene exposure was also studied to further investigate adsorbate-induced morphological changes. Issues relevant to the stability of Ag catalysts for general oxidation reactions were addressed.

2:40pm SS1+EM-MoA3 Kinetics and Dynamics of Substrate and Metal Atoms on TiO@sub2@, G. Thornton, I. Brookes, H. Raza, C.L. Pang, S. Haycock, Manchester University, UK INVITED

TiO@sub2@ substrates have been used as platforms to test ideas about oxide surface reconstruction and metal growth on oxides. This work is motivated by the importance of such interfaces in a number of applications which include catalysis and gas-sensing. As part of this work we have recently studied two aspects of TiO@sub2@ surface science associated with temperature and time dependent structural changes using STM and non-contact AFM. The first involves the study of the 1x1 to 1x3 phase transition of TiO@sub2@(100). In addition to the 1x1 and the high temperature equilibrium 1x3 microfacet termination previously observed, intermediate 1x3 structures are imaged. The relationship between the 1x1 termination and the 1x3 microfacet phase suggests that the latter reconstruction is formed by removing material rather than growing from a lower lying terrace. Intermediate structures point to a mechanism of the phase transition which involves discrete bond breaking steps. Turning to Cu growth on TiO@sub2@(110), at room temperature and at <0.1 ML most of the metal atoms are initially mobile, with some 2D island formation. The cluster size of about 6 Å diameter suggests that they consist of 7 atoms arranged in a centred hexagon. Such an arrangement fits between the bridging O rows. 3D clusters are formed at higher coverage consistent with Volmer-Weber growth. At lower temperatures 1D metastable strings of Cu atoms are formed in the [001] direction, which collapse to 2D islands and subsequently 3D clusters at higher coverage.

3:20pm SS1+EM-MoA5 Nucleation and Growth of Pt Nanoclusters on TiO@sub 2@ Rutile and Anstase Surfaces, Y. Liang, Pacific Northwest National Laboratory; A.W. Grant, University of Washington; D.R. Baer, S. Gan, Pacific Northwest National Laboratory

Understanding the interaction of ultra-thin metal overlayers with oxide surfaces impacts a wide range of technological applications. One of those is the oxide-supported metal catalysts where unusual surface chemisorption and activity have been observed. In this presentation, we report an investigation of nucleation and growth of Pt on rutile and anatase surfaces using scanning tunneling microscopy, x-ray photoelectron spectroscopy, and low energy electron diffraction. Results show that vapor deposition of 0.1 ML of Pt on a rutile TiO@sub 2@(110) surface at ambient temperature leads to the formation of randomly distributed three-dimensional Pt nanoclusters on the 1x1 surface. However, this random distribution is strongly perturbed by the presence of surface line defects produced by extended sputtering and annealing cycles. As the density of the line defect increases, majority of Pt nanoclusters are preferentially attached at the ends of line defects instead of randomly distributed on the rutile surfaces. This result suggests that the line defects on TiO@sub 2@(110) surfaces have stronger interaction with Pt and thus serve as nucleation sites for Pt growth. Based on the change of distribution of Pt clusters as a function of line defect density, the diffusion length of Pt on rutile surfaces is obtained. In addition to rutile, we also investigate the nucleation and growth of Pt on anatase surface. We have successfully grown anatase single crystal thin films on SrTiO@sub 3@ substrates using oxygen plasma assisted molecular beam epitaxy. Investigation of nucleation and growth of Pt on anatase surface is currently in progress. The results will be presented at the meeting and compared with those obtained on the rutile TiO@sub 2@ surfaces.

3:40pm SS1+EM-MoA6 Role of Surface Vacancies and Water Products in Metal Nucleation: Pt/MgO(100), A. Bogicevic, D.R. Jennison, Sandia National Laboratories

Metal atom adsorption on oxide surfaces, resulting in clusters or thin films, involves a variety of structure-determining chemical interactions. While surface steps have long been known to promote nucleation, it has been speculated in several experimental studies that the most common defect in well prepared surfaces, isolated surface oxygen vacancies, may act as nucleation sites. However, this has not been substantiated via experiment or theory. Here we examine this question and, for completeness, how water dissociation products affect nucleation, since there have been several reports that these are common low-density contaminants on prepared oxide surfaces. Our density-functional calculations reveal that isolated F@sub s@ and V@sub s@ surface vacancies on MgO(100) ionize single Pt atoms, roughly tripling their adsorption energy. This trapping inhibits Pt atoms from binding to other Pt atoms, resulting in a negative addimer binding energy. Hence, isolated surface vacancies demote nucleation, contrary to popular belief. A defect that does promote nucleation is the F@sub s@V@sub s@ divacancy, which increases the addimer binding energy by 20%. Amongst water and its dissociation products, adsorbed hydroxyl ions are found to have a similar but even stronger effect. We discuss the implications of these results for the temperature dependence of nucleation and the generality of these results for other metals and oxides.@footnote 1@ @FootnoteText@ @footnote 1@ Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE under Contract DE-AC04-94AL85000.

4:00pm SS1+EM-MoA7 Metal Particles on Single Crystal Oxides as Model Catalysts, J.H. Larsen, J.T. Ranney, A.W. Grant, D.E. Starr, J.E. Musgrove, C.T. Campbell, University of Washington

The growth morphology and reactivity of model oxide-supported metal catalysts are intimately connected. On some well-defined oxides, vapor-deposited metals form two-dimensional islands, typically up to a critical coverage below 1 monolayer (ML). The local electronic environment of the supported metal particles is modified as compared to the surface of the bulk metal, and so changes in reactivity are expected. Above the critical coverage, three-dimensional growth sets in and it becomes possible to measure reactivities as a function of island thickness. Several metal on metal oxide systems were studied. The surface growth mode was investigated using low energy ion scattering (LEIS) and x-ray photoelectron spectroscopy (XPS). In order to probe the nature of the reaction sites on the surface, the decomposition of hydrocarbons was also studied with

temperature programmed desorption (TPD). From these experiments, the dependence of the metal reactivity on the lateral dimensions of the twodimensional metal islands and the thickness of three-dimensional metal clusters was determined. It was found that Pt particles on ZnO(0001)-Zn exhibit reactivity towards methanol decomposition which is characteristic of low-index Pt facets, even below the critical coverage of ~ 0.6 ML where only two-dimensional islands are present. The adsorption energy of some metal on metal oxide systems was furthermore measured as a function of coverage using single crystal adsorption calorimetry. The adsorption energy is a fundamental quantity that gives important insight into the energetic origins of the growth and reactivity of metal particles supported on metal oxides.

4:20pm SS1+EM-MoA8 High-Pressure STM Studies of Pt Nano-clusters on Al@sub 2@O@sub 3@/NiAl(110), L. Österlund, M.O. Pedersen, P. Thostrup, K.H. Hansen, E. Laegsgaard, I. Stensgaard, F. Besenbacher, University of Aarhus, Denmark

A novel system in which an STM is incorporated into a high pressure cell has been constructed. The system permits in-situ studies of surfaces with atomic resolution at pressures ranging from UHV to one atmosphere. In the present paper, we have investigated the morphology and structure of well-ordered Pt nano-clusters deposited on thin layers of aluminum oxide created by oxidation of NiAl(110). >From the shape, i.e. the height and width, and from atomic resolved images of the top facets of the clusters, we can quantitatively determine the adhesion energy of the metal cluster to the oxide, using calculated surface free energies for the cluster facets. We have investigated the change in the morphology of the Pt nano-clusters exposed to up to 1 bar of hydrogen and oxygen.

4:40pm SS1+EM-MoA9 Cu Interaction with Al@sub 2@O@sub 3@ Substrates: Effects of Defects and Coverage, C. Niu, K. Shepherd, J.A. Kelber, University of North Texas

We report UHV surface science studies of the wetting and nucleation behavior of Cu on sapphire(0001). Such fundamental wetting and nucleation interactions are of increasing importance in microelectronics, joining and brazing, as well as in catalysis. This study focuses on the effects of defects and kinetic factors for well-defined systems that are critical to an understanding of behavior for "real world" systems. On clean sapphire, Cu is initially present as Cu(I) to a coverage of 0.35 ML [ML = monolayer], after which a second, metallic Cu layer begins to grow. This behavior is in agreement with recent theoretical calculations by A. Bogicevic and D. R. Jennison[Phys. Rev. B (in press)]. The behavior of Cu on sapphire at elevated temperatures is coverage dependent. For @theta@@sub Cu@ < 0.35 ML, Cu(I) remains stable on the surface for temperatures up to \sim 1000K. However, in the presence of Cu(0), e.g. @theta@@sub Cu@ = 0.75 ML, Cu(I) reacts to form additional Cu(0) at about 500K. Pre-sputtering of the sapphire surface prior to Cu deposition inhibits Cu(I) formation and enhances Cu(0) formation at low coverage, correlating with the sputterinduced dehydroxylation of the sapphire surface and creation of oxygen vacancies. These data indicate that variations of a small number of surface defect densities can explain the large number of contradictory results obtained for the Cu/alumina systems. The significance of these findings to "real world" applications (e.g. Cu on oxidized Ta and other microelectronics diffusion barriers) will be discussed.

5:00pm SS1+EM-MoA10 Nucleation and Growth of Tungsten on SiO@sub 2@ During Atomic Layer Deposition Using Sequential Surface Reactions, *J.W. Elam, C.E. Nelson, R.K. Grubbs, S.M. George,* University of Colorado, Boulder

The atomic layer deposition of tungsten (W) can be achieved by separating the binary reaction WF@sub 6@ + Si@sub 2@H@sub 6@ --> W + 2SiHF@sub 3@+ 2H@sub 2@ into two half-reactions. Successive application of the WF@sub 6@ and Si@sub 2@H@sub 6@ half-reactions in an ABAB... sequence produces W atomic layer controlled growth. The nucleation and growth of W on SiO@sub 2@ was examined during alternating exposures to Si@sub 2@H@sub 6@ and WF@sub 6@. Auger electron spectroscopy studies at 573 K revealed an initial nucleation phase that was followed by a layer-by-layer W growth regime. Nucleation occurred during the first 10 sequential Si@sub 2@H@sub 6@ and WF@sub 6@ surface reactions. Layer-by-layer W deposition then proceeded at a growth rate of 2.5 Å per AB reaction cycle. This W growth rate is consistent with one W monolayer per AB reaction cycle. The Auger data was fit well assuming Frank-van der Merwe layer-by-layer growth. These studies reveal that the sequential surface reactions can facilitate metal wetting of oxide surfaces and conformal layer-by-layer metal growth. Additional Auger experiments yielded the adsorption kinetics for both Si@sub 2@H@sub

6@ and WF@sub 6@ during W atomic layer deposition. The WF@sub 6@ half-reaction had an activation energy E=7 kcal/mol and required WF@sub 6@ exposures of 30 L for the WF@sub 6@ half-reaction to reach completion. The Si@sub 2@H@sub 6@ had virtually no temperature dependence and the Si@sub 2@H@sub 6@ half-reaction saturated following 200 L Si@sub 2@H@sub 6@ exposures at 573 K.

Surface Science Division Room 607 - Session SS2-MoA

Reactions on Metals

Moderator: F. Zaera, University of California, Riverside

2:00pm SS2-MoA1 Surface Chemistry on Stepped Pt Surfaces - What Happens at the Steps?, J.T. Yates, Jr., C.E. Tripa, T.S. Zubkov, University of Pittsburgh; M. Mavrikakis, J.K. Norskov, Technical University of Denmark, Denmark INVITED

H.S. Taylor postulated in 1925 that step sites on metallic surfaces are active sites for catalytic reactions. This postulate has become one focus of surface science research since the 1970's. We have studied both photochemical processes and thermally driven processes which occur specifically at metallic step sites. The photodecomposition of adsorbed O@sub 2@ on Pt(335) and Pt(779) surfaces has been used to study the reaction of photogenerated O atoms with CO molecules on both step and terrace sites producing CO@sub 2@. A surface-aligned photochemical process is observed. In addition, the chemisorption of N@sub 2@ on the step sites of these two crystals has been investigated by infrared spectroscopy and by kinetic methods. Linear arrays of weakly-based N@sub 2@ molecules have been observed and their properties will be described. N@sub 2@ does not adsorb on the (111) terrace sites separating the steps.

2:40pm SS2-MoA3 Investigations of the Role of Edges on the Reaction Kinetics on Nanometer-sized Catalyst Particles using Monte Carlo Simulations, *H. Persson*, *P. Thormahlen*, Chalmers University, Sweden; *V.P. Zhdanov*, Boreskov Institute of Catalysis, Russia, Sweden; *B. Kasemo*, Chalmers University, Sweden

From basic research on single crystals of catalytic materials, it is today well established that the rate of a catalytic reaction may vary considerably from one crystal face to another@footnote 1@ and that defect sites such as steps, kinks, surface vacancies, adatoms etc, may have different catalytic activities than the perfect terrace sites.@footnote 2@ In addition, there are (for supported catalysts) additional types of sites located at the particle-support boundary. It is therefore not surprising that a wide variety of behaviours of catalytic activity versus particle size have been observed,@footnote 3@ sometimes differing considerably from single crystals. The collective set of such differences and the challenge to understand and explain them is referred to as the "structure gap" in catalysis. This presentation will be focussed on Monte Carlo simulations of the kinetics of supported nm catalyst particles, being large enough to have attained bulk-electronic properties.@footnote 4,5,6,7@ The basic underlying mechanisms for the phenomena we will analyse are: (i) the different catalytic activities on different facets of a small supported crystalline particle become coupled in a strongly non-linear fashion due to diffusion occuring over facet boundaries, (ii) different kinetic rate constants at the facet boundaries of a supported particle compared to those for the perfect facets give rise to new kinetics, (iii) and spillover by diffusion of reactants, between the particle and its support, also create new kinetics. The main focus will be on how edges may affect the reaction kinetics. @FootnoteText@ @footnote 1@ R. Imbihl and G. Ertl, Chem. Rev. 95 (1995) 697. @footnote 2@ J.T. Yates, J. Vac. Sci. Technol. A 13 (1995) 1359. @footnote 3@ P.L.J. Gunter et al Catal. Rev. Sci. Eng. 39 (1997)77 @footnote 4@ V.P. Zhdanov, B. Kasemo, Surf. Sci. 405 (1998) 27. @footnote 5@ V.P. Zhdanov, B. Kasemo, Phys. Rev. Lett. 81 (1998) 2482. @footnote 6@ H. Persson et al., J. Vac. Sci. Techn. A (1999), in press. @footnote 7@ H. Persson et al, Catal. Today (1999), in press.

3:00pm SS2-MoA4 Dissociation and Desorption of NO and N@sub 2@ on Rh(100) and Rh(111), Effect of Surface Structure on Elementary Reaction Steps, *M.J.P. Hopstaken*, *J.W. Niemantsverdriet*, Eindhoven University of Technology, The Netherlands

Removal of NO@sub x@ is an important issue in automotive exhaust catalysis. On the molecular level, dissociation of NO on rhodium is the crucial step in the reduction of NO by CO, H@sub 2@ or hydrocarbons. Here we use TPD/SIMS to study reactions of NO on Rh(100) and compare with similar results on Rh(111).@footnote 1@ On both surfaces the

reaction rates of the different elementary steps depend highly on coverage. At low coverage, dissociation of NO is completed around 250 K and 340 K for the Rh(100) and the Rh(111) surface, respectively. When the surface is saturated with NO, dissociation only starts when NO desorbs i.e. when empty sites become available. However, inhibition of NO dissociation at higher coverages cannot be explained by site blocking alone. Monte Carlo simulations strongly indicate that the activation energy for dissociation of NO on Rh(111) increases when other adsorbates such as N, O, and NO are present. At low coverages we find an activation energy of 45 kJ/mole for dissociation of NO on Rh(100), which is 20 kJ/mole lower than on Rh(111). Desorption of NO from both surfaces proceeds at similar rates. However, formation of N@sub 2@ is slower on Rh(100). Apparently, bond breaking of NO is faster and formation of a N-N bond is slower on the more open Rh(100) surface. This can be explained on the basis of surface chemical reactivity theories.@footnote 2@ Unexpectedly, the oxidation of CO to CO@sub 2@ proceeds much faster on Rh(100) than on Rh(111). This, together with the higher rate of dissociation and lower rate of N@sub 2@ formation, has important consequences for the kinetics of the CO + NO reaction on the different rhodium surfaces. @FootnoteText@ @footnote 1@ H.J. Borg, J.P.C.-J.M. Reijerse, R.A. van Santen and J.W. Niemantsverdriet, J. Phys. Chem. 101 (1994) 10052. @footnote 2@ R.A. van Santen, J.W. Niemantsverdriet, Chemical Kinetics and Catalysis, Plenum Press, New York, 1995.

3:20pm SS2-MoA5 Interactions between CO and NO on Rh Loaded Ceria Films, D.R. Mullins, Lj. Kundakovic, S.H. Overbury, Oak Ridge National Laboratory

CO and NO were adsorbed sequentially on model catalysts composed of submonolayer amounts of Rh deposited on highly crystalline thin films of reduced cerium oxide. The chemical state of the adsorbed species was monitored by soft x-ray photoelectron spectroscopy (SXPS). It has previously been shown that a reduced ceria substrate promotes the dissociation of CO and NO on supported Rh, with essentially full dissociation occurring by 400 K or 500 K for adsorbed NO and CO, respectively. At a constant temperature of 200 K, a saturation coverage of CO blocks subsequent adsorption of NO, and vice versa. However, the reaction of CO or NO with the dissociation products of the other molecule leads to new states in the C 1s and N 1s SXPS spectra that do not occur if either gas is adsorbed separately. If NO is dosed first and then heated to decompose it into atomic N and O, subsequent CO exposure at 200 K leads to new high binding energy states in the C1s and O 1s spectra which appear after annealing to 400 K. The binding energies of these states are consistent with formation of CO@sub 2@ on Rh. Additional features occur in the C1s and N 1s spectra indicative of the formation of other forms of N and C, as yet unassigned. If CO is dosed and dissociated first, then CO@sub 2@ is not formed upon subsequent exposure to NO. However, the features associated with the unassigned, adsorbed species do appear upon annealing. The only products observed in thermal desorption are CO and N@sub 2@ and, in particular, no CO@sub 2@ is desorbed. Additional experiments are in progress to identify the unassigned species and to determine the mechanisms of their formation. * 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-AC05-960R22464.

3:40pm SS2-MoA6 Non-linear Behaviour in the NO-H@sub 2@ Reaction over Pt Group Metals: A Comparison, *C.A. de Wolf*, Leiden University, The Netherlands; *M.Yu. Smirnov*, Boreskov Institute of Catalysis, Russia; *M.O. Hattink*, *B.E. Nieuwenhuys*, Leiden University, The Netherlands

Oscillations in the NO+H@sub2@ reaction have been observed over the single crystal surfaces of Rh(533), Rh(311), Rh(111) and Pt(100).@footnote 1@ The following N-containing products can be formed: N@sub2@, NH@sub3@ and N@sub2@O. Recently, we observed oscillations over Ir(110)@footnote 2,3@ and Ir(210). The rate of N@sub2@ formation oscillates out of phase with the rate of NH@sub3@ and H@sub2@O formation. No N@sub2@O is formed. By using synchrotron radiation we could perform fast XPS measurements during a heat and cool cycle in the reaction mixture.@footnote 4@ These measurements show that there is a strong repulsive interaction between adsorbed N and O and that N buildsup on the surface during the NH@sub3@ formation. This information was used to propose a model for the oscillations in which the surface oscillates between an N covered surface which blocks the hydrogen adsorption and an O covered surface, which is accessible to hydrogen. A comparable model was suggested for Rh. However, the H@sub2@/NO ratio, the period and the shape of the oscillations are different for these metals. This is probably

caused by differences in the rate of the various reactions that take place. The NO+H@sub2@ reaction over Ru(0001) shows a different picture. In this case hardly any NH@sub3@ is formed during a heat and cool cycle even under H-rich conditions and instead of a build-up of N a build-up of O on the surface was obtained. No oscillations have been observed so far. A comparison of the non-linear behaviour in the NO+H@sub2@ reaction of these various metals will be made. @FootnoteText@@footnote 1@N.M.H. Janssen, P.D. Cobden, B.E. Nieuwenhuys, J. Phys.: Condens. Matter 9 (1997) 1889-1917 @footnote 2@C.A.de Wolf, B.E.Nieuwenhuys, A. Sasahara, K.Tanaka, M.M. Slinko, M.Yu. Smirnov, Surf. Sci. 411 (1998) L904-L909 @footnote 3@C.A. de Wolf, B.E. Nieuwenhuys, M.M. Slinko, M.Yu. Smirnov, accepted for publication in the Proc. of IVC-14 to be published in Surface Science @footnote 4@C.A. de Wolf, S. Lizzit, A. Baraldi, M. Kiskinova, B.E. Nieuwenhuys, in preparation.

4:00pm SS2-MoA7 Chemical Diffusion, Percolation, and Order-Disorder Transitions in a Model for CO-Oxidation with c(2x2)-O Ordering, *D.-J. Liu*, *E.W. James, J.W. Evans*, Iowa State University

Pattern formation during CO-oxidation on single crystal surfaces is mediated by the chemical diffusion of adsorbed CO in a disordered environment of coadsorbed relatively immobile oxygen. We analyze COdiffusion in a lattice-gas models for this reaction which incorporates c(2x2) ordering of adsorbed oxygen,@footnote 1@ and thus preferential diffusion at higher oxygen coverages of CO along anti-phase boundaries between c(2x2)-O domains. This constitutes a novel type of problem involving transport in a disordered medium, where CO-diffusion is blocked by percolation of the c(2x2)-O domains. We further show that such percolation is strongly influenced by (but not necessarily coincident with) a c(2x2) order-disorder transition in the oxygen overlayer. The latter constitutes a non-equilibrium analogue of order-disorder transitions familiar in equilibrated adlayers with short-range repulsive interactions. Precise results characterizing diffusion, percolation, and the order-disorder transition are obtained from extensive Monte Carlo simulations. @FootnoteText@ @footnote 1@ Y. Suchorski, J. Beben, E.W. James, J.W. Evans, and R. Imbihl, Phys. Rev. Lett. 82 (1999) 1907.

4:20pm SS2-MoA8 CO-oxidation Reaction as a Probe of Oxygen States at Oxygen-rich Ru(0001), A. Böttcher, Fritz-Haber-Institut der MPG, Germany It has been demonstrated that the oxidation of a Ru(0001) surface proceeds via four well characterized stages:(a) chemisorption, (b) oxygen penetration, (c) interfacial growth, (d) lateral and scale growth. The physical properties of the resulting oxygen phases were determined by means of thermal desorption spectroscopy (TDS), ultraviolet photoionization spectroscopy (UPS(21.2eV)) and low energy electron diffraction (LEED). The CO-oxidation reaction as performed over oxygenrich surfaces has been used as a sensitive probe of various oxygen states. The analysis of the integral yield and the reaction kinetics reveals four well distinguishable oxygen species which are characteristic for the consecutive oxidation stages. In the high temperature regime (T>550K) the very efficient reaction is limited only by the diffusion of oxygen atoms from the subsurface region toward the topmost layer. The activation energy for this limiting reaction step ranges from 0.1 to 0.3 eV. In the low temperature regime (T

4:40pm SS2-MoA9 Metastable States of Nitrogen Atoms Adsorbed on Ru(0001), *L. Diekhöner*, *H. Mortensen*, *A. Baurichter*, *A.C. Luntz*, Odense University, Denmark

There has been a tremendous amount of work in recent years in the study of nitrogen interacting with ruthenium, in part because of its possible role as an alternative ammonia catalyst. There is still considerable disagreement as to the maximum coverage of adsorbed N allowed on Ru surfaces. We report here a novel way to produce high coverage states of nitrogen atoms adsorbed on Ru(0001) using an atomic N atom beam for dosing. Low doses produces the well known low coverage overlayers. At higher atom beam doses, we find sequential fillings of several previously unknown higher coverage states on the surface, ultimately forming a maximum coverage of 1 ML N/Ru atom. A large decrease in Ru-N bond strength with N coverage is apparent in our results and is in good agreement with recent density functional calculations. A combination of these calculations and our experiments indicates that the higher coverage states are in fact metastable relative to associative desorption, stabilized only by an increase in the barrier between the gas phase and the adsorbed state with coverage as well. Independent confirmation of the higher barriers for the high coverage states was also obtained via laser induced thermal desorption (LITD). In these experiments the kinetic energy distribution of the N@sub 2@ formed in associative desorption was measured by time of flight (TOF)

techniques. We find N@sub 2@ desorbing with high translational energy distributions, much higher than seen in earlier desorption experiments from low coverages. Preliminary analysis indicates barriers that are at least in excess of 1.5 eV.

5:00pm SS2-MoA10 Atomic Scale Chemistry: Desorption of Ammonia from Cu(111) Induced by Tunneling Electrons, L. Bartels, Columbia University; M. Wolf, Fritz-Haber-Insitut der Max-Planck-Gesellschaft, Germany; T. Klamroth, Freie Universität Berlin, Germany; P. Saalfrank, University College London, United Kingdom; A. Kühnle, G. Meyer, K.-H. Rieder, Freie Universität Berlin, Germany

Excitation experiments on individual ammonia molecules on Cu(111) were performed with a low-temperature scanning tunneling microscope (STM) at 15 K. It could be shown that multiple electronic excitation of ammonia molecules can lead to an excitation of their substrate bond sufficient to caues desorption of the molecules from the substrate. This frequently results in their transfer to the STM tip apex. Tunneling spectra acquired with bare metal tips at the adsorption site of ammonia are compared with spectra acquired with ammonia decorated tip apices. The dependence of the desorption yield on the tunneling current at different biases shows a change of the order of the desorption process which nicely correlates with the number of incomming electron energies necessary to make up the binding energy. Excitation with either polarity, i. e. electron and hole attachment, can cause desorption. The change of the net desorption yield at different biases can be related to the standard model of the tunnel junction. Hartree Fock calculations allow to deduce from spectroscopic data that the ammonia modified Cu 4s state near the Fermi edge is responsible for the desorption process.

Surface Science Division Room 606 - Session SS1+EM-TuM

Nitrides and Compound Semiconductors

Moderator: A.C. Kummel, University of California, San Diego

8:20am SS1+EM-TuM1 Reconstructions and Growth Kinetics of GaN Surfaces with and without Adlayers, R.M. Feenstra, Carnegie Mellon University INVITED

Reconstructions of the gallium nitride (0001) Ga-face and N-face surfaces have been studied using scanning tunneling microscopy, with growth performed by molecular beam epitaxy. Distinct families of reconstruction are observed on each face, with most of the structures involving the presence of one of more adlayers of gallium bonded to underlying nitrogen atoms. For the N-face, this Ga-adlayer is in a 1x1 arrangement and further reconstructions are formed by additional Ga adatoms weakly bonded on the Ga-adlayer. For the Ga-face, the Ga-adlayer is incommensurate with the GaN lattice. For both the Ga- and N-face, growth under Ga-rich conditions yields smooth surfaces whereas growth under N-rich conditions produces rough surfaces. The latter case is indicative of limited surface diffusion rates. However, in the presence of surfactant layers such as Mg or As, smooth growth is also obtained in the N-rich regime. For sufficiently high surface coverage of Mg, a remarkable transition is observed in which Ga-polar material converts to N-polarity, with the inversion domain boundary extending along the c-plane. For growth of InGaN alloys, the role of surface metal layers (mainly indium) is also found to play an important role in the growth kinetics and incorporation efficiency. @FootnoteText@ Work supported by Office of Naval Research and National Science Foundation, and performed in collaboration with V. Ramachandran, H. Chen, A. Smith, D. Greve, J. Northrup, J. Neugebauer, W. Sarney, and L. Salamanca-Riba.

9:00am SS1+EM-TuM3 Increase of Electrical Conductivity in p-GaN by Immersion in H@sub2@O@sub2@ Solution*, B. Liu, M.H. Ahonen, P.H. Holloway, University of Florida

Immersion in a peroxide solution was found to increase electrical conductivity in p-GaN films. Auger electron spectroscopy (AES), currentvoltage and Hall measurements were used for characterization. All samples in this study were grown on the c-plane of sapphire substrates by metallorganic vapor phase epitaxy (MOVPE) with a carrier concentration of 1.1x10@super 17@ cm@super -3@. The samples were first cleaned in boiling aqua regia (3HCl+3HNO@sub 3@) for 10min, rinsed in DI water, and blown dry with N@sub 2@. Metal contacts (10nmNi/100nmTi/100nmAu) were deposited with an electron beam evaporator (~10@super -6@ Torr). After metal deposition, samples were immersed in a H@sub 2@O@sub 2@ solution (1H@sub 2@O@sub 2@ : 5H@sub 2@O or 1H@sub 2@O@sub 2@: 1H@sub 2@O, in volume) for different time (30sec to 300sec). This was followed by DI water rinse and N@sub 2@ blowing dry. Surface composition analysis using AES showed differences in N concentration versus treatments with the highest increase of N (5.67at%) found after immersion in 1H@sub 2@O@sub 2@ : 1H@sub 2@O for 300sec. Corresponding to this increase in N, improved electrical conductivity was confirmed by current-voltage data. The highest (a factor of two) increase of conductivity was measured for the sample with the highest increase of N concentration. No increase of carrier concentration was found in these samples with Hall measurement. The increase of N atoms at the sample surface and improvement of electrical conductivity will be discussed based on the chemical reaction of H@sub 2@O@sub 2@ with GaN and the effects of N vacancies in p-GaN. * This work is supported by EPRI and DARPA under agreement W08069-07.

9:20am SS1+EM-TuM4 Structure of GaN(0001)-1*1: Holography Study of Mg Adsorption on GaN(0001) Surface, G.J. Lapeyre, S.H. Xu, H. Cruguel, Y. Yang, Montana State University; J.F. Schetzina, North Carolina State University

The adsorption site and surface atomic structure of Mg on GaN(0001)-1*1 surface has been studied by photoelectron holographic imaging technique. The results clearly show that Mg adsorbs on T4 site and there is one monolayer Ga adatoms on the surface. They are on H3 sites.

9:40am SS1+EM-TuM5 Angle Resolved Photoemission Studies of the Surface Electronic Structure of GaN(0001), K.E. Smith, Y.C. Chao, P. Ryan, J. Downes, C.B. Stagarescu, R. Singh, T.D. Moustakas, Boston University; D. Hanser, R.F. Davis, North Carolina State University

The physical properties of GaN are under intense study due to its use in optoelectronic and high temperature semiconductor devices. However, the surface electronic structure of GaN remains poorly understood. Numerous reconstructions of GaN are observed, but very little is known about the detailed electronic structure of clean, ordered GaN surfaces. We report the results of an extensive synchrotron radiation excited angle-resolved photoemission study of n-type and p-type wurtzite GaN(0001)1x1 surfaces. GaN thin films were grown both by MOCVD on SiC, and by MBE on Al@sub 2@O@sub 2@. Surfaces were cleaned by repeated cycles of N@super 2+@ ion bombardment followed by annealing in UHV. We have observed a number of different surface states on these materials. For n-type MBE samples we find a non-dispersive surface state just below the valence band maximum that is highly sensitive to surface contamination and disorder. This state shows no dispersion perpendicular to the surface and exists across the surface Brillouin zone in a region devoid of bulk states. Polarization measurements reveal that this feature originates from a state with sp@sub z@ character. Destruction of this state only partially removes the observed band bending. For n-type MOCVD samples, cleaned in an identical fashion, we find at least two surface states. One is similar to that seen on the MBE material, while the second is a highly dispersive back bonding state, extending to the bottom of the valence band at points in the surface Brillouin zone. Removal of these states does not alter the observed band bending. For p-type MBE samples, we also find a surface state in the fundamental band gap, above the valence band maximum. Such states are not observed for the n-type material. We will discuss the surface electronic structure of GaN in the context of these measurements. @FootnoteText@ Work supported in part by NSF grant DMR 95-04948. Experiments were performed at the NSLS, which is supported by US DOE.

10:00am SS1+EM-TuM6 The Reaction of Oxygen with GaN(0001), B.D. Thoms, Georgia State University, US; V.J. Bellitto, Y. Yang, Georgia State University; D.D. Koleske, A.E. Wickenden, R.L. Henry, Naval Research Laboratory

In addition to optoelectronic applications, Group III Nitrides also exhibit properties appropriate for their use in high power and high temperature transistors. Oxidation of the surface influences several aspects of device fabrication including surface passivation and the production of metal contacts. We have characterized the reaction of oxygen with MOCVDgrown GaN(0001) using low energy electron diffraction (LEED), Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), high resolution electron energy loss spectroscopy (HREELS), and temperature programmed desorption (TPD). AES of GaN(0001) following exposure to O2 at room temperature results in an increased O(KLL) Auger intensity which saturates after approximately 200 L. AES following heating shows that oxygen is present to temperatures of 900 C. No surface reconstruction is observed by LEED, but rather a reduction in contrast between diffraction spots and background with increasing oxygen exposure. The reaction with oxygen produces a reduction in the ELS intensity at loss energies of 3.5 and 6 eV. A similar reduction is observed after exposure to atomic hydrogen, consistent with the reaction of both oxygen and hydrogen with surface dangling bonds. Oxygen exposure also produces an increase in ELS intensity at 10 eV. In HREEL spectra acquired following oxygen exposures up to 200 L, no adsorbate vibrational features are resolved from Fuchs-Kliewer phonon losses at integer multiples of 700 cm-1. These data are consistent with the chemisorption of oxygen on Ga sites.

10:20am SS1+EM-TuM7 Deep Level Electronic States of Clean GaN (0001)(1x1) Surfaces Prepared by In Decapping, *A.P. Young*, *L. Brillson*, Ohio State University; *C. Tu*, University of California, San Diego

The tremendous interest in the properties of GaN surfaces and interfaces has created a need for new techniques for preparing clean, ordered surfaces under ultrahigh vacuum (UHV) conditions. Furthermore, the electronic properties associated with different interface preparations are not well understood at present. In contrast to surfaces prepared by N+ bombardment or Ga overcoat annealing cycles at 900C, clean and ordered GaN (0001) (1x1) surfaces can be produced directly from MBE-grown surfaces after removal of an In cap layer at 650C. These surfaces are comparable to those clean, ordered surfaces reported elsewhere. We have used electron-excited nanometer luminescence spectroscopy (EENLS) to measure these states in the band gap of MBE-GaN deposited on a GaN/sapphire composite substrate. The GaN was cleaned in UHV via

thermal desorption of a thin (~50 ML) metallic In layer deposited prior to removal of the specimen from the growth chamber. This relatively low temperature desorption presents a benign method of transporting and processing GaN for device applications. Auger Electron Spectroscopy (AES) results show that if the In can uniformly cover the surface, it can prevent contamination during atmospheric exposure without reacting or diffusing into the GaN layer. The as-prepared surface morphology, measured via ex situ atomic force microscopy (AFM), indicated significant islanding of the In on the surface with approximate lateral size of 250 nm and height of 30 nm. Furthermore, a Ga signal, probably in the form of an oxide, was observed via AES indicating that some of the surface was not covered by In. The In was selectively desorbed from the GaN without reacting to produce InGaN. 8 ML of Ga were then deposited and the surface flashed once to 690C to reduce residual O and C contamination yielding a sharp (1x1) low energy electron diffraction (LEED) pattern. EENLS at a probe energy of 350 V (probe depth » 3 nm) indicated substantial "yellow" (YL) emission within the bandgap centered at 2.22 eV (FWHM = 0.4 eV) with only minimal near band edge (NBE) emission. YL emission remains constant while NBE increases with depth of excitation, indicating only states intrinsic to the GaN bulk. Subsequent AFM reveals Ga droplets residual to the flash annealing. Thus, In decapping introduces no new states at the clean, ordered GaN surface.

10:40am SS1+EM-TuM8 Characterization of MOCVD ZnO Buffer Layers for CIS Solar Cells, *L.C. Olsen*, Washington State University; *G.J. Exarhos*, Pacific Northwest National Laboratory; *F.W. Addis, L. Huang*, Washington State University

This paper concerns studies carried out to characterize MOCVD ZnO films grown for buffer layers in CIGS solar cells which have exhibited efficiencies between 12 and 14%. Further understanding of properties of these devices are required in order to increase efficiencies above 18% as demonstrated by CIGS cells with CdS buffer layers. Work is focusing on buffer layers grown with a two step process involving nucleation of ZnO at 250 C and subsequent growth at 100 C to achieve a total film thickness on the order of 800 A. The purpose of this work is to characterize the physical and electro-optical properties of MOCVD ZnO layers, and relate the results to device processing. All ZnO films examined were grown onto copper-indiumdiselenide (CIS) substrates. XPS examination of films for which the growth was terminated at various stages of the two-step process show that good coverage of CIS is achieved after 100 A of growth, although some outdiffusion of indium does occur. XPS analyses of 800 A films indicate the MOCVD ZnO films have no major impurities and that films are slightly oxygen deficient. Ellipsometry studies indicate that results for the index of refraction and extinction coefficient vs photon wavelength are well understood if one assumes that there are no secondary phases between the ZnO buffer layer and CIS, and that the ZnO band structure is characterized by three transitions, one at 3.2 to 3.4 eV, one at 3.8 to 4.0 eV, and one at 4.8 to 5.2 eV. The transitions are fairly consistent with theoretical results for the ZnO band structure. Raman spectroscopic studies of the ZnO buffer layers are also being carried out. Finally, results for ZnO buffer layers grown with the two-step process will be compared to characteristics of films grown with different procedures and which yield poor performing cells.

11:00am SS1+EM-TuM9 Photoelectron Diffraction of GaSe Bilayer Grown on Si(111), S. Meng, B.R. Schroeder, A. Bostwick, University of Washington; E. Rotenberg, Lawrence Berkeley National Laboratory; F.S. Ohuchi, M.A. Olmstead, University of Washington

Initial nucleation of GaSe on Si(111)7x7 results in formation of a pseudomorphic bilayer, which passivates the substrate dangling bonds and serves as the interface for further film growth. Component-resolved photoelectron diffraction (PED) and low-energy electron diffraction show this bilayer is oriented in a single domain, with the Ga-Se bond aligned with the substrate Si-Si bond. Combining scanned-angle and scanned-energy PED with theoretical calculations reveals the Ga and Se atomic positions. Ga sits directly atop surface Si, and the resultant interface bonding leaves Se lone-pair states on the surface. This makes the Si(111):GaSe surface highly resistant to contamination, and even additional GaSe does not stick for T@sub substrate@@>=@550°C. The measured PED patterns of Ga and Se 3d states show strong forward focusing along Ga-Se bond as well as diffraction rings from in-plane Se-Se scattering. The Ga-Se bond angle is between that for layered GaSe and cubic Ga@sub 2@Se@sub 3@. PED also shows strong (>20%) angular variation of the Ga3d spin-orbit branching ratio, while the Se 3d branching ratio is constant within 5%. This is likely associated with differences in photoionization matrix element and

propogation of 3/2 and 5/2 states for the different local environments. * Supported by NSF DMR9801302.

11:20am SS1+EM-TuM10 An Example of a Compound Semiconductor Surface that Mimics Silicon: The InP (001) (2x1) Reconstruction, L. Li, Q. Fu, B. Han, M. Begarney, D. Law, C. Li, R.F. Hicks, University of California, Los Angeles

An InP (001) (2x1) reconstruction was prepared by metalorganic vaporphase epitaxy. Scanning tunneling micrographs and infrared spectra of adsorbed hydrogen revealed that the (2x1) is terminated with a complete layer of buckled phosphorous dimers, giving rise to p(2x2) and c(4x2)domains. A surface band gap of 1.2 ± 0.2 eV was measured by scanning tunneling spectroscopy. The buckling can be explained by electron correlation among the dangling bonds of pairs of phosphorous dimers. This allows the surface to achieve a lower energy, semiconducting state. This reconstruction mimics the Si (100) (2x1), which is terminated with buckled silicon dimers.

11:40am SS1+EM-TuM11 STM Studies of Sulfur Passivated InP(100), G.P. Lopinski, R.A. Wolkow, National Research Council, Canada; C.D. MacPherson, Nortel Networks, Canada

While sulfur passivation of InP(100) has been extensively studied by a number of techniques the details of the surface structure are still not definitively established. In this work we report STM studies of sulfur passivated InP(001) surfaces, prepared by wet chemical treatment in ammonium sulfide followed by annealing in UHV. Although the as prepared surface is disordered due to the presence of excess sulfur, highly pitted terraces evolve for annealing temperatures above 300C. Further annealing to 450C results in emergence of atomically flat terraces. LEED observations indicate the existence of a (3x1) phase in addition to the previously reported (2x1) structure. Atomically resolved STM images reveal the coexistence of local (3x1) and (2x1) periodicity. These surfaces are found to be stable with respect to brief air exposures.

Surface Science Division Room 607 - Session SS2-TuM

Model Catalysts

Moderator: A.G. Sault, Sandia National Laboratories

8:20am **SS2-TuM1 The Microscopic Mechanism of Methanol Synthesis over the Zn-promoted Cu(111)**, *J. Nakamura*, University of Tsukuba, Japan; *I. Nakamura*, National Institute for Resources and Environment, Japan; *H. Nishimura*, *H. Nakano, M. Sano*, University of Tsukuba, Japan; *T. Fujitani*, National Institute for Resources and Environment, Japan

We had reported that the Zn-deposited Cu(111) could be regarded as a model of Cu/ZnO catalysts in terms of the turnover frequency of methanol formation and the activation energy. After establishing the catalyst model, we had further tried to look into the detailed mechanism on the promotional role of the Zn as well as the microkinetics using in-situ IRAS, XPS and STM apparatuses connected to a high pressure reactor. Very reactive formate species adsorbed in an inclined bidentate state was detected by IRAS, which was found to be responsible for the promotional effect of the Zn. Also the microkinetic picture was established for formate synthesis and formate decomposition. Interesting relationships between the ordered structure of formate observed by STM and the kinetics of decomposition were shown. That is, various ordered structures of formate intermediates synthesized from CO@sub 2@ and H@sub 2@ at 1 atm were very different from the structure of formate prepared by adsorption of formic acid, which cause a difference in the pre-exponential factor of the rate constant for the formate decomposition. This was explained by that a nearest neighbor formate species interfered with the OCO plane vibration of formate, which is probably necessary to overcome the transition state of the decomposition. The STM images of the Zn-deposited Cu(111) showed that Zn atoms were substituted for Cu atoms, leading to a Cu-Zn surface alloy. Upon the deposition of Zn, the alloying started at the step edges of the Cu(111) surface, and then the Zn atoms migrated toward the terrace. The migration rate was measured by time-resolved STM.

8:40am SS2-TuM2 Vacuum and Electrochemical Characterization of a Model Pt(111) Catalyst Modified with Vapor-deposited Ru, *D.S.W. Lim, T.H. Madden, V.K. Medvedev, E.M. Stuve,* University of Washington; *T.J. Jarvi,* United Technologies Research Center

A practical liquid fuel cell anode catalyst must oxidize fuel in the presence of adsorbed carbon monoxide (CO), whether the actual fuel is methanol in

the direct methanol fuel cell, or hydrogen from reformed hydrocarbons. While platinum (Pt) exhibits the greatest reactivity for fuel oxidation, it alone is unable to oxidize CO at potentials low enough to be practical. Pt modified with ruthenium (Ru) can however oxidize CO at lower potentials, although the details of the Ru enhancement have not yet been established. Also, the lack of reproducible performance of both model and industrial Pt / Ru fuel cell catalysts indicates that the preparation / processing effects on catalyst structure and performance have not been adequately assessed. In this work, a Pt(111) surface is modified with Ru via physical vapor deposition and characterized in ultra-high vacuum using AES, LEED, and TDS. The crystal is then transferred directly to an electrochemical cell where blank and methanol-oxidation voltammetry are performed. Early results using an industrial electron-beam Ru deposition source suggest simultaneous multi-layer growth of the Ru adlayer on Pt(111) at room temperature. Room temperature blank voltammetry indicates new features in the low-potential region due to Ru on Pt(111). Methanoloxidation voltammetry indicates reduced peak currents due to lack of dissociative adsorption of methanol on surface Ru at room temperature. These electrochemical characteristics due to Ru on Pt(111) can largely be reversed by a mild 300 deg C anneal in vacuum. We recently developed a small electron-beam Ru deposition source in our lab which allows highly precise Ru deposition under good vacuum conditions. More detailed vacuum and electrochemical characterization using this source for the Ru / Pt(111) system will be discussed. This work was supported by the Office of Naval Research, the National Science Foundation, the Link Foundation, and the University of Washington.

9:00am SS2-TuM3 Structurally Ordered Magnesium Vanadate Model Catalysts for Oxidative Dehydrogenation, A.G. Sault, J.A. Ruffner, Sandia National Laboratories

A fundamental understanding of the nature of the active sites in mixed metal oxide oxidation catalysts has proven elusive. The complex nature of these materials makes fundamental studies of active sites difficult. The use of single crystal surfaces to overcome this complexity is limited by the insulating nature of oxides, which restricts the use of many surface analytical probes. For simple oxides, some researchers have used ultrathin epitaxial oxide films to overcome these problems. Such films allow STM studies that provide unprecedented atomic detail regarding metal oxide surfaces. We are employing similar methods to study mixed metal oxide surfaces. Using RF sputter deposition, we have grown thin (<85 Å) films of Mg@sub 3@(VO@sub 4@)@sub 2@, a known selective oxidative catalyst. Bulk and surface analysis of films grown on Si wafers show the desired stoichiometry. By depositing Mg@sub 3@(VO@sub 4@)@sub 2@ on a 500 Å Au layer grown on an oxidized Si wafer, films strongly orientated in the (042) plane of Mg@sub 3@(VO@sub 4@)@sub 2@ can be grown. This plane consists of close packed oxygen layers, with Mg and V ions in octahedral and tetrahedral sites, respectively. Heating the films above 623 K in vacuum or 100 Torr propane results in partial reduction of V(V) to V(IV) and segregation of V to the surface. Treatment in oxygen reverses these changes. This reversible redox chemistry is consistent with the known mechanism for catalytic oxidation, which involves participation of lattice oxygen. We will report STM images of these surfaces, and detail the effects of heat treatments in reactive environments (e.g., oxygen/propane mixtures) on the structure and composition of these films. The formation of defects such as oxygen vacancies will be of special interest as lattice oxygen plays an important role in catalysis over mixed metal oxides. Through these studies we hope to provide the first detailed atomic scale view of active sites in this important class of catalysts.

9:20am SS2-TuM4 The Atomic-scale Structure of MoS@sub 2@ Nanocluster Catalysts Studied by STM, S. Helveg, J.V. Lauritsen, E. Laegsgaard, I. Stensgaard, University of Aarhus, Denmark; B.S. Clausen, H. Topsoe, Haldor Topsoe Research Laboratories, Denmark; F. Besenbacher, University of Aarhus, Denmark

Hydrodesulfurization (HDS) catalysis has recently attracted an increased interest partly augmented by the new severe environmental legislation. The activity of the industrial HDS catalysts has uniquely been related to the edge structure of MoS@sub 2@ nano-crystals. However, very little is known about the actual shape of the nano-crystalline MoS@sub 2@ particles and the exact edge structures. To obtain such structural insight, we have prepared a model system of 30 Å wide MoS@sub 2@ nano-clusters dispersed on the Au(111) model surface. High resolution Scanning Tunneling Microscopy (STM) studies unequivocally reveal that the MoS@sub 2@ nano-clusters are of triangular shape, and from atomically resolved STM images of the edge structures, we tentatively conclude that the edges are S restructured Mo terminated edges.

9:40am SS2-TuM5 Linking Surface Science and Catalysis, I. Chorkendorff, Technical University of Denmark, DENMARK INVITED Surface Science has in the past provided much of the framework and tools for understanding heterogeneous catalysis. Nevertheless, the pressure and structure gap still continues to provide unforeseen and interesting phenomena, which are necessary prerequisites in order that real catalytic processes under high-pressure conditions can be understood and modeled. It is therefore mandatory to identify which reaction pathways are prevailing and what structure and composition are present at increased pressure. In a number of examples it will be demonstrated how, by combining in situ high pressure experiments on well defined single crystals with DFT calculations, it is possible to gain a further insight in this direction. For example is it well known from UHV experiments that steps or defects may influence the surface reactivity substantially, but the influence on catalytic process have been of more speculative nature. It will be shown. how steps and/or defects increases the sticking of N@sub2@ on Ru(0001) by 8 to 9 orders of magnitude!! Since this is the rate-limiting step in the ammonia synthesis on Ru, it will naturally have a profound impact on the understanding of the ammonia synthesis, which was also studied. Turning to model system for alloy catalyst it will be demonstrated how the surface composition and availability for performing chemical reaction can be strongly dependent on gas induced segregation phenomena. A brief overview of the determining parameters will be given showing that the surface composition of alloys is dynamically dependent on temperature and the chemically potential of the gasses involved and cannot in many cases be determined from UHV experiments alone.

10:20am SS2-TuM7 Flow Reactor Studies of Nanofabricated Model Catalysts; Activity and Reconstruction, *S. Johansson, E. Fridell, B. Kasemo,* Chalmers University of Technology, Sweden

Nanofabrication of model catalysts using the electron-beam lithography technique offers a way to produce geometrically well-defined model catalysts. Component interaction, particle separation and particle size (in the 10 nm range) can be controlled. Multi-layer structures can be obtained by repeating the fabrication-process. Furthermore, re-structuring can be accomplished by heat treatment afterwards in different gas mixtures. These nanofabricated catalysts are well suited to study, e.g., spillover effects in catalytic systems. A micro-reactor for catalytic evaluation of these nanofabricated model catalysts has been designed. It operates at atmospheric pressure and allows samples with a small total active surface area (below 1 mm@super 2@). This implies small gas-flows in the order of approx. 1-10 mm@super 3@/s. The small active surface-area comes from a limitation in the electron-beam lithography process to make large numbers of small structures in a reasonable time, due to the serial processing. The minimum Pt-surface-area needed for catalytic activity evaluation has not yet been determined for this system. Differences in the CO-reaction rate in the kinetically controlled region is measured as a function of interaction length between Pt and CeO@sub x@, where the total surface area of Pt has been kept constant. Morphology changes of nanofabricated Pt-discs with diameters up to 700 nm has been studied. Structural changes occur in reactant mixtures, e.g., CO+O@sub 2@ in Ar, at elevated temperatures (500°C). Disintegration of the larger Pt-discs into several smaller crystalline Pt-particles is observed.

10:40am SS2-TuM8 Increasing the C-O Bond Anharmonicity of Methoxy on Cu(100) with Coadsorbates, J.M. White, H. Ihm, K.C. Smith, H. Celio, University of Texas, Austin

The C-O bond ahnarmonicity of methoxy induced by coadsorbates on Cu(100) has been studied using reflection absorption infrared spectroscopy (RAIRS). The analysis of the anharmonicity was carried out through the IR spectrum of a localized two-phonon bound state, the 2@nu@'@sub C-O@ excitation. For methoxy without coadsorbates, the vibrational frequencies of the C-O stretching mode and its overtone exhibit large coverage dependent shifts caused by dipole-dipole interactions. The anharmonicity of the C-O bond is @omega@@sub e@@chi@@sub e@=8.5 cm@sup -1@, which is 34% lower than that found for the gas phase methanol. Atomic oxygen markedly shifts the 2@nu@'@sub C-O@ band from 1951 cm@sup -1@ to 1940 cm@sup -1@, which consequently increases the anharmonicity by 11 cm@sup -1@. We have also compared results for methoxy from the thermal decomposition of methyl nitrite (CH@sub 3@ONO) on Cu(100) at different temperatures. We find that the 2@nu@'@sub C-O@ band can detect the presence of coadsorbed NO since the vibrational properties of the 2@nu@'@sub C-O@ band for both systems (methoxy-A-Cu(100) where A=O or NO) are quite similar. The definite correlation of the changes to the vibrational properties of methoxy induced by coadsorbates was achieved

by using temperature programmed desorption (TPD) and Auger electron spectroscopy (AES).

11:00am SS2-TuM9 Studies of the Oxidation Reactions of Methanol on a Heated Silver Membrane, *R.J. Beuhler, R.M. Rao, M.G. White,* Brookhaven National Laboratory

A polycrystalline Ag-membrane is being used as a model substrate for investigating the kinetics and dynamics of Ag-catalyzed oxidation reactions, such as the epoxidation (EO) of ethylene and the partial oxidation of methanol. These Ag-catalyzed reactions are carried out on a large-scale commercially, and despite considerable effort to understand the reaction mechanisms, much still remains uncertain. We have been attempting to study these oxidation reactions under collision free conditions (pressures less than 10@super -5@ torr), allowing both electron impact mass spectroscopy and state-selective laser ionization techniques to be used for product analysis. The main advantage of the membrane is that high surface coverages of adsorbed O@sub (a)@ can be prepared by diffusion of oxygen atoms produced by dissociative adsorption at the high pressure side of the heated Ag foil. The oxygenated Ag-foil is found to be very active in promoting the partial oxidation of methanol to formaldehyde. At a methanol pressure of 10@super -6@ torr, the reaction rate is on the order of 10@super 15@ molecules/cm sec@super 2@, with a measurable lower limit of about 5 x 10@super 13@ molecules/cm sec@super 2@. During the initial heating of the foil, activation of the surface is observed. In complementary studies, O 1s XPS measurements have been performed on the Ag-foil surface to identify the chemical state of the adsorbed oxygen, and (2+1) REMPI laser spectroscopy has been used to extract ro-vibronic and velocity distributions for desorbed molecular oxygen formed by the recombination reaction O@sub (a)@ + O@sub (a)@ = O@sub 2(g)@.

11:20am **SS2-TuM10 Improved Catalytic Activity and Selectivity by Photon Irradiation**, *D. Chakarov*, Chalmers University of Technology and University of Göteborg, Sweden; *S. Ljungström*, Competence Centre for Catalysis, Sweden; *J. Bergeld*, *D. Ingert*, *V.P. Zhdanov*, *B. Kasemo*, Chalmers University of Technology and University of Göteborg, Sweden

Photo-catalysis is the enhancement of a chemical reaction by combined action of a catalyst and photons, on the reaction rate and/or selectivity. In heterogeneous photo-catalysis, the reaction occurs on a solid surface, with the reactants in gaseous or fluid state. The photons usually excite hot (photo) electrons that by transient attachment to one of the reactants enhance the reaction. In the present work, we explore the possibilities to increase the efficiency of catalytic emission cleaning by photo-catalysis. The approach includes both experimental and theoretical studies of the different parameters that may influence the photo-catalytic reactions, such as catalyst composition and wavelength dependence. The experiments are performed with conventional noble metal car exhaust catalysts at atmospheric pressure, nanofabricated model catalyst, and extended single crystals at UHV. Theoretical treatment includes studies of hot electron excitation-transport-attachment processes and Monte Carlo simulation. We present results concerning the reaction kinetics and light-off behavior for different CO + O2 and CO + NO mixtures on different catalysts. The main observations to date are: The light-off temperature can be reduced substantially (by up to 80 degrees) by photon irradiation at 365 nm. The single photon, non-thermal origin of this photocatalytic effect is confirmed by power- and wavelength- dependence measurements. The different characteristics of the photocatalysis on supported platinum, compared to single crystal Pt (111) in UHV, are discussed in terms of case specific adsorbate coverages, hot electron excitation, and reaction mechanisms.

11:40am SS2-TuM11 Direct Observation of Propylene Transformation Chemistry on and in the Pores of Silver Exchanged Faujasite Catalyst, *S. Sambasivan*, Brookhaven National Laboratory; *D.A. Fischer*, National Institute of Standards and Technology; *A. Kuperman*, Dow Chemical Company; *B.M. DeKoven*, Intevac Inc.

For the first time Near-Edge Soft X-ray Absorption Spectroscopy Fine Structure (NEXAFS) electron yield (surface sensitive about 50 Å) and fluorescence yield (bulk sensitive) have been applied simultaneously to characterize the adsorbed state of propylene in the surface and the bulk of the silver exchanged faujasite (LZY-52) catalyst. This technique is non-destructive, element specific, and a direct probe of the bonding and concentration of the adsorbed species, and reactive intermediates on a highly complex zeolite catalyst. Propylene adsorption on Ag/LZY-52 faujasite at 125 K showed that a bulk adsorbed state was a weakly interacting gas-phase like species with a highly intense carbon 1s to @pi@ *intensity which begins to desorb upon heating from 150 K to 300 K. On the other hand the propylene adsorbed on the surface forms a strongly

chemisorbed intermediate with a small of carbon 1s to @pi@ * intensity but a strong @sigma@ * intensity indicating a formation of a sigma complex which is stable up to 250 K. A very small adsorption of propylene was observed on a zeolite with similar cage structure, high Si/Al ratio and no silver loading. The difference in the nature propylene adsorption in the bulk and surface of Ag/LZY-52 is discussed with respect to the difference in acidity and the size of the Ag particles in the surface and bulk zeolite. The NEXAFS technique is demonstrated as a practical new probe of molecular level reaction chemistry in catalyst materials.

Surface Science Division Room 606 - Session SS1+EM-TuA

Oxides: Growth and Structure

Moderator: E.G. Seebauer, University of Illinois, Urbana

2:00pm SS1+EM-TuA1 Noncommutative Band Offset at @alpha@-Cr@sub 2@O@sub 3@/@alpha@-Fe@sub 2@O@sub 3@(0001) Heterojunctions, S.A. Chambers, Y. Liang, Pacific Northwest National Laboratory

We have measured the valence band discontinuity at artificially structured, epitaxial heterojunctions of @alpha@-Cr@sub 2@O@sub 3@(0001) and @alpha@-Fe@sub 2@O@sub 3@(0001) grown on @alpha@-Al@sub 2@O@sub 3@(0001) substrates. Oxygen-plasma-assisted molecular beam epitaxy was the growth technique, and band offsets were measured by core-level and valence-band photoemission. Layered film structures of these two materials maintain the in-plane lattice parameter of @alpha@-Fe@sub 2@O@sub 3@(0001). Thus, the @alpha@-Cr@sub 2@O@sub 3@(0001) layers are under a 2.3% tensile stress. The valence band offsets are 0.3±0.1 eV and 0.7±0.1 eV when the top layer is Fe@sub 2@O@sub 3@ and Cr@sub 2@O@sub 3@, respectively. The noncommutativity in band offset appears to be due to a growth-sequence-dependent interface dipole caused by different extents of intermixing for the two kinds of interfaces.

2:20pm **SS1+EM-TuA2 Ultrathin Iron Oxide Films**, *R.L. Stockbauer*, *J. Karunamuni, A. Koveshnikov, R. Madjoe, R.L. Kurtz*, Louisiana State University

Thin films of spin polarized conductors are receiving increased attention as potential contacts for devices such as spin-valves and high-sensitivity disk sensors. We have succeeded in producing ultra thin films of FeO and Fe@sub 3@O@sub 4@ and characterized their morphology using STM and LEED. The oxides are grown by depositing thin films of Fe on a Cu(100) surface at room temperature. The Cu substrate has terraces ca. 100Å wide with steps perpendicular to the [010] direction. The Fe grows layer-by-layer in islands uniformly distributed on the Cu terraces. The oxides are formed by heating to 840K in 10@super -6@ Torr O@sub 2@. The change in the morphology of the surface after oxidation is truly striking. At low Fe coverage (<2ML), FeO completely rearranges the Cu substrate. Large terraces up to 1µm wide are now observed. The FeO itself forms long stripes typically $0.2\mu m$ wide and up to $10\mu m$ long parallel to the [011] direction. Shorter stripes are observed in the perpendicular direction. The FeO stripes display two superstructures. A coarse structure consists of a series of dark bands parallel to the stripe direction and spaced at 360Å intervals. The fine structure is a 20.5Å hexagonal pattern. A comparison of LEED data and simulations indicates that the overlayer is FeO(111) with stripes aligned along the [110] directions. Oxidizing Fe films thicker than 2ML results in the oxide phase of device interest, Fe@sub 3@O@sub 4@. These patches show a 170Å banded structure and the same size hexagonal superstructure but rotated 30° from that observed for the FeO . LEED data, simulations, and thermochemistry are consistent with the overlayer being Fe@sub 3@O@sub 4@(111) rotated 15° from the [001] azimuth. Surprisingly, these highly oriented oxide films do not show strong angular dependence in photoemission. MOKE, circular dichroism, and spin polarized measurements are underway to determine the magnetic properties of the oxide films.

2:40pm SS1+EM-TuA3 Islanding, Facetting, and the Lattice Relaxation in the Growth of @alpha@-Fe@sub 2@O@sub 3@ on @alpha@-Al@sub 2@O@sub 3@, S.I. Yi, Y. Liang, S. Thevuthasan, S.A. Chambers, Pacific Northwest National Laboratory

The growth of @alpha@-Fe@sub 2@O@sub 3@ on c- and r-oriented @alpha@-Al@sub 2@O@sub 3@ by oxygen-plasma-enhanced molecular beam epitaxy has been investigated with reflection high-energy electron diffraction, non-contact atomic force microscopy, X-ray photoelectron spectroscopy, X-ray photoelectron diffraction, low-energy electron diffraction, and high-energy ion scattering. The epilayer is facetted due to compressional stress on the c-plane during growth of the first two monolayers. The epilayer structure is significantly distorted, with considerable in-plane strain. However, the film exhibits a constant Fe 2p binding energy with respect to the O 1s binding energy for all thicknesses, revealing the growth of phase-pure @alpha@-Fe@sub 2@O@sub 3@ throughout. A growth-mode transition begins at approximately two monolayers from strained wetting layer to the formation of clusters of rhombohedral islands when a relatively slow growth rate of 1 Å/min is used. However, this transition occurs over several monolayers at a growth temperature of 400 @super o@C. A film with high structural order and orientational stability grows as the islands coalesce to form new and larger terraces. This transition to island-mediated growth can be kinetically impeded for higher growth rates of 0.1-0.3 Å/sec.@footnote 1@ In contrast, the growth-mode transition will occur more rapidly if temperatures of 450 to 500 @super o@C are used along with the slower growth rate. However, sustained growth at temperatures in excess of 500 @super o@C results in the simultaneous formation of Fe@sub 3@O@sub 4@ (111) and/or @gamma@-Fe@sub 2@O@sub 3@ (111) along with @alpha@-Fe@sub 2@O@sub 3@(0001). In contrast to growth in the cplane, the epilayer shows only facetted growth on the r-plane, regardless of the deposition rate and substrate temperature. This result may be due to the lower surface symmetry of the r-plane compared to the c-plane. @FootnoteText@ @footnote 1@ S. I. Yi, Y. Liang, S. A. Chambers, to be published in JVST A, Jul/Aug, 1999

3:00pm **SS1+EM-TuA4 Surface Reconstructions of Fe@sub 3@O@sub 4@(001)**, *B. Stanka, W. Hebenstreit,* **U. Diebold**, Tulane University; *S.A. Chambers,* Pacific Northwest National Laboratory

We have investigated the structural changes to the Fe@sub 3@O@sub 4@(001) surface which are induced by different sample treatments. The samples consisted of ~5000 Å thick films of Fe@sub 3@O@sub 4@(001), grown with oxygen-plasma-assisted molecular beam epitaxy (OPA-MBE) on MgO(001) substrates. To study the surface termination, structure, morphology, and composition, scanning tunneling microscopy (STM), low energy electron diffraction (LEED), low energy He@sup +@ ion scattering (ISS), and x-ray photoelectron spectroscopy (XPS) were used. A (@sr@(2) x @sr@(2))R45° reconstruction relative to bulk-terminated Fe@sub 3@O@sub 4@ is induced by heating in oxygen (10@sup -6@ - 10@sup -7@ mbar) at temperatures between 250°C and 500°C after a through-air transfer from the MBE chamber. Our STM results show an appearance consistent with a B-layer termination, which consists of a layer of octrahedrally coordinated Fe and tetrahedrally coordinated O, along with one O vacancy per unit cell. This surface is autocompensated, or charge neutral, and is therefore expected to be stable. Further annealing in UHV causes a transformation to either a (1 x n) or a (2@sr@(2) x @sr@(2))R45 structure. In both cases, a (@sr@(2) x @sr@(2))R45 reconstructed surface can be regained reproducibly by annealing in oxygen. Interestingly, at no time do we observe the other autocompensated termination, which consists of one-half monolayer of tetrahedrally coordinated Fe(III), despite its observation in other laboratories. Thus, it appears that the surface termination is critically dependent on the method of surface preparation.

3:20pm SS1+EM-TuA5 The Surface Structure of @alpha@-Al@sub 2@O@sub 3@(0001) Studied by LEED, C.F. Walters, Sandia National Laboratories; E.A. Soares, M.A. Van Hove, Lawrence Berkeley National Laboratory; K.F. McCarty, Sandia National Laboratories

The surface structure of @alpha@-Al@sub 2@O@sub 3@(0001) has been investigated using normal-incidence low-energy electron diffraction. High quality sapphire samples were produced by ex-situ annealing in air, followed by in-situ cleaning using atomic deuterium at an elevated sample temperature. To investigate the possible occurrence of different surface structures and/or stoichiometries, the samples were processed, subsequent to the atomic deuterium cleaning, using several different procedures. These included annealing the sample in oxygen, and exposing the cooled sample to atomic deuterium. The experimental data were compared to results of calculations performed using an automated tensor LEED program. Several different models were used as the starting point for the analysis. These included termination by: an oxygen layer, a single aluminum layer, a double aluminum layer, and a "hydroxyl" covered single aluminum layer. Additionally, we have analyzed mixtures of these terminations, with the mixtures including different species, as well as the same species but containing different crystallographic planes (i.e., terraced surfaces with fractional unit cell step heights). For each sample preparation, the best structural model was determined via an analysis of the Pendry R-factor that took into account the effect of the additional fitting parameters for the models containing mixed terminations. The bestfit models derived from the tensor LEED analysis will be discussed with respect to the preparation method used, as well as compared to the results of recent first-principles calculations. This work supported by USDOE-OBES-Division of Materials Sciences.

3:40pm SS1+EM-TuA6 Formation of Epitaxial Al@sub 2@O@sub 3@ on Ni@sub 3@Al(111) Studied by STM, HREELS, UPS, @DELTA@@PHI@, and LEED, A. Rosenhahn, J. Schneider, J. Kandler, T. Pelster, Universität Bonn, Germany; R. Linke, Eindhoven University of Technology, The Netherlands; C. Becker, K. Wandelt, Universität Bonn, Germany

The formation of oxides on the Ni@sub 3@Al(111) single crystal surface has been studied in the temperature range from 300K to 1000K by STM, HREELS, UPS, @DELTA@@PHI@, and LEED. The experiments reveal a strong temperature dependence of the structure and the chemical composition of the resulting oxides, which is caused mainly by a rising aluminum mobility with increasing temperature. Adsorption of oxygen at room temperature creates a disordered surface which appears rough in STM images and shows a diffuse LEED pattern. At 600K STM images show patches of different appearance on the alloy surface. At low coverages the small oxidic nuclei possess a triangular shape, and HREELS measurements show a Al@sub 2@O@sub 3@-like composition. At higher coverages two areas with different appearance can be distinguished in STM, accompanied by the observation of mixed Ni/Al-oxide vibrations in HREELS. At 800K STM measurements show highly ordered triangular shaped oxidic islands. A moiré structure can be observed which corresponds to a superstructure due to an unrotated single O/Al overlayer, that has also been found by LEED and HREELS measurements. The electronic structure of the film being very similar to that of O/Al(111). Adsorption at 1000K finally leads to the growth of an oxidic film, that proceeds from steps exclusively. The oxide exists in two rotational domains that can be detected in LEED and STM. Both HREELS and UPS measurements show the formation of a Al@sub 2@O@sub 3@-doublelayer. Only at this temperature the chemical order of the underlying Ni@sub 3@Al(111) substrate is completely restored.

4:00pm SS1+EM-TuA7 Surface Structure Determination of Yttrium-Stabilized ZrO@sub 2@(001) Surface Using X-Ray Photoelectron Diffraction, S. Thevuthasan, S.I. Yi, Pacific Northwest National Laboratory; Y.-J. Kim, Taejon National University of Technology, Korea; T.T. Tran, S.A. Chambers, C.H.F. Peden, Pacific Northwest National Laboratory

The physical and chemical properties of oxide surfaces are strongly influenced by several structural properties. As such, there is a growing interest in determining surface termination and relaxation in single crystal oxides. The yttrium-stabilized ZrO@sub 2@(001) surface can in principle be either O terminated or Zr terminated. However, neither of these surfaces is autocompensated as a (1x1) structure. The Zr terminated @sr@2x@sr@2)R45@super o@ reconstruction is autocompensated. It was recently reported that the CeO@sub 2@(001)surface, which is similar to ZrO@sub 2@(001), is terminated with 0.5 monolayers of oxygen.@footnote 1@ We have carried out low-takeoff-angle x-ray photoelectron diffraction (XPD) measurements using Zr 3d, Y 3d and O1s core levels on a oxygen-plasma-cleaned ZrO@sub 2@(001) surface to determine the surface structure. Low-energy electron diffraction data show broad (1x1) spots that are characteristic of many oxide surfaces, and no half-order spots are visible. Currently single and multiple scattering simulations and R-factor analysis are being performed using model clusters generated using both O and Zr terminated surfaces. Preliminary analysis indicates that the surface is Zr terminated with the first layer spacing contracted by 23% relative to the bulk interlayer spacing. Detailed analysis is in progress and results will be presented at the meeting. @FootnoteText@ @footnote 1@G.S. Herman, Phys. Rev. B Rapid Comm. (in press). Work supported by the U.S. Department of Energy (DOE), Offices of Basic Energy Sciences, Division of Chemical Sciences and the DOE's Environmental Management Science Program.

4:20pm SS1+EM-TuA8 Epitaxial Growth and Characterization of Zirconium-Doped CeO@sub 2@(111) Thin Films on Yttria-Stabilized Zirconia(111), T.T. Tran, Pacific Northwest National Laboratory; Y.-J. Kim, Taejon National University of Technology, Korea; S. Thevuthasan, G.S. Herman, Pacific Northwest National Laboratory

Doning of the ceria lattice with 7r has been shown to enhance the oxygen storage capacity and the rate of oxygen release, and thus the catalytic properties of noble metals supported on these oxides.@footnote 1@ The ability to obtain a detailed knowledge of the effect of the surface structure and zirconium doping levels on oxygen exchange rates requires high-quality single crystalline materials. In a previous study, pure and Zr-doped CeO@sub 2@(001) thin films were grown on SrTiO@sub 3@(001).@footnote 2@ Due to the good lattice match and identical crystal structure, yttria-stabilized zirconia (YSZ) was chosen as the substrate for the growth of CeO@sub 2@(111) in this study. Both pure and Zr-doped CeO@sub 2@(111) thin films were grown on YSZ(111) by oxygen-plasmaassisted molecular beam epitaxy. After deposition, the films were

compositionally and structurally characterized by in-situ reflection highenergy electron diffraction (RHEED), low-energy electron diffraction (LEED), x-ray photoelectron diffraction (XPD), and x-ray photoelectron spectroscopy (XPS), as well as by ex-situ Rutherford backscattering spectrometry. RHEED, LEED, and XPD results indicated that the materials are well-ordered at the surface for zirconium doping levels up to 40%. Furthermore, a +4 oxidation state was confirmed for both Zr and Ce using XPS. RBS results showed that Zr was found to incorporate substitutionally at cation sites in the ceria lattice. @FootnoteText@ @footnote 1@ P. Fornasiero, G. Balducci, J. Kaspar, S. Meriani, R. Di Monte, and M. Graziani, Catal. Today, 29, 47 (1996); Hamada, H., Catal. Today, 22, 21 (1994); Ozawa, M., M. Kimura, and A. Isogali, J. Alloys Comp., 193, 73 (1993). @footnote 2@ Y. Gao, G.S. Herman, S. Thevuthasan, C.H.F. Peden, and S.A. Chambers, J. Vac. Sci. Technol. (in press).

4:40pm SS1+EM-TuA9 Structure and Dynamics of KTaO@sub 3@(001) via Elastic and Inelastic Helium Atom Scattering@footnote 1@, J.A. Li, T.W. Trelenberg, E.A. Akhadov, S.A. Safron, J.G. Skofronick, Florida State University; L.A. Boatner, Oak Ridge National Laboratory

Although bulk KTaO@sub 3@ is considered an incipient ferroelectric which remains cubic at all temperatures, He diffraction on the (001) surface, cleaved in situ, shows reconstruction of the (1x1) surface to (2x1). The surface behavior, however, seems to depend on its thermal history as, for example, in the following observations: 1)After the sample is cleaved at about 300K and cooled to about 190K, He diffraction reveals a (1x1) surface which appears to be stable indefinitely. 2) If the target is then warmed from 190K to about 220K, reconstruction to the (2x1) phase takes place gradually over a period of about 2 days, whereas if it is warmed to about 260K, the (2x1) phase becomes evident after about 3 hours. 3)When the target is instead taken from 190K to approximately 60K and then to about 260K, the (2x1) surface is apparent immediately. 4)Restoration to (1x1) can be achieved (a) in a few hours or (b) immediately by warming the surface to about 330K or to about 360K, respectively. In addition, there is considerable hysteresis in the intensities of the He diffraction spots for the (2x1) surface over the thermal cycle from 260 K to 50 K to 260 K. Helium time-of-flight (TOF) spectra were obtained to determine the surface phonon dispersions of the (1x1) and (2x1) surfaces for several surface temperatures between 80K and 300K. These appear very similar over the entire surface Brillouin zone. The dominant peaks in the TOF spectra correspond to a dispersionless mode at about 13.5meV, which stiffens slightly as the temperature is raised. However, the lowest energy branch which is quite flat at low temperatures seems to soften near the zone center as the temperature increases. @FootnoteText@ @footnote 1@Supported by U. S. Department of Energy grant number DE-FG02-97ER45635.

5:00pm SS1+EM-TuA10 Deposition of Highly Oriented Mg@sub 3@(VO@sub 4@)@sub 2@ Thin Films for Use in Catalysis Studies, J.A. Ruffner, A.G. Sault, Sandia National Laboratories

Magnesium vanadates are potentially important catalytic materials for the conversion of alkanes to alkenes via oxidative dehydrogenation. However, little is known about the active sites at which the catalytic reactions take place. It may be possible to obtain a significant increase in the catalytic efficiency if the effects of certain material properties on the surface reactions could be quantified and optimized through the use of appropriate preparation techniques. Given that surface reactivity is often dependent upon surface structure and that the atomic level structure of the active sites in these catalysts is virtually unknown, we desire thin film samples consisting of a single magnesium vanadate phase and a well defined crystallographic orientation in order to reduce complexity and simplify the study of active sites. We report on the use of reactive RF sputter deposition to fabricate very highly oriented, stoichiometric Mg@sub 3@(VO@sub 4@)@sub 2@ thin films for use in these surface analysis studies. Preliminary depositions of Mg@sub 3@(VO@sub 4@)@sub 2@ onto amorphous substrates resulted in amorphous thin films. However, deposition of Mg@sub 3@(VO@sub 4@)@sub 2@ onto well-oriented, lattice-matched thin film "seed" layers such as Ti (0002), Au (111) or Pt (111) resulted in very strong preferential (042) crystallographic orientation (pseudo-hexagonal planes parallel to the substrate). This strong preferential growth of the Mg@sub 3@(VO@sub 4@)@sub 2@ suggests epitaxial (single-crystal) growth of this mixed metal oxide on the underlying metal seed layer. The effects of the substrate material, seed layer material, deposition temperature, and post-deposition anneal temperatures on thin film properties such as stoichiometry, crystallographic orientation, and chemical interactions will be reported.

Surface Science Division

Room 6C - Session SS2+EM-TuA

Semiconductor Surface Chemistry

Moderator: R.M. Feenstra, Carnegie Mellon University

2:00pm SS2+EM-TuA1 Medard W. Welch Award Address: Halogen Etching of Si with Emphasis on Atomic-Scale Processes, J.H. Weaver¹, University of Minnesota INVITED

Etching is the process of producing a pattern on a surface, and it is central to a great many technologies. Indeed, etching (material removal) plays a complementary role to growth (material addition), and product fabrication includes both etching and growth. This talk will review recent progress made in understanding surface etching of semiconductors. Emphasis will be on atomic-scale changes in surface morphologies for Si(100) etched with halogens, where the parameters that are controlled are the flux and the fluence of the beam and the reaction temperature of the substrate. The kinds of information that can be gained from atomic-resolution scanning tunneling microscopy will be highlighted. Etch morphologies will be linked to site-specific desorption energies, with consideration of terrace pitting and the formation of nanometer-scale patterns. The sequence of events leading to dihalide desorption and the role of vacancies will be described. Comparison of results for F-Si(100) and Cl-Si(100) shows the formation of defects in the second layer for F, a process that results in roughening rather than layer-by-layer etching observed for Cl.

2:40pm SS2+EM-TuA3 Micrometer-scale "Grooves" and Step Bunching during Extended Oxidation-induced Etching of Si(001) Surfaces, J.F. Nielsen, The Ohio State University; M.S. Pettersen, Otterbein College; J.P. Pelz, The Ohio State University

We have used in-situ STM and ex-situ AFM to observe large-scale step rearrangement on Si(001) surfaces that were heated by DC current at ~1000@super o@C for 3-43 hrs in ~10@super -5@ Torr of oxygen. Depending on sample miscut and current direction, these conditions produced either (1) no significant step rearrangement, (2) large scale (5-10µm) step-bunched regions (with separation increasing roughly as t@super 1/2@), or (3) large "grooves", consisting of a highly-ordered sinusoidal step array with in-phase alignment. The grooved and stepbunched phases can coexist on the same wafer, forming neighboring semicoherent patches extending over hundreds of microns. The interface between the two phases is remarkably sharp. The step-bunching was also observed on surfaces heated in vacuum (no oxygen), and may be similar to electromigration-related behavior reported by Doi et al.@footnote 1@ Regular arrays of "crossing steps" are also seen on the step bunched regions. It is not yet clear whether oxygen is required for the formation of the grooves. The grooves appear to be qualitatively different from the "wavy" steps reported by Tromp and Reuter@footnote 2@ in that they extend coherently over large areas and are not confined to sample regions of extremely low-miscut. We are currently mapping out the precise conditions necessary to produce each surface phase, and are using the wide terraces resulting from step-bunching in on-going studies of spontaneous step creation on ultra-flat Si(001) surfaces. @FootnoteText@ @footnote 1@ T. Doi, M. Ichikawa, and S. Hosoki, Phys. Rev. B. 55, 1864 (1997) @footnote 2@ R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. 68, 820 (1992).

3:00pm SS2+EM-TuA4 The Structure of Steps on Hydrogen-Passivated Si Surfaces, A. Laracuente, L.J. Whitman, Naval Research Laboratory

Steps play a critical role during epitaxy, so knowing their structure is crucially important to understanding how films grow. There has been a considerable effort to determine the step structure on Si surfaces oriented near (001).@footnote 1@ On surfaces tilted toward (111), there are four distinct step configurations, single- and double-layer A-type and B-type steps, commonly denoted as S@sub A@, S@sub B@, D@sub A@, and D@sub B@. B-type steps are almost always "rebonded," with two extra atoms per unit cell at the step edge. The extra atoms halve the dangling bond density along each step and thereby make this structure energetically preferred over a non-rebonded configuration. On surfaces tilted more than 3°, only rebonded D@sub B@ steps occur. Because most industrial Si film growth happens in the presence of hydrogen, an accurate picture of such growth requires an understanding of how H affects the Si step structure and dynamics. It was recently predicted theoretically that non-rebonded steps should be energetically more favorable on H-terminated Si.@footnote 2@ We have now verified this prediction experimentally on a

range of surfaces oriented from (001) to (114). We find that S@sub B@ steps "unrebond" after H-passivation, as predicted, completely altering the step energetics. Similarly, H passivation splits a large fraction of D@sub B@ steps into S@sub A@+S@sub B@ step combinations. These changes in step structure have a dramatic effect on the step dynamics and the resulting surface morphology, generally leading to much rougher surfaces. We will discuss how these changes can explain a variety of previous observations about the effects of H on Si film growth. @FootnoteText@ @footnote 1@ A. A. Baski, S. C. Erwin, and L. J. Whitman, Surf. Sci. 392, 69 (1997). @footnote 2@ S. Jeong and A. Oshiyama, Phys. Rev. Lett. 81, 5366 (1998).

3:20pm SS2+EM-TuA5 Microscopy of Si(001) Surface Defects Produced by keV He Ion Irradiation at Low Temperatures, K. Kyuno, D.G. Cahill, R.S. Averback, University of Illinois, Urbana-Champaign; J. Tarus, K. Nordlund, University of Helsinki, Finland

The interactions of bulk point defects (interstitials and vacancies) with silicon surfaces influences microstructures and dopant profiles created by low-energy ion implantation. To gain insight on the migration of ioninduced defects and their interactions with surfaces, we use variable temperature scanning tunneling microscopy (STM) to measure the areal density of surface defects created by 5 keV He ion irradiation of Si(001) at low temperatures. Samples are irradiated to a dose of 1.7 and 3.4x10@super 13@ ions cm@super -2@ at 80, 130, 180, and 294 K, and imaged at the same temperature. Because of the background density of surface vacancies, we focus our analysis of the STM images on the densities of adatoms, dimers, and clusters formed by the ion bombardment. The density of these protrusions at 80 and 130 K is approximately linear in dose, independent of temperature, and in reasonable agreement with our molecular dynamics calculations of surface defect concentrations. At 180 K, the measured density of protrusions is enhanced by a factor of ~3; we interpret this result in terms of the onset of bulk defect migration. Surprisingly, the Si(001) surface appears to be a relatively inefficient trap for bulk defects under our experimental conditions; our results can be explained by the migration and trapping of defects formed within less than 1 nm of the surface.

3:40pm SS2+EM-TuA6 A Variable Temperature Scanning Tunnelling Microscopy Study of Si(100) Etching Dynamics, C.F. Herrmann, J.J. Boland, University of North Carolina

The etching behavior of bromine on the Si(100) surface was investigated using variable temperature scanning tunneling microscopy (VT-STM). The clean Si(100) was initially dosed with bromine to passivate the surface. The passivated surface was then heated slowly and imaged simultaneously with no additional bromine exposure. STM images were taken at several temperatures from 600K to 750K to study the etching dynamics of Si(100) with bromine. The initial distribution of vacancies peaked at a single dimer unit and decayed monotonically to higher lengths. After further heating, repartitioning was observed and dimer vacancies of odd lengths were preferentially formed. The motion of single dimer vacancies was also observed in addition to a novel etching structure. The implications for chemical etching are discussed.

4:00pm SS2+EM-TuA7 Dissociative Adsorption and Recombinative Desorption of H2 on Si(100)-2x1, F.M. Zimmermann, X. Pan, Rutgers University

The interaction of hydrogen with Si(100) is of considerable technological importance since hydrogen desorption is the rate-limiting step in lowtemperature chemical vapor deposition of Si. Furthermore, this system is intriguing from a fundamental point of view, due to a multitude of unusual and remarkable experimental observations, such as desorption kinetics intermediate between first order and second order, and the so-called 'barrier puzzle': A large barrier to adsorption is seen in adsorption experiments, whereas in desorption dynamics experiments the desorbing molecules paradoxically show no signs of having traversed such a barrier. Using surface second harmonic generation, we have measured the adsorption and desorption kinetics as a function of surface temperature. H coverage, and exposure pressure. These measurements reveal more highly unusual kinetic behavior. Contrary to what is expected from Langmuirian site-blocking considerations, the sticking probability increases markedly with coverage, indicating a self-catalyzed adsorption mechanism. In addition, the sticking probability exhibits a pronounced dependence on exposure pressure, ruling out most 'simple' adsorption mechanisms. The observations are interpreted in terms of a self-catalyzed, barrier-less, interdimer adsorption mechanism (observed with the STM by Biedermann, Knoesel, Hu, and Heinz, submitted to Phys. Rev.). Our model quantitatively

explains the measured adsorption and desorption kinetics (temperature, coverage, and pressure dependence), and provides a natural explanation of the vexing barrier puzzle. Fitted model parameters are in very good agreement with independently obtained experimental and theoretical values.

4:20pm SS2+EM-TuA8 Novel Mechanisms for Plasma Etch Front and CVD (Chemical Vapor Deposition) Growth Front Roughening, Y.-P. Zhao¹, J.T. Drotar, G.-C. Wang, T.-M. Lu, Rensselaer Polytechnic Institute

Plasma etching and chemical vapor deposition (CVD) are major tools for thin film processing in microelectronic industry. Although kinetic roughening of thin films has attracted considerable attention in recent years, very little work has been focused on the study of surface roughening mechanisms during plasma etching and chemical vapor deposition. Here, we report a novel etch front roughening phenomenon during the plasma etching of Si(100) substrates. The surface power spectrum shows an obvious wavelength selection which does not occur in conventional noiseinduced roughening. The average local surface slope is almost invariant while the vertical roughness grows as a power law in time, w ~ t^@beta@, with a growth exponent @beta@ = 0.91 ± 0.03. We develop a general nonlocal model to describe the roughening process in plasma etching based on the gas transport kinetics for a large Knudsen number. The flux of the reactive particles redistributes according to the re-emission mechanisms that are influenced by the surrounding morphology. Our extensive numerical calculations and Monte Carlo simulations for various re-emission modes show that @alpha@ (roughness exponent) ~ @beta@ ~ z ~ 1 for plasma etching, which is consistent with our experimental results. Our calculations demonstrate that the proposed model is universal in describing the roughening of plasma etching. In addition, the reverse of this model can be used to describe CVD growth. Our Monte Carlo simulations show that @alpha@ ~ @beta@ ~ 0, z ~ 2 for CVD growth. Detailed comparisons between local and non-local dynamic growth models, as well as the growth and etching processes will also be presented. @FootnoteText@ Work supported by NSF.

4:40pm SS2+EM-TuA9 Resonance-Enhanced Multiphoton Ionization Studies of the Etching of Silicon by Molecular Chlorine, *T.A. Barckholtz, L. McDonough, S.R. Leone,* University of Colorado, Boulder

Laser ionization time-of-flight mass spectrometry is a powerful technique for characterizing the neutral products of the etching of semiconductor materials. We previously showed that single photon ionization (SPI), which uses the 9th harmonic of a Nd:YAG laser, provides excellent characterization of the neutral products of the etching of silicon by molecular chlorine, both thermally@footnote 1@ and during ion-enhanced etching.@footnote 2@ Two drawbacks of using the SPI technique are the low laser power available (ca. 10 µJ/pulse) and the lack of resolution of the state distributions (electronic, vibrational, rotational) of the products. To address these deficiencies, we recently implemented a Nd:YAG-pumped dye laser on an etching apparatus that enables resonant electronic multiphoton ionization (REMPI) schemes for the detection of the neutral species. Because of the greater laser power available (several mJ/pulse), the detection sensitivity has been dramatically increased. For example, the REMPI signal intensity of neutral atomic Si during thermal etching is approximately 200 times greater than the SPI intensity. Furthermore, complete state resolution of the Si spin-orbit (@super 3@P@sub 2@, @super 3@P@sub 1@, and @super 3@P@sub 0@) and metastable (@super 1@D@sub 2@) states is obtained. For SiCl, due to its broad rotational and vibrational distributions, the detection sensitivity is increased by a smaller factor, and only partially resolved state distributions are possible. We plan to use the enhanced sensitivity and partial state resolution to investigate the mechanism for the ion-enhanced etching of silicon by chlorine in greater detail than was possible with the SPI technique. The results of these studies will be compared with the predictions of published molecular dynamics simulations. @FootnoteText@ @footnote 1@Materer, N.; Goodman, R. S.; Leone, S. R. JVST A 1997, 15, 2134-2142. @footnote 2@Goodman, R. S.; Materer, N.; Leone, S. R. JVST A, submitted for publication.

5:00pm SS2+EM-TuA10 Femtosecond Photo-induced Dynamics on a Cleaned and a Chlorinated Si(111) Surfaces, S. Haraichi, F. Sasaki, Electrotechnical Laboratory, Japan

A photo-induced chemical etching of Si is considered as a powerful candidate of the next-generation device fabrication thechnology from the view point of extremely low damage. However the atomic and/or dynamic

mechanisms of the photo-induced reaction of Si/halogen systems have not been well understood. We have investigated photo-induced dynamics on a cleaned and a chlorinated Si(111) surfaces using femtosecond secondharmonic generation (SHG). For the pump-probe measurements, Tisapphire laser at 1300nm and 800nm with a 100fs pulse width were used as the probe and the pump beams, respectively. With the wavelength at 1300nm, a contribution of absorption is negligible and the surface specific information can be obtained. SHG intensities from a cleaned 7x7 surface decay rapidly just after the pump beam coincides with the probe beam and increase with a rapid and a slow time constants of around 1ps and more than several tens ps. These results were probably due to an immediate photo-excitation and two kinds of relaxation of 7x7 surface states. On the other hand, SHG intensities from a chlorinated Si surface increase rapidly just after the pump beam irradiation and decay with a time constant of around several ps, based on Si-Cl bonding states. On both a cleaned and a chlorinated Si surfaces, the time constants show no significant dependence on the pump beam fluency under the critical fluency of the etching reaction.

Surface Science Division Room 607 - Session SS3-TuA

Diffusion on Surfaces

Moderator: T.L. Einstein, University of Maryland

2:00pm SS3-TuA1 Mechanisms and Energetics in Diffusion of O2-Molecules and H-atoms on Si(1x1)-7x7 Surfaces, *R.L. Lo, I.S. Hwang, M.S. Ho,* Academia Sinica, Republic of China

Using a variable temperature STM, atom and molecular dynamics on solid surfaces can be observed directly and the energetics studied in detail. It is possible to trace the path of single particle movement, measure site and path specific hopping rates and the rate parameters of individual atoms and molecules on solid surfaces as well as to probe the mechanisms. We find that on Si(111)-7x7 surface, O2 molecules adsorb on top of adatom sites while H atoms adsorb on top of rest atom sites. Diffusion and hopping of H and O2 on this surface is achieved by hopping of chemical bonds via intermediate states. We have identified the intermediate states and also derived site and path specific activation energies and frequency factors, and the potential energy curves for the hopping of O2 and H on this surface. The physical significance of these measurements will be discussed. Research supported by NSC of ROC and Academia Sinica. 1. I-S Hwang, R-L Lo and T. T. Tsong, Phys. Rev. Lett. 78, 4797 (1997). 2. R-L Lo, I-S Hwang, M-S Ho and T. T. Tsong, Phys. Rev. Lett. 80, 5584 (1998).

2:20pm SS3-TuA2 Real-Time Imaging of Step Motion on Cu(100) with the Low Energy Electron Microscope@footnote 1@, C.L.H. Devlin, S. Chiang, X.D. Zhu, University of California, Davis

The low energy electron microscope (LEEM) is capable of real-time, realspace imaging of metal and semiconductor surfaces, at the scale of tens of nanometers. We have recently used a new instrument at UC Davis to image the motion of steps on the Cu(100) surface. We have seen a number of intriguing effects at the relatively low temperature range of 100 to 300°C. Impurities pin the step positions, affecting the shapes of the steps over regions of many microns. The kink density of the steps decreases with additional sample cleaning, with the steps becoming more rectilinear. Evidence exists for several different phases on the surface as a function of temperature, as the contrast on terraces changes markedly on the scale of 10-20 nm with increasing temperature. The size of an area corresponding to a particular phase also changes. In some cases, rapid fluctuations of the contrast at the boundaries are evident as the phase shrinks. For curved steps, wave-like motions have been observed along the length of steps. Steps have also been observed to move into and out of an impurity at constant temperature. An X-ray photoemission spectrometer and a commercial variable temperature scanning microscope (VT-STM) (50-800K) have recently been added to the UC Davis LEEM system and are being used to further characterize the Cu(100) system. @FootnoteText@ @footnote 1@Funded by National Science Foundation (DMR-95-12231).

2:40pm SS3-TuA3 Diffusion and Dynamics of 2D Clusters on Crystal Surfaces, G. Rosenfeld, University of Twente, The Netherlands; L.K. Verheij, D.C. Schloesser, IGV, Forschungszentrum Jülich, Germany; G. Comsa, University of Bonn, Germany INVITED

Using fast scanning tunneling microscopy, the diffusion and shape fluctuation of nanoscale vacancy clusters on a Cu(111) surface have been studied. The diffusion constant has been determined as a function of

cluster size and temperature, and the underlying atomic scale diffusion processes have been deduced.@footnote 1@ The results are discussed with respect to simple scaling theories. Via detailed analysis of cluster shapes and shape fluctuations both the anisotropy and the absolute value of the line tension, i.e., the specific free energy of cluster edges, have been determined.@footnote 2@ The experimental data yield a comprehensive set of energies believed to be representative for the diffusion and stability of 2D metal clusters on fcc(111) surfaces. @FootnoteText@ @footnote 1@ D.C. Schloesser, L.K. Verheij, G. Rosenfeld, G. Comsa, to be published @footnote 2@ D.C. Schloesser, L.K. Verheij, G. Rosenfeld, G. Comsa, Phys. Rev. Lett. 82, 3843 (1999).

3:20pm **SS3-TuA5 Sulfur's Effect on Cu(111) Surface Morphology**, *J. de la Figuera*, *K. Pohl, M.C. Bartelt, N.C. Bartelt, P.J. Feibelman, R.Q. Hwang*, Sandia National Laboratories

Numerous studies have demonstrated the dramatic effects that small amounts of an adsorbate can have on film growth and surface morphology. The origin for these effects range from kinetic limitations to thermodynamic considerations. We have recently observed that extremely small amounts of sulfur can significantly affect the smoothing of Cu(111). Cu islands of monolayer height decay several orders of magnitude faster in the presence of ~0.01 ML of sulfur as compared to the clean case. Using time-resolved STM, we have monitored the rate and morphology of the decay to identify the origin of this phenomenon. In agreement with these observations, first-principles calculations predict a dramatic change in the ratio of Cu step formation energies in the presence of a row of S atoms at the steps. Sulfur atoms bind more strongly to the A-type step. The ratio of the equilibrium lengths of the A- and B-type steps is about 1:1.1 on the clean surface, but about 2.4:1 when the step edges are S-saturated. We discuss the observed superfast island decay in terms of atomic processes at and near island edges, including S-mediated near-irreversible detachment of Cu atoms, enhanced diffusion of Cu adatoms and small clusters on the terraces, and more efficient downward transport. This work is supported by the Office of Basic Energy Sciences Division of Materials Sciences of the U.S. DOE (DE-AC04-94AL85000).

3:40pm SS3-TuA6 Influence of Adsorbates on the Self-diffusion of Pt Adatoms and the Stability of Pt Dimers, *S. Horch*, University of Aarhus, Denmark; *T.R. Linderoth*, University of Aarhus, Denmark, Sweden; *S. Helveg*, *L. Petersen*, *E. Laegsgaard*, *I. Stensgaard*, *F. Besenbacher*, University of Aarhus, Denmark

Surface diffusion of atoms is an important phenomenon in areas of materials processing such as chemical vapor deposition (CVD) and sintering. In these particular areas, the diffusion are modified by atoms adsorbed from the gas phase. Here we try to derive mechanistic insight into this effect from observations, using the Scanning Tunneling Microscope, of adsorbate promoted self-diffusion on the Pt(110)-(1x2) surface.@footnote 1@ In the case of hydrogen, we directly image an activated Pt-H complex (with H bound on top the Pt adatom) which has a diffusivity enhanced by a factor of 500 at room temperature, relative to Pt adatoms on the clean surface. The influence of other adsorbates also on the binding energy of Pt dimers is currently being investigated. @FootnoteText@ @footnote 1@ S. Horch, H. T. Lorensen, S. Helveg, E. Laegsgaard, I. Stensgaard, K. W. Jacobsen, J. K. Norskov and F. Besenbacher, Nature 398 (1999) 134.

4:00pm **SS3-TuA7 Study of Subsurface Hydrogen in Pd(111) by STM**, *M.K. Rose*, Lawrence Berkeley National Laboratory; *A. Borg*, Norwegian University of Science and Technology, Norway; *D.F. Ogletree*, *M. Salmeron*, Lawrence Berkeley National Laboratory

Using Variable Temperature Scanning Tunneling Microscopy we have studied hydrogen atoms embedded in the topmost layers of Pd(111) and the influence of these impurities on surface adsorbates. Hydrogen is imaged beneath surface three-fold hollow sites at 20K. Subsurface hydrogen atoms exhibit attractive interactions leading to aggregation into clusters. We observe diffusion of two distinct hydrogen species within the subsurface layer above 200K, with activation energies differing by approximately 10%. Significant variation in the diffusion barriers is found in the presence of surface adsorbates. Interlayer diffusion is not observed below 220K, which sets lower bounds on the surfacesubsurface and subsurface-bulk diffusion barriers and provides a benchmark for ab-initio total energy calculations. Scanning Tunneling Spectroscopy of subsurface hydrogen has been performed and the results are compared with tightbinding calculations. Adsorbed molecules interact strongly with subsurface H. In the case of CO, binding occurs preferentially at sites separated by @sr@3 lattice vectors from surface hollow sites above embedded

hydrogen. For O@sub 2@, thermal dissociation proceeds adjacent to H sites. Subsurface H clusters provide nucleation sites for ordered adsorbate structures, pin adsorbate domain boundaries, and hinder adsorbate diffusion.

4:20pm SS3-TuA8 Enhanced Interlayer Mass Transport and Dynamics of Film Smoothening on a Symmetry-broken Ag(111) Surface, H. Yu, C.-S. Jiang, University of Texas, Austin; Ph. Ebert, Forschungszentrum J@um u@lich, Germany; X.-D. Wang, C.K. Shih, University of Texas, Austin

We have studied the dynamics of the film flattening process at room temperature and higher annealing temperatures of Ag films deposited at low temperature on GaAs(110) surfaces. We will present a scanning tunneling microscopy movie, which shows the evolution of the film morphology over 13 hours at room temperature. The initial surface contains a distribution of surface heights up to five monolayers. The vacancy islands at the lowest layer and the islands at the top layer both decay very rapidly with the same decay constants. The remaining islands (of a surface with three monolayers exposed) decay with a much slower rate and we observed a freeze of decay after about 7 hours. Consecutive annealing up to 400 K induces a further decay of the roughness, such that finally nearly only two layers are exposed. The island size increased during room temperature and consecutive annealing steps considerably and the steps align preferentially along the high symmetry directions of the twofold superstructure present on the Ag surface. These results demonstrate the existence of a considerably enhanced interlayer mass transport and a different symmetry behavior compared to those observed for Ag homoepitaxy on Ag(111) surfaces. The enhanced interlayer mass transfer is interpreted in terms of a very low Ehrlich-Schwoebel barrier.

4:40pm SS3-TuA9 Ion-Enhanced Surface Diffusion: Experiment and Simulation, E.R. Blomiley, Z. Wang, E.G. Seebauer, University of Illinois, Urbana

Low-energy ion enhancement of thin film deposition has become an increasingly widespread technique for lowering growth temperatures and improving film properties. Rational process optimization has remained difficult, however, because the beneficial effects of enhanced surface diffusion are often opposed by the deleterious effects of sputtering and ion embedding. Good explanations for important aspects of the governing physical processes remain lacking. We have recently reported for the first time direct quantitative measurements of low-energy (<70 eV) ionenhanced diffusion, using the Ge/Si(111) adsorption system with noble gas ions as the bombarding species. The present work extends that work to examine the effects of incident bombardment angle. Experiments with second harmonic microscopy show that below about 750°C, diffusional enhancement increases monotonically as the incident angle increases from normal toward grazing. However, above 750°C diffusional effects change nonmonotonically in a manner more akin to sputtering yields. Molecular dynamics simulations show these effects arise from ion-induced adatomvacancy pair formation.

5:00pm SS3-TuA10 The Effect of As@sub 4@ Flux on the Ga Diffusion on the GaAs(001)-(2x4) Surface, D.W. Bullock, V.P. LaBella, Z. Ding, P.M. Thibado. University of Arkansas

The activation energy for an individual Ga atom to hop across the technologically important GaAs(001) 2x4 reconstructed surface as a function of As@sub 4@ flux was measured. This study was motivated by the ongoing development of short-period III-V semiconductor superlattices for electronic and optoelectronic applications grown by molecular beam epitaxy (MBE). This study was carried out in an ultrahigh vacuum MBE system with an in situ scanning tunneling microscope (STM) to study III-V single cryst al surfaces and interfaces on the atomic scale. The diffusion measurement was achieved by measuring the number density of islands as a function of substrate temperature and As@sub 4@ flux, and comparing it to random walk computer simulations of the grow th process. The Ga atom's relative probability to stick to existing island edges and its relative diffusion anisotropy are estimated. Interestingly, it was discovered that increasing the As@sub 4@ pressure forces the Ga atoms to diffuse more isotropically. This work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1 - 1058

Surface Science Division Room 4C - Session SS-TuP

Poster Session

SS-TuP1 Vacuum TPD from Traditional and Nano-fabricated Pt/Alumina Model Catalysts, *E. Fridell, T.R. Linderoth, B. Kasemo,* Chalmers University, Sweden

Temperature Programmed Desorption (TPD) is a valuable method to identify adsorbed species and investigate desorption kinetics. The usual method of performing TPD for (practical) catalyst samples is in a flow reactor under inert gas flow. The interpretatio n of the resulting spectra is hampered by complications associated with thermal gradients in the samples, re-adsorption of the desorbed species, gas phase transport under viscous flow conditions, etc.To remedy these problems, we have constructed an equip m ent allowing UHV-TPD from both model samples and "real" catalysts: The samples can be pre-treated at atmospheric pressures and high temperatures in a reactor cell mounted onto a UHV system. They are then exposed to the adsorbing gas before being transla ted to a position in front of a mass spectrometer for TPD in vacuum. The catalyst washcoat is applied directly onto, e.g., a metal foil which can be cooled or heated resistively providing precise temperature control. The equipment is intended primarily fo r catalysts made by traditional wetdeposition, but also for new "nano-fabricated" samples. To produce the latter, several methods are employed, for example we use colloidal particles adsorbed onto a surface as masks for sputtering of vacuum deposited metal/oxide films. After removing the colloidals the resulting 2D model catalysts consist, e.g., of Pt particles of uniform sizes and with controlled spatial separations on an alumina surface. In this presentation the equipment will be described and results of just initiated measurements concerning CO/oxygen adsorption on Pt/alumina catalysts will be presented.

SS-TuP2 Growth Mode of Au on SiO@sub 2@ Ultrathin Film, K. Luo, Texas A&M University; D.Y. Kim, Hallym University, Korea; D.W. Goodman, Texas A&M University

Au clusters supported on SiO@sub 2@/Mo(110) have been studied by xray photoemission spectroscopy(XPS), low energy ion scattering(LEIS), temperature programmed desorption(TPD) and low energy electron diffraction(LEED). At both 100 K and 300 K, the growth mode of Au at fractional monolayer coverages is quasi-two dimensional. With higher coverages, three dimensional growth of Au was found. No strong chemical interaction was observed between gold and silica. By annealing Au/SiO@sub 2@/Mo(110) to 1000 K, sintering of gold clusters was observed. The Au desorption activation energy was measured by temperature programmed desorption to be about 42 kcal/mol, lower than the sublimation energy of 90 kcal/mol for bulk gold.

SS-TuP3 Nucleation and Growth of Faceted Features on the Platinum Covered W(111) Surface, *K. Pelhos*, Rutgers, The State University of New Jersey; *J.B. Hannon, G.L. Kellogg*, Sandia National Laboratories; *T.E. Madey*, Rutgers, The State University of New Jersey

Low energy electron microscopy (LEEM) and scanning tunneling microscopy (STM) have been used to investigate the faceting of W(111) as induced by Pt. The atomically rough W(111) surface, when fully covered with a complete physical monolayer (1.7 x 10@super 15@ atoms/cm@super 2@) film of Pt and annealed to temperatures higher than ~750 K, experiences a significant morphological restructuring: the initially planar surface undergoes a faceting transition and forms three-sided pyramids with {211} faces. LEEM investigations show that when Pt is dosed onto the heated surface, the transition from planar to faceted structure proceeds through the nucleation and growth of spatially separated faceted regions starting at 2/3 physical monolayers coverage. STM reveals the atomic structure of the partially faceted surface, with large planar regions, dotted by clusters of pyramids of various sizes. On the other hand, when the initially planar sample is first completely covered with a physical monolayer of Pt and gradually heated, LEEM does not show any spatial separation in the faceting transition. STM observations of the initial stages of this transition show a continuous uniform roughening of the surface towards the faceted phase.

SS-TuP4 Adsorption of O@sub 2@ on Al(111) - No Evidence for "Hot Adatoms", M. Schmid, P. Varga, Technische Universität Wien, Austria Based on a scanning tunneling microscopy (STM) study,@footnote 1@ it has been suggested that adsorption of O@sub 2@ on Al(111) results in a high transient mobility of the two oxygen atoms created by dissociation of the oxygen molecule. It was suggested that these atoms move at least 80 Å apart before they come to rest at the surface.@footnote 1@ We have performed experiments under the same conditions. High-resolution STM images enable us to identify the features considered single O adatoms in ref. 1 as two O atoms in adjacent fcc hollow sites. We also find groups of three and four oxygen atoms, however. The dynamics of the O dimers point to an attractive interaction of O atoms in adjacent fcc hollow sites. These findings do not completely rule out the possibility of a large transient mobility and subsequent diffusion of individual O atoms, finally forming stable dimers. We consider it more likely, however, that only few O@sub 2@ molecules do not stay in adjacent hollow sites during adsorption and the single O adatoms created thereby diffuse until they coalesce with one of the dimers or larger O groups on the surface. With decreasing tunneling distance, Al atoms with three and two O neighbours appear as protrusions, explaining images with protrusions earlier attributed to single O adatoms. @FootnoteText@ @footnote 1@H. Brune et al., Phys. Rev. Lett. 68, 624 (1992); J. Chem. Phys. 99, 218 (1993).

SS-TuP5 Adsorption Dynamics of Oxygen on Al(111), A.J. Komrowski, University of California, San Diego; Y. Liu, Syagen Technologies, Inc.; 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. A previous study of Al(111) reacted with thermal O@sub 2@ at low coverages observed isolated features separated by >80 Angstroms which were attributed as dissociated O atoms.@footnote 1@ We have studied the oxidation of Al(111) using supersonic molecular beam techniques and scanning tunneling microscopy. The adsorption of monoenergetic O@sub 2@ on the Al(111) surface shows a change in the chemisorption site distribution (single reacted sites vs. doubles) with incident translational energy. We will contrast the O@sub 2@--Al(111) reaction against data from the reaction of supersonic oxygen atoms with Al(111) and compare the chemisorption results between activated and non-activated processes. @FootnoteText@ @footnote 1@ Brune, H. et. al. J. Chem. Phys. v99, 2128 (1993).

SS-TuP6 Water Dissociation on Boron-Doped Single Crystal Ni@sub3@(Al,Ti) (110) Surface, J. Wang, B. Zhou, Y.W. Chung, Northwestern University

Previous work demonstrated that water dissociates into hydrogen on Ni@sub3@(Al, Ti) (100) surfaces. There is clear evidence that this dissociation reaction results in the reduced ductility of many polycrystalline aluminum-based alloys in a moist environment. Ductility measurements further showed that addition of boron suppresses this moisture-induced embrittlement. To explore the effect of boron on water dissociation, we first dosed the surface of clean Ni@sub3@(Al, Ti) (110) with controlled amounts of boron, using a specially designed low-energy boron ion source, followed by low-temperature exposure to D@sub2@O and temperatureprogrammed desorption. Results indicated that water dissociates into atomic hydrogen on clean Ni@sub3@(Al, Ti) (110) boron-free surface, which was further verified by x-ray photoemission studies. This dissociation reaction is strongly suppressed by boron adsorption at a coverage of 0.5 monolayer. Auger studies on boron modified surfaces showed that boron is oxidized in this process. The chemical state of water was followed by x-ray photoemission. These studies indicated that addition of boron suppresses water dissociation into atomic hydrogen. By co-adsorption of D@sub2@O and oxygen on boron-modified Ni@sub3@(Al, Ti) (110) surfaces, the effect of oxygen was also investigated by temperature-programmed desorption. The significance of this observation will be discussed.

SS-TuP7 Ethene Adsorption on Cu(111), Cu@sub 3@Pt(111), CuPt@sub 3@(111), and Pt(111), T. Pelster, Universität Bonn, Germany; R. Linke, Eindhoven University of Technology, The Netherlands; J. Breitbach, A. Frey, Universität Bonn, Germany; M. Tanemura, Nagoya Institute of Technology, Japan; M. Grüne, R.-J. Linden, C. Becker, K. Wandelt, Universität Bonn, Germany

The adsorption of ethene on Cu(111), Cu@sub 3@Pt(111), CuPt@sub 3@(111), and Pt(111) at 100K has been investigated using high resolution energy electron loss spectroscopy (HREELS), temperature programmed desorption (TPD), ultraviolet photoelectron spectroscopy (UPS), and work function change measurements. On Pt(111) ethene forms at 100K a well known di-@sigma@-complex, whereas on Cu(111) ethene adsorbs in a

weakly bonded @pi@-complex which shows typical vibration spectra very similar to gaseous ethene. On Cu@sub 3@Pt(111) and CuPt@sub 3@(111) both species can be found, with higher intensity of the @pi@-complex on the Cu@sub 3@Pt(111) and the di-@sigma@-complex on the CuPt@sub 3@(111) surface, respectively. A full peak assignment in HREELS spectra gives a strong indication for a reduction of the C-C bond order of the di-@sigma@-species going from Cu@sub 3@Pt(111) to Pt(111). This can be attributed to an electronic effect due to the dilution of Pt by Cu. Both TPD and UPS support these results. Surprisingly, ethene does not dehydrogenate on the alloys when the surface is heated in contrast to ethene on Pt(111). This can be explained by the lack of appropriate sites on Cu@sub 3@Pt(111). On CuPt@sub 3@(111) the issue is more complex since on this surface such sites are available. On this surface the process might therefore be kinetically hindered.

SS-TuP8 HREELS and XPS Studies of Fe(C@sub 5@X@sub 5@)@sub 2@ / Ag(100) where X=H, D, or Me, C.M. Woodbridge, D.L. Pugmire, M.A. Langell, University of Nebraska, Lincoln

Although metallocenes show great potential as novel Chemical Vapor Deposition (CVD) source molecules, very little is known about how they bond to metal surfaces. Therefore, systematic investigation of ferrocene adsorption to different single crystal substrates are essential for understanding and controlling CVD processes involving metallocenes. We have used HREELS and XPS to study ferrocene, Fe(C@sub 5@H@sub 5@)@sub 2@, deuterated ferrocene, Fe(C@sub 5@D@sub 5@)@sub 2@, and its methylated derivative on Ag(100). HREELS was used to confirm the molecular nature of the adsorbed metallocene, determine the orientation and quantify interactions between ferrocene and the silver substrate. XPS was used to evaluate the chemical state of iron and carbon in the ferrocene films and to quantify the adsorbate surface concentration. Specific information about orientation and chemical shifts as a function of ferrocene exposure will also be presented.

SS-TuP9 Insertion Process of Conjugated Molecules into n-Alkanethiol Self-Assembled Monolayers on Au(111), *T. Ishida*, JRCAT-NAIR and PRESTO-JST, Japan; *W. Mizutani*, JRCAT-NAIR, Japan; *U. Akiba*, Tokyo Institute of Technology, Japan; *N. Choi*, JRCAT-ATP, Japan; *M. Fujihira*, Tokyo Institute of Technology, Japan; *H. Tokumoto*, JRCAT-NAIR, Japan

Since conjugated molecules are a good candidate for the components of nanoscale devices, functions of organic molecules have been investigated in search of their potential applications. To analyze the property of such conjugated molecules, insertion of such a molecule into pre-assembled nalkanethiol SAMs on Au(111) is attracted recently. We have investigated using STM insertion process of conjugated molecules, benzylmercaptane 4-biphenylmethanethiol (BP), and [1,1':4',1"-Terphenyl]-4-(BM). methanethiol (TP) into alkanethiol SAMs. These conjugated molecules were inserted into boundaries between structural domains of n-alkanethiol SAMs at the initial stage of insertion reaction. The insertion process rate increased with the number of phenyl rings of the conjugated molecule, i.e., the most of alkanethiols were replaced by BP and TP for 3-4 h and 2 h, respectively. On the other hand, BMs were inserted in the domain boundaries even after one day insertion reaction. These results suggested that the interaction energy difference between the conjugated molecules and alkanethiols strongly affected the insertion reaction.

SS-TuP10 Adsorption and Thermal Decomposition of 1,3-butadiene and 2butyne on Ru(001), *M.J. Weiss*, *C.J. Hagedorn*, *W.H. Weinberg*, University

of California, Santa Barbara The low temperature (80 K) molecular adsorption and subsequent thermal decomposition of 1,3-butadiene and 2-butyne are studied on Ru(001) using temperature programmed desorption and high resolution electron energy loss spectroscopy (HREELS). After heating to 300 K, the 1,3-butadiene decomposes to yield a (CH)@sub 4@ surface metallacycle. This result is particularly interesting in that the (CH)@sub 4@ species has been implicated as an intermediate in the production of 1,3-butadiene (and other molecules) during thiophene hydrodesulfurization. 2-butyne adsorbs at a coverage of 0.27 molecules for every surface ruthenium atom, a coverage which is equal to that observed for the adsorption of acetylene on this surface. The 2-butyne decomposes to yield surface hydrocarbon fragments whose HREEL spectra resemble those of vinylidene, acetylide, and methylidyne. Slight differences in the spectra, however, suggest that the fragments observed in the present work may actual be analogous species containing four carbon atoms.

SS-TuP11 A Study of Boron Effects on the Reaction of Co and SiGe at Various Temperatures, *H.J. Huang*, *K.M. Chen*, National Chiao Tung University, Taiwan, R.O.C.; *T.C. Chang*, *G.W. Huang*, *L.P. Chen*, National Nano Device Laboratory, Taiwan, R.O.C.; *C.Y. Chang*, National Chiao Tung University, Taiwan, R.O.C.

The boron effects on Co and SiGe interfacial reaction were studied with RTA from 500°C to 1000°C. The undoped and in-situ boron-doped strained Si@sub 0.91@Ge@sub 0.09@, Si@sub 0.85@Ge@sub 0.15@ layers were prepared at 550°C by ultra-high vacuum chemical vapor deposition system for silicidation. The resulting films were characterized by sheet resistance measurement, Auger electron spectroscopy, X-ray diffractometry, high resolution X-ray diffractometry, secondary ion mass spectroscopy, scanning electron microscopy, and transmission electron microscopy. Co(Si@sub 1y@Ge@sub y@) cubic structure was formed from 500°C to 700°C RTA with different Ge content. For the boron-doped sample, Ge content (y = 0.064, 0.054) in Co(Si@sub 1-y@Ge@sub y@) was less than undoped sample (y= 0.12, 0.11) after 500°C RTA, which can be discovered by X-ray diffraction. This implied that boron atoms retarded the incorporation of Ge into the Co(Si@sub 1-y@Ge@sub y@) ternary phase. It also led to large piled-up of Ge at the reaction interface. On the other hand, according to the X-ray rocking curve, boron-doped sample led to less relaxation of strained SiGe layer. Furthermore, from sheet resistance measurement, the formation of CoSi@sub 2@ was a little slower in boron doped sample than in undoped sample. This may be due to the decrease of Co diffusivities, which was caused by the boron accumulation at the Co/SiGe reaction interface. At temperature above 800°C, CoSi@sub 2@ was formed and the underlying SiGe layer was almost totally consumed. From the AES and TEM analyses, Ge segregation to the surface and the CoSi@sub 2@ grain boundary was observed.

SS-TuP12 Vacancy Mediated Growth of Ga@sub 2@Se@sub 3@ Thin Films, Z. Qian, Z. Dai, F.S. Ohuchi, University of Washington; K. Ueno, A. Koma, University of Tokyo, Japan; S. Meng, M.A. Olmstead, University of Washington

Ga@sub 2@Se@sub 3@ thin films were grown on GaAs(100) and Si(111) substrates by molecular beam epitaxy (MBE). In spite of large differences in lattice and symmetry found in GaAs(100) and Si(111), reflection high energy electron diffraction (RHEED) showed that the Ga@sub 2@Se@sub 3@ thin films were epitaxially grown on both surfaces. Electronic structures were determined by ultraviolet photoelectron spectroscopy (UPS) and electron energy loss spectroscopy (EELS). For the Ga@sub 2@Se@sub 3@ thin films growth on GaAs(100) substrate, transmission electron microscopy (TEM) revealed that vacancies were distributed on one set of the [111] crystal planes of @alpha@-Ga@sub 2@Se@sub 3@ structure by forming a @sr@3x@sr@3 configuration, resulting in the formation of vacancy ordered @beta@-Ga@sub 2@Se@sub 3@ structure. In this structure, modulation periodicity along [110] crystal directions was three times larger than that of @alpha@-Ga@sub 2@Se@sub 3@, and the crystal structure was consistent to the model proposed by Lübbers and Leute for bulk material (J. Solid State Chem., 43 (1982) 339). Very different nature of the growth habit was observed on the Si(111). High population of planer defects observed in the thin film was regarded as the result of Ga vacancy ordering in the crystal structure of Ga@sub 2@Se@sub 3@. We claim that the vacancies play an important role in determining the thin film structure in addition to lattice and symmetry matching conditions in the heteroepitaxy.

SS-TuP13 Surface Morphology of Ge(111) and Ge(001) Etched by keV Xe Ions, J.C. Kim, D.G. Cahill, R.S. Averback, University of Illinois, Urbana-Champaign

In situ scanning tunneling microscopy (STM) was used to study the surface morphology and defects created by keV Xe@super +@ ion etching of Ge(111) and Ge(001). Starting surfaces were prepared by etching single crystal Ge wafers at ~ 510 @super o@C by 5 keV Xe@super +@ ions with ion flux of 2.7 x 10@super 13@ ions cm@super -2@s@super -1@ and fluence of 5 x 10@super 16@ ions cm@super -2@; the samples were subsequently cooled and etched at lower temperatures with various ion fluences and ion energies, and imaged at room temperature. Ge(111) and Ge(001) surfaces remain crystalline after being etched at T @>=@ 295 @super o@C. Crater-like surface features, which were not observed on the starting surfaces and will be called pits, were observed on both Ge(111) and Ge(001) surfaces etched at 295 @super o@C and 325 @super o@C. These pits are ~ 200 Å in diameter and are surrounded by closely spaced steps. Pits were observed on the Ge surfaces etched by Xe@super +@ ions with energies as low as 650 eV. Etching of a Ge(111) buffer layer, which was grown at ~ 365 @super o@C with the thickness of 1000 Å in an in situ

MBE chamber, at 295 @super o@ was performed to examine the interaction of 5 keV Xe@super +@ ions with the surface prepared without etching at high temperature and revealed no pits. These results that pits were observed following 650 eV Xe@super +@ ion etching and not observed following etching of an MBE buffer layer suggest that these large surface features are not the result of the individual surface cascades as has been observed for 20 keV Ga ions. The pits initially grow in size and number and eventually disappear after the samples were etched for approximately one hour, leading to different surface roughening morphologies at 295 @super o@C and 325 @super o@C. Rutherford backscattering spectroscopy (RBS) data show that Xe atoms are implanted below the starting surface, subsequent ion etching at lower temperatures causes a broadening of Xe peak in RBS spectra. Our data suggest that interaction of bulk defects, e.g. Xe bubbles or vacancy clusters, with surface can have a strong influence on the evolution of surface morphology during ion etching at keV energies.

SS-TuP14 Surface Core Level Shift on GaN(0001) Surface, *Y. Yang*, *S.H. Xu*, *H. Cruguel*, *G.J. Lapeyre*, Montana State University; *H.J. Ho*, TopoMetrix Co. Synchrotron radiation photoelectron spectroscopy (SRPES) has been employed to investigate the electronic structure of clean wurzite GaN(0001) surface. The Ga 3d, N 1s and valence band emissions are measured by recording the energy distribution curves (EDC). A surface-shifted core level component is observed in the Ga 3d emission. It is located at 0.6 eV higher binding energy than the bulk component. The surface component is sensitive to atomic H adsorption. Experiment with deposition of ultra-thin Mg layer strongly support that it is attributed to the first layer Ga atoms. On the same sample, the surface core level shift of N 1s is identified at 1.0 eV lower binding energy side of the bulk component. The origin of the observed surface core level shifts will be discussed. Atomic-force-microscopy (AFM) image with line profiles are also acquired to determine the surface morphology.

SS-TuP15 Raman-scattering Study of In(As,Sb)/InSb Superlattices, B. Marcos, R. Cuscó, Institut Jaume Almera (CSIC), Spain; R.A. Stradling, Imperial College, U.K.; L. Artús, Institut Jaume Almera (CSIC), Spain

InAs@sub 1-x@Sb@sub x@ alloys display the smallest bandgap in the III-V group for x=0.6. By growing In(As,Sb)/InAs superlattices even smaller effective bandgaps can be obtained, making these layer structures very interesting for applications to mid- and far-infrared semiconductor lasers and light-emitting diodes operating at wavelengths from 4 to beyond 10 µm. In a previous paper@footnote 1@ we reported a Raman-scattering study of the optical phonon modes of InAsSb/InAs strained-layer superlattices(SSL) for different Sb compositions, but to our knowledge no study has been reported so far on the phonons of the other end system SSLs, namely the InAsSb/InSb SSLs. In the present work we report Raman measurements on InAsSb/InSb SSLs for several As concentrations below 20%. The InAsSb alloy displays a two-mode behaviour,@footnote 2@ and consequently the InSb-like and InAs-like LO modes of the alloy are expected. In fact, despite the low As concentration of the alloy, in the (Z|XY|-Z) Raman spectra we could observe not only the InSb-like LO mode of the alloy but also the InAs-like LO mode. The strain-induced relative shift of this peak is well accounted for by elastic strain calculations. In the (Z|XX|-Z) configuration an additional peak is observed below the InSb-like LO mode of the alloy that can be tentatively assigned to interface modes. @FootnoteText@ @footnote 1@ L. Artús, R. A. Stradling, Y. B. Li, S. J. Webb, W. T. Yuen, S. J. Chung, and R. Cuscó, Phys. Rev. B 54, 16 373 (1996). @footnote 2@ Y. B. Li, S. S. Dosanjh, I. T. Ferguson, A. G. Norman, A. G. de Oliveira, R. A. Stradling, and R. Zallen, Semicond. Sci. Technol. 7, 567 (1992).

SS-TuP16 The Adsorption and Thermal Decomposition of Monomethylamine Adsorbed on Si(100), A.J. Dennis, C.P.A. Mulcahy, S.M. Casey, University of Nevada, Reno

Monomethylamine (MMA) adsorption on the Si(100)-(2x1) surface has been studied using Auger electron spectroscopy (AES), low-energy electron diffraction and temperature-programmed reaction spectroscopy (TPRS). It is shown that at room temperature MMA chemisorbs dissociatively on this surface. TPRS data show that the decomposition of the adsorbed MMA proceeds via two different mechanisms. The surface bound adsorbates can decompose via reactions that form gaseous hydrogen and hydrogen cyanide products; however, they may also decompose via a reaction channel producing gaseous ammonia. AES results show that repeated decomposition of MMA on Si(100) leads to the slow deposition of carbonand nitrogen-based films. Kinetic analysis of the TPRS data will be discussed along with results from ab initio calculations modeling MMA adsorption on nine-atom silicon clusters.

SS-TuP18 The Formation of di-@sigma@ Bond in Chemisorbed Benzene and Chlorobenzene on Si(111)-7x7, Y. Cao, G.Q. Xu, National University of Singapore, Singapore

The adsorption of aromatics on Si surfaces has attracted great interests recently. In the present study, the adsorption of benzene and chlorobenzene on Si(111)-7x7 has been studied using high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). Both chemisorbed and physisorbed benzene were observed at an adsorption temperature of 110 K. Chemisorbed benzene desorbs molecularly at 350 and 364 K while physisorbed molecules desorb at 180 K. In the HREELS studies, two separate energy losses at 2920 and 3025 cm@super -1@ were observed for chemisorbed benzene, attributable to the C-H stretching vibrations of sp@super 3@ and sp@super 2@ carbon atoms, respectively. In addition, the formation of Si-C bond is also evidenced at a vibrational frequency of 540 cm@super -1@. Our results clearly demonstrate that benzene is di-@sigma@ bonded to the adjacent adatom and rest-atom on Si(111)-7x7, forming a 1,4cyclohexadiene-like structure. The adsorption behaviour for chlorobenzene is guite similar to that of benzene. However, due to the substitution effect of the Cl atom on ring of benzene, a regional-selective adduction of 2,5sites in chlorobenzene on Si(111)-7x7 is observed, resulting the formation of 2,5-chlorocyclohexadiene like adduct.

SS-TuP19 Dissociative Adsorption of Molecular Hydrogen on Si(001): Energy Dependence, Angular Distribution and Reaction Mechanism, *M. Duerr, M.B. Raschke, U. Hoefer,* Max Planck Institut fuer Quantenoptik, Germany

The dissociative adsorption of molecular hydrogen on Si(001) surfaces was investigated by means of supersonic molecular beam techniques and optical second harmonic generation (SHG). Sticking on the flat surfaces shows strong activation with beam energy as well as surface temperature.@footnote 1@ Preparing single-domain surfaces by selectively passivating the step sites of vicinal Si(001) surfaces, polar and azimuthal distributions of the sticking coefficient could be measured. The polar distributions are found to be peaked towards the surface normal. However there is a strong azimuthal dependence, the distribution is considerably narrower (cos@super 12@) for incident angles perpendicular than parallel to the dimers (cos@super 3.5@). For multi-domain surfaces, the reduction of the sticking coefficients is more pronounced than it is to be expected by the reduction of normal energy. Therefore the energetic corrugation dominates the adsorption process. Temperature dependence of the sticking coefficient, deviation from normal energy scaling and azimuthal anisotropy result from the covalent bindings on the semiconductor surface, which lead to a strong corrugation of the potential energy surface and the strong influence of lattice vibrations on reaction dynamics. Proposed defect mediated mechanism, leading to an enhancement of sticking under glancing incidence can be excluded. @FootnoteText@ @footnote 1@ M. Duerr, M. B. Raschke, and U. Hoefer, J. Chem. Phys. (submitted).

SS-TuP20 Silicide Island Nucleation Behavior for Co/Si(111) Studied with STM and LEEM, T.H. McDaniels, P.A. Bennett, Arizona State University

We have measured the coverage and temperature dependence of island nucleation during deposition of Co on Si(111)-7x7 using STM for low temperature and LEEM for high temperature. Below 500C, 3 distinct structures occur: "lowered" regions mostly on the unfaulted half of the 7x7 unit cell, "raised" regions mostly on the faulted half, and flat island structures with a 2x2 pattern of silicon adatoms. Island density vs coverage follows a growth exponent near 1, suggestive of i=0 behavior (stable nucleus contains a single atom), and the temperature dependence is relatively weak. From 600-900C, the islands are atomically flat CoSi2, and they form only at step edges following completion of a 1x1-RC ("ring-clusters") layer. Island density is now much lower and strongly temperature dependent with an activation energy of approximately 2.0eV.

SS-TuP21 Nickel Graphite Intercalation Compound formed by High Temperature Deposition of Ni on SiC, K. Robbie, Linköping University, Sweden, Canada; T. Jemander, N. Lin, R. Erlandsson, G.V. Hansson, L.D. Madsen, Linköping University, Sweden

While studying the growth of sputter-deposited nickel on 6H SiC (0001) substrates, an unexpected islanded structure was formed. Nickel, deposited at room temperature and annealed to 950 C to form Ni@sub 2@Si, is the most common approach for forming ohmic contacts to n-type

SiC. In this study aimed at gaining understanding of the contact formation process, we sputter-deposited Ni layers of varying nominal thickness (subto 1000 monolayers) onto hydrogen-etched on-axis SiC substrates at temperatures ranging from ambient to 1000 C and subsequently annealed to 1000 C. In-situ analysis was performed with RHEED, LEED and/or STM. Unlike all previous experience with Ni deposited onto SiC, we observed the formation of islands of two types, one of which had very steep sidewalls (>60 degrees) and an extremely flat top with a peculiar "stitched" surface structure. Microspot AES analysis has shown that the islands are composed of Ni and C, or Ni, Si, and C, and that the carbon is bound graphitically in both types. Investigations with STM, AFM, and AES, and comparison to literature, has led us to believe that a new type of graphite intercalation compound was formed in the flat topped islands with a composition of approximately NiC@sub 12@, and that Ni on the top graphite sheet produced the "stitched" surface structure observed by STM. Previously, only alkali metals and transition metal chlorides have been shown to intercalate into the galleries of graphite, and the reactivity and instability of these compounds has limited their use in spite of their very exciting electronic, magnetic, and other physical properties.

SS-TuP22 Surface Modification in Heteroepitaxy : Laminar, Crystalline Silicon on CaF@sub 2@, B.R. Schroeder, S. Meng, A. Bostwick, University of Washington; E. Rotenberg, Lawrence Berkeley National Laboratory; M.A. Olmstead, University of Washington

CaF@sub 2@/silicon heterostructures are strong candidates for obtaining visible light emission from silicon. However, the heteroepitaxial growth of laminar, crystalline silicon on CaF@sub 2@(111) substrates is hindered by two factors 1) CaF@sub 2@ surface energy is much lower than that of Si and 2) a strong etching reaction between Si and F. We have overcome these difficulties through surface modification 1) use of arsenic as a surfactant 2) electron irradiation to remove surface fluorine. Low energy (40 eV) electron irradiation removes fluorine (amount of F removed scales linearly with the electron dose) but the films become extremely reactive with oxygen and/or water vapor (even under UHV conditions). Arsenic termination stabilizes this surface and serves as a surfactant for the subsequent silicon growth. X-ray photoelectron spectroscopy shows Ca-Si bonds at the interface and As-Si bonds at the surface. The silicon surface has a bulk-like termination, characteristic of Si(111):As, as evidenced by the 1X1 LEED pattern. X-ray photoelectron diffraction shows that the grown silicon layer is crystalline, rotated 180@super o@ with respect to the CaF@sub 2@ substrate (Type B interface), and completely covers the CaF@sub 2@. Supported by DOE grant DE-FG03-97ER45646/A002.

SS-TuP23 X-ray Photoemission and Near Edge Absorption Studies of Rhenium (VII) Sorption onto Fe-bearing Materials, *P. Liu*, *W.W. Lukens*, *Jr.*, *E.J. Moler*, *D.K. Shuh*, Lawrence Berkeley National Laboratory

Technetium (@sup 99@Tc) is a radioactive byproduct of nuclear fission. and its concentration may set the regulatory limit for disposal of nuclear wastes. Therefore, the high solubility and mobility of TcO@sub 4@@sup -@ needs to be addressed. A solution is to reduce Tc@sup 7+@ to Tc@sup 4+@, which is much less soluble and mobile. One method is by adsorbing Tc@sup 7+@ onto surfaces of reducing agents. While previous experiments demonstrated that Tc@sup 7+@ ions were sorbed on and reduced by some materials, the products and the mechanism of sorption and reduction are not fully characterized or understood. Rhenium (Re) has similar redox properties as Tc, and can be treated as a surrogate for Tc in selected systems. Since Re is non-radioactive, experiments are more efficiently performed. A class of possible reductants are Fe, Fe oxides, and sulfides. Sorption samples were prepared by immersing powders of Fe metal, FeO, FeS, and FeS@sub 2@, respectively, in 0.010M Re(VII) solution for 24 hours or longer, during which time the powder and the solution were constantly mixed. The reacted powders were extracted after the mixtures were centrifuged and the solutions decanted. The photoemission of Re 4d and 4f core levels, and NEXAFS of Re N@sub III@ experiments were carried out at the Advanced Light Source. The results reveal that the amount of absorbed Re decreases from Fe metal, through FeO, FeS, to FeS@sub 2@; and that different species of Re are sorbed on surfaces of different Fe-bearing materials, with more oxidized species tending to dominate on the less sorbed surfaces. Together with the pH measurements of the residual solutions, the results suggest that the sorption and reduction of Re on the surfaces of Fe-bearing materials are partially controlled by the final pH of the solution-particle mixture.

SS-TuP24 Epitaxial Growth of Thin Ag Films on Al(001) and Al(110) Surfaces@footnote 1@, N.R. Shivaparan, M.A. Teter, R.J. Smith, Montana State University

We report the results of a characterization of Ag films (0 to 60 Å thick), deposited onto Al(001) and Al(110) surfaces at room temperature, using high energy ion backscattering and channeling, x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). For the Al(001) surface, measurements of the backscattered ion yields from Al and Ag atoms show that the Ag atoms occupy fcc lattice sites and shadow Al substrate atoms. However, the ion scattering yields and photopeak intensities do not follow layer-by-layer model growth curves. Together with the evolution of the Ag 3d core level binding energies and the valence band shape as a function of Ag coverage, these results support a model of interface strain relief by means of Ag-Al alloy formation, with the interface ultimately covered by an ordered, epitaxial Ag film. For the Al(110) surface the observations are closer to those expected for layer-by-layer Ag growth, but still show evidence of some Al diffusion into the well-ordered Ag overlayer. @FootnoteText@ @footnote 1@ Work supported by NSF Grant No. DMR-9710092 and by NASA EPSCoR Grant NCCW-0058 .

SS-TuP25 The Reactivity of Short Chain Alcohols on VC (100), R.L. Guenard¹, University of Houston; S.S. Perry, University of Houston, US

The reactions of small chain alcohols on the nonpolar (100) surface of single crystal VC have been studied using temperature programmed desorption (TPD). The surface was prepared by argon ion sputtering followed by electron beam heating to 1400K. The sample was sputtered and annealed between coverages, as well, in order to insure the removal of any oxides formed in the reaction with an alcohol. The results of these experiments showed that VC exhibits selective reactivity towards alcohols including, dehydrogenation and alkene formation. In these TPD measurements, methanol adsorbed both molecularly and dissociatively onto VC. The products of temperature induced desorption being H@sub2@ and CH@sub4@. A molecular desorption reaction path was also observed. For ethanol and isopropanol, the resulting products of temperature induced desorption were notably different from that of methanol. A @beta@-hydride elimination mechanism results in the formation of water and an alkene. Ethylene and water are evolved from the surface when dosed with ethanol, while propene and water are the products evolved when isopropanol is dosed. In both cases the alkene product is separated from the surface at a temperature greater than water desorption. This reactivity of short chain alcohols, observed near room temperature on VC (100), illustrates potential pathways of lubricant degradation and highlights the possible need for passivating additives.

SS-TuP26 Extremely Efficient Electron Stimulated Desorption of Hydrogen from GaN(0001), V.J. Bellitto², Georgia State University; B.D. Thoms, Georgia State University, US; D.D. Koleske, A.E. Wickenden, R.L. Henry, Naval Research Laboratory

To achieve high etch rates and anisotropy during etching of GaN, high temperatures, reactive chemicals, and/or high ion energies are required. The use of electron or photon stimulated processes for etching may be one method to avoid the use of reactive chemicals, damage produced by high ion energies, and materials limitations imposed by high temperatures. Electron stimulated desorption (ESD) of H from GaN(0001) has been observed and characterized using electron energy loss spectroscopy (ELS). Bombardment with 90 eV electrons produces a reversal of H induced changes in the ELS data at 3.5, 6.6, and 11.7 eV. We attribute the electronstimulated desorption of hydrogen from surface Ga-H to be responsible for these reversals. The reversal of H induced changes to ELS was monitored versus electron exposure to determine the ESD cross section. We measured a cross section for ESD of H of 2 x 10 @super -17@ cm@super 2@ with a reduction of ~3 for the ESD of D to 7 x 10 @super -18@ cm@super 2@. The cross section for the ESD of H from GaN(0001) is 2 to 4 orders of magnitude greater than reported on Si surfaces. On GaN the cross section for ESD of D is ~3 times smaller than for H, while on Si(100) the ESD of D is ~50 times less than for H. Assuming the ESD of H from GaN(0001) occurs through an electronically excited state, as in the Menzel-Gomer-Redhead (MGR) model, the presence of a large cross section and small isotope effect would indicate slow quenching of the excited electronic state. In general, longlived surface electronic excitations would result in enhanced efficiencies for electron- or photon-stimulated processes. This extremely fast ESD of H also has consequences for electron spectroscopies (LEED & ELS) of H/GaN using similar electron energies and current densities. For example, under the

¹ Morton S. Traum Award Finalist ² Morton S. Traum Award Finalist

conditions used in these experiments (90 eV, 33 μ A/cm@super 2@), 34 % of the surface H is removed in the first minute of electron exposure. In essence, the H is removed from GaN(0001) more quickly than many electron spectroscopies can be performed.

Surface Science Division Room 606 - Session SS1-WeM

Surface Structure

Moderator: J. Hinch, Rutgers University

8:20am SS1-WeM1 Temporal Diffraction: A New Method for Studying Surface Kinetics, E.H. Conrad, The Georgia Institute of Technology INVITED An understanding of surface kinetics is crucial to many areas of 2D and 3D film growth. A variety of techniques are currently available to extract surface kinetics parameters such as diffusion coefficients, atom attachment rates to islands and steps, etc. Most of these techniques, however, are limited to low coverages (i.e., single atom kinetics) and a limited temperature range (usually far from equilibrium). We have been developing a new technique, Temporal LEED Spectroscopy (TLS), that should be applicable over a much larger range of temperatures and up to hydrodynamic diffusion densities where equations are applicable.@footnote 1@ This technique uses the inherent intensity fluctuations, @delta@I(t) = I(q,t)-, in a surface diffraction experiment that are caused by the motion of steps, atoms, grain boundaries, etc. From these fluctuations a self auto-correlation function, G(@tau@)) <@delta@I(t)@delta@I(t+@tau@)>, is constructed that contains the essential kinetics information. I will present a short discussion of how the technique works and the limits on its sensitivity and time resolution. As a specific example, I will show how kinetics information from a system of fluctuating steps on a vicinal surface can be extracted. Data will be presented for two systems where the step motion is governed by different rate limiting kinetics: stepped W(430) and stepped Si(111) surfaces. @FootnoteText@ @footnote 1@ E.H. Conrad, A. Menzel, S. Kiriukhin and M.C. Tringides, Phys. Rev. Lett. 81, 3175 (1998).

9:00am SS1-WeM3 Similarities in Tensile and Compressive Strain Relief in Growth of Cu and Ag on Ru(0001)@footnote 1@, A.P. Baddorf, Oak Ridge National Laboratory; H. Zajonz, Brookhaven National Laboratory; D.M. Zehner, Oak Ridge National Laboratory; D. Gibbs, Brookhaven National Laboratory

Growth and dynamics of strained films of Cu and Ag on Ru(0001) have been studied at temperatures between 300 and 925 K using x-ray diffraction. A diverse series of structures are observed, which appear to be prevalent in heteroepitaxial growth on hexagonal surfaces. Thin films of both Cu and Ag are initially strained, in the first case from tensile stress of a 5.8% lattice mismatch and in the second from compressive stress of a 6.3% mismatch. Both Cu and Ag form stripe phase reconstructions, in which strain is reduced by uniaxial contraction or expansion along the [100] direction of the film. In Cu films, the stripe phase appears during formation of the second layer, the first being pseudomorphic, while in Ag films the first layer forms the stripe phase. For Cu, the stripe phase undergoes an abrupt incommensurate/commensurate transition to a registry dependant on temperature. Differences in thermal expansion may explain this temperature dependence. A second registry is correlated with third layer growth of Cu, however the third layer is metastable. At higher coverages, both Cu and Ag stripe phases coexist with (111) oriented 3-dimensional islands. For Cu, island formation follows stripe phase development, however for Ag, unstable islands appear first and participate in formation of the stripe phase. Structures grown in equilibrium at high temperature are compared with those grown at room temperature and imaged with scanning tunneling microscopy as well as with results from semi-empirical calculations. @FootnoteText@ @footnote 1@ORNL is managed by Lockheed Martin Energy Research Corp. under US DOE contract DE-AC05-96OR22464. BNL is supported by US DOE DE-AC02-98CH10886.

9:20am SS1-WeM4 Step-Step Interactions on TaC(910)@footnote 1@, J.-K. Zuo, Oak Ridge National Laboratory and Southwest Missouri State University; T.-J. Zhang, University of Tennessee and Oak Ridge National Laboratory; J.F. Wendelken, Z. Zhang, D.M. Zehner, Oak Ridge National Laboratory

TaC, an ionic crystal with an extremely high melting point of ~3983 C, exhibits a strong faceting behavior for (n10) surfaces after heating to ~2000°C.@footnote 2@ These facets are very regular when n = 1, 2 or 3 but become less regular when n = 9. Through a scanning tunneling microscopy based study of the step distribution and structure on TaC(910), we determine that the observed morphology results from the interplay of a step-step repulsive interaction with both short- and long-range attractive interactions. The surface is dominated by bunched double-height steps

where the bunches are separated by relatively long intervening (100) terraces having irregular widths. The step-separation distribution is highly skewed and sharply peaked at 13 atomic rows, the average spacing within a step bunch, while the (910) orientation is maintained with an average step-separation of about 18 rows. A Monte Carlo simulation shows that a weak, long-range, attractive interaction, -B/x@super a@, must be added to a strong, medium-range, repulsive interaction, A/x@super 2@, to fit the measured distribution. In addition, a short range attractive interaction is required for the creation of multiple-height steps that are oriented in the [010] direction. Possible physical origins for each of these interactions will be discussed. @FootnoteText@ @footnote 1@ ORNL is managed by Lockheed Martin Energy Research Corp. under U.S. DOE Contract No. DE-AC05-960R22464. @footnote 2@ J.-K. Zuo, J. M. Carpinnelli, D. M. Zehner and J. F. Wendelken, Phys. Rev. 53, 16013 (1996).

9:40am SS1-WeM5 Phosphide Phases on Cu(001): a Helium Atom Scattering Study, L.V. Goncharova, J. Braun, A.V. Ermakov, B.J. Hinch, Rutgers University

PF@sub 3@ and PH@sub 3@ adsorbs molecularly on Cu(001) at low surface temperatures. As these molecules are susceptible to electron induced decomposition; helium atom scattering proves to be a powerful diagnostic tool. On raising the surface temperature competition between desorption and decomposition occurs. Decomposition is complete after annealing to room temperature. A low coverage of phosphorous induces a poorly ordered c(6x8) phase. Subsequent annealing to 500K substantially improves the long range ordering of this structure. For PF@sub 3@ exposures at room temperature, no adsorption is observed. In contrast, PH@sub 3@ adsorbs dissociatively. Under these exposure conditions a c(6x6) phase is observed. Both $c(6 \times 8)$ and $c(6 \times 6)$ phases display low rainbow angles implying phosphorus incorporation into the surface plane. We shall discuss possible structures for these low-corrugation, phosphorusin-copper phases.

10:00am **SS1-WeM6 Ordered Alloying of Pd with the Mo(001) Surface**, *D. Wu, Z.Q. He*, *M.S. Altman*, *W.K. Lau*, *C.T. Chan*, Hong Kong University of Science and Technology, P.R. China

The interaction of Pd with the Mo(001) surface has been studied with low energy electron microscopy (LEEM) and diffraction (LEED), and first principles total energy calculations. A significant change of surface morphology is revealed by LEEM during the development of a Pd-induced c(2x2) periodic structure. The creation of a large number of islands upon Pd deposition is consistent with the formation of a subsitutional alloy. Accommodation of Pd in excess of the ideal c(2x2) coverage leads to the formation of a c(2x8) structure, although with no apparent change of surface morphology. The c(2x8) structure is stable at the interface between Mo and thicker Pd overlayers. Theoretical calculations demonstrate that the substitutional alloy is energetically favored compared to an overlayer structure at half monolayer coverage. Proliferation of antiphase domain walls in the c(2x2) subsitutional alloy is proposed to explain the c(2x8) periodic structure. Theoretical calculations indicate that a pseudomorphic Pd overlayer is more stable than substitutional alloys at one monolayer coverage, and that the Pd-covered Mo(001) surface would be unstable with respect to faceting to the (112) orientation if the pseudomorphic growth can be realized. However, experiment reveals that there is a kinetic limitation to the formation of the pseudomorphic structure and that faceting is preempted by the formation of more complex surface alloy structures.

10:20am SS1-WeM7 Alkali-Metal-induced 3x1 Reconstruction of the Ge(111) Surface, G.S. Lee, Korea Research Institute of Standards and Science, Korea; J. Kim, Korea Advanced Institute of Science and Technologies; I. Chizhov, H. Mai, R.F. Willis, The Pennsylvania State University

We present the scanning tunneling microscopy (STM) images of the 3x1 reconstruction of the Ge(111) surface induced by the adsorption of Na and Li. Both filled- and empty-state images of Ge(111)3x1-Na consist of double-row zigzag chains. For Ge(111)3x1-Li, the filled-state image shows single-width rows with sparsely distributed block features between the rows, while the empty-state image is characterized by double rows of dimer-like features. For both surfaces, the dual-polarity images taken simultaneously reveal lateral shift and phase reversal of the rows upon polarity reversal. The apparent dissimilarity of the STM images is contradictory to the expectation that the Ge(111)3x1 surface, like the Si(111)3x1 surface, is a substrate reconstruction which is not specific to the kind of alkali metals. The interpretation of the images of both Ge(111)3x1 surfaces will be

discussed by comparing with those of the Si(111)3x1 surfaces, and the recently proposed structural model for the Si(111)3x1 reconstruction.

10:40am SS1-WeM8 High-Resolution Structural Analysis of Te/Ge(001), B.P. Tinkham, Northwestern University; P.F. Lyman, University of Wisconsin, Milwaukee; O. Sakata, D.A. Walko, Northwestern University; M.J. Bedzyk, Northwestern University, Argonne National Laboratory

We propose models for the surface structure of Te/Ge(001). Te has proven to be an effective surfactant for Si/Ge heteroepitaxy.@footnote 1@ Thus, the study of Te/Ge(001) will determine more precisely the method of surfactant action. Our group has performed high-resolution XSW (X-Ray Standing Wave) and LEED (Low-Energy Electron Diffraction) studies at Te coverages of 1 and .5 monolayer. We are presently investigating these structures with surface x-ray diffraction in order to allow us to fully describe the surface structure, including the composition and structure of the Te dimers. STM will also be used to verify the competing models suggested by the x-ray measurements. @FootnoteText@ @footnote 1@ H.J Hosten, J. Klatt, G. Lippert, E.Bugiel, and S. Higuchi, J. Appl. Phys. 74, 2507 (1993).

11:00am SS1-WeM9 A Novel STM Imaging Mechanism Used to Resolve the Atomic Structure of the As-Rich GaAs(001)-(2x4) Surface, V.P. LaBella, D.W. Bullock, P.M. Thibado, University of Arkansas; P. Kratzer, M. Scheffler, Max-Planck-Gesellschaft, Germany

Motivated by the importance of GaAs in the compound semiconductor device market. The atomic arrangement of the technologically important GaAs(001)-(2x4) reconstructed surface is determined using scanning tunneling microscopy (STM) and first-principles, electronic structure calculations. The bias-dependent STM images reveal the relative position and depth of atomic-scale features within the trenches between the top layer As dimers, which are in agreement with the @beta@2 (2x4) structural model. The bias-dependant simulated STM images reveal that a retraction of the top most dangling bond orbitals is the unique mechanism that enables the STM tip to image the trench structure. This work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1-1058).

11:20am SS1-WeM10 Dislocations, Phason Defects, and Domain Walls in a One-dimensional Quasiperiodic Superstructure of a Metallic Thin Film, *Ph. Ebert,* Forschungszentrum J@um u@lich, Germany; *K.-J. Chao, Q. Niu, C.K. Shih*, University of Texas, Austin

We investigated disorder and structural defects in a one-dimensional quasiperiodic superstructure of a thin Ag film on GaAs(110) surfaces by scanning tunneling microscopy. The superstructure forms sequences with long and short separations exhibiting a self-similarity. We demonstrate that the modulation can be described best with a Fibonacci sequence and deviations are due to structural defects. We identify dislocations, phason defects, and domain walls. The static stress field of dislocations is found to be a source of phason defects.

11:40am SS1-WeM11 The Surface Reconstructions of InP(001), Z. Ding, V.P. LaBella, D.W. Bullock, P.M. Thibado, University of Arkansas

Motivated by the increasing use of InP in high speed opto-electronic devices that are fabricated using molecular beam epitaxy (MBE), the surface reconstruction phases of the technologically important InP(001) surface are studied. This study is performed in a combined ultrahigh vacuum MBE and scanning tunneling microscopy (STM) multi-chamber facility that incorporates a solid source phosphorus evaporation source and a novel temperature measurement system accurate to within ± 2 @super o@C. Both reflect ion high energy electron diffraction (RHEED) and STM are used to map out the InP(001) surface reconstruction phase's dependence upon substrate temperature and phosphorus pressure. A c(4x4), a (2x1), and a (2x4)/c(2x8) reconstruction are all observed. Thi s work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1-1058).

Surface Science Division Room 607 - Session SS2+AS+PS-WeM

Ion-Surface Interactions I

Moderator: L. Hanley, University of Illinois, Chicago

8:20am SS2+AS+PS-WeM1 Trapping and Desorption of Energetic Cu Atoms on Cu(111) and (001)Surfaces at Grazing Incidence, *D.E. Hanson*, *A.F. Voter, J.D. Kress*, Los Alamos National Laboratory; *X.-Y. Liu*, Motorola, Inc.

Cu is widely used as an interconnect in semiconductor chips. It is deposited by ionized physical vapor deposition on sub-micron features that have sidewalls nearly parallel to the incident ion beam. Molecular dynamics (MD) simulations have shown that, for angles of incidence (with respect to normal) up to 20 degrees, the sticking probability is unity for all energies; the impact atom penetrates and loses all of its kinetic energy to the surface. As the impact angle increases, the probability for the impact atom to reflect increases, reducing the sticking probability. Surprisingly, for angles above 70 degrees, the sticking probability increases with impact angle. We have performed MD simulations of Cu atoms impacting both Cu(111) and (001) surfaces at grazing incidence and find that this unexpected increase in sticking probability is a consequence of trapping (or surface skipping). An energetic Cu atom (10 ¾ E ¾ 100 eV) can become trapped by the mean attractive potential above the surface, oscillating normal to the surface. While in this trapped state, it can traverse hundreds of Å as it dissipates energy to the surface. Until the atom either desorbs or comes to rest, it experiences an average energy loss rate that is piecewise linear, typically comprised of two or more roughly linear (dE/dt = constant) regions. The process can be characterized by two parameters: the desorption probability at each oscillation and an average energy loss rate (per oscillation) that is independent of energy. These parameter values are the same for both the (111) and (001) surfaces. A phenomenological model based on these parameters is presented, and the predictions of sticking probability, average energy transfer to the surface, and total distance traveled along the surface, agree with full MD simulations. The dependence of the desorption probability on the surface temperature, was also studied.

8:40am SS2+AS+PS-WeM2 Dynamics of NO@super +@ Abstraction of Oxygen on Al(111), *M. Maazouz*, *P.L. Maazouz*, *D.C. Jacobs*, University of Notre Dame

Energetic collisions between molecules and surfaces can activate a number of reaction processes, such as electron transfer, activated dissociative chemisorption, dissociative scattering, atom abstraction, and sputtering. The branching into each of these channels can be affected by the initial internal energy (electronic, vibrational, and rotational) and collision energy of the molecule. Reactive collisions of NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v=1) with oxygen-covered Al(111) are explored across a range of hyperthermal energies (5-80 eV). A laser forms the incident ions from the neutral NO via resonance-enhanced multiphoton ionization (REMPI). This produces NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v) in a selected vibrational level (v=0-6) of the ground electronic state. Scattered products include O@super -@, NO@super -@, and NO@sub 2@@super -@. The latter product arises from an atom abstraction channel and is the main focus for the present study. The NO@sub 2@@super -@ formation shows a strong dependence on the oxygen coverage and the NO@super +@ primary energy. Detailed reaction mechanisms leading to NO@sub 2@@super-@ emergence will be discussed.

9:00am SS2+AS+PS-WeM3 Oxygen Negative Ion Emission from Al(100) Bombarded by Li@super+@ Ions, J.A. Yarmoff, W.K. Wang, B.-L. Young, B.C. Corbitt, University of California, Riverside; Z. Sroubek, Academy of Sciences of Czech Republic

The intensity of oxygen negative ions sputtered from metal surfaces (V, Mo, Cu) by rare gas ions is known to increase by up to 3 orders of magnitude when the surface work function is lowered by alkali metal adsorption. A resonant charge transfer process from the surface bands to the oxygen affinity level is apparently responsible for the negative ion formation, and such a process is strongly dependent on the surface potential. We have measured the intensities and kinetic energy distributions of O@super-@ sputtered from Al(100) via bombardment by 200 eV Li@super+@ ions. In contrast to experiments with rare gas ions, the O@super-@ intensity is found to be relatively independent of the work function changes induced by Cs deposition (@DELTA@@phi@ = - 3 eV). For O@super-@ kinetic energies above 20 eV there is no increase in the yield,

and it increases by only a factor of 2-3 at lower O@super-@ kinetic energies. The energy distribution depends exponentially upon the O@super-@ kinetic energy, and has a cutoff at about 120 eV. These results suggest that the yield of oxygen particles sputtered from clean Al(100) by Li@super+@ is already nearly completely ionized due to the local potential perturbation caused by the projectile. Thus, a further lowering of the surface potential by the deposition of alkali adsorbates has little effect. This is clear evidence of the localized nature of the resonant charge exchange process, and the first evidence that such a local effect can be induced by the primary particle.

9:20am SS2+AS+PS-WeM4 Matrix Dependent He+ Neutralization by Adsorbates: An ISS Study of S and Cl on TiO@sub 2@(110), W. Hebenstreit, E.L.D. Hebenstreit, U. Diebold, Tulane University

We have studied the adsorption of S and Cl on TiO@sub 2@(110) with lowenergy He@super +@ ion scattering spectroscopy (ISS) , X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). Because of its high surface sensitivity, ISS is ideally suited to determine the chemical composition of surfaces. While it is well known that quantification of ISS spectra is influenced by trajectory-dependent blocking, the element-specific neutralization of the probing ion is generally assumed not to be matrix dependent. We found that the neutralization of He+ ions (400 - 2450 eV, scattering angle 139°) scattered on Cl or S (adsorbed on TiO@sub 2@(110)), depends strongly on sample pretreatment and adsorption site. Cl (~ 1 ML) and S (~ 2/3 ML) give rise to pronounced peaks in ISS spectra when adsorbed on the sputtered TiO2 sample (1 keV Ar@super +@, flux 1.5 10@super 16@ cm@super -2@), but both species cannot be detected after adsorption at RT on the annealed, stoichiometric TiO@sub 2@(110) surface (coverage ~ 1/3 ML). STM shows that the adsorbates are located on the rows of 5-fold coordinated Ti atoms. When dosed at 573 K, S adsorbs at the position of bridging oxygen atoms, where it forms a (1x3) superstructure. In this case S becomes "visible" again for ISS. All spectra (on sputtered and annealed substrates) show a decrease in the O and Ti ISS signal due to blocking induced by the adsorbates. Subsurface positions of the adsorbates in the "invisible cases" can be excluded by STM. The difference in neutralization is due to different electronic structures of the substrate surface: (a) semiconducting with a 3 eV band gap when annealed; (b) metallic due to defect states and oxygen deficiency after sputtering. In case of S located at the position of bridging oxygens, neutralization is affected by the different local bonding.

9:40am SS2+AS+PS-WeM5 Hyperhhermal Ion - Surface Interactions, J.W. Rabalais, University of Houston INVITED

The chemical and physical phenomena accessible by means of low energy ion beams on surfaces will be discussed. Such energetic reactive ions can stimulate selected physical and chemical processes, such as film deposition, growth, synthesis, and shallow implantation within a nonequilibrium UHV environment. The 'low energy' or 'hyperthermal' range is considered to be 5 eV to a few keV. The lower limit is of the order of chemical bond energies. In this limit, chemical bonding interactions become significant. the binary-collision approximation (BCA) becomes questionable, and inelastic interactions can alter the ion trajectories. In the high energy limit, the sputtering yield becomes equivalent to or higher than the beam flux, classical ion trajectory simulations using the BCA provide a satisfactory description of the collision events, and the impinging ions are implanted in the subsurface layers. Mass-selected ion beam deposition (IBD) allows independent control over parameters such as ion energy and type, ion fluence and dose, substrate temperature, and background gases. The advantages of IBD for stimulation of chemical reactions, control of film stoichiometry, low temperature epitaxy, good film-substrate adhesion, and for growth of materials with metastable structures, isotopic purity, and high densities will be contrasted with the disadvantages, such as production of defects, imperfections, and amorphous materials and the limited thicknesses of IBD films. Examples of the use of mass- and energyselected beams for hyperthermal surface reactions, film growth, synergism between ion energy and substrate temperature, and shallow implantation will include: Si+ ion homoepitaxy, the growth SiO2 from pulsed Si+ and O+ beams, low energy Ti+ beams for growth of titanium silicide on silicon and mixed Ti-Al oxides on sapphire (a-Al2O3), growth of diamond-like carbon, growth of Ag(111) on a Ni(100) surface, and survival probabilities of scattered TiClx cluster ions.

10:20am SS2+AS+PS-WeM7 Dissociation and Energy Distribution Processes in XY@super -@(CO@sub 2@)@sub n@ (XY = ICl, I@sub 2@, and Br@sub 2@) Collision onto Silicon Surface, S. Koizumi, Genesis Research Institute, Inc., Japan; H. Yasumatsu, A. Terasaki, T. Kondow, Toyota Technological Institute, Japan

Collisional dissociation induced by impact of a cluster anion, ICl@sup -@(CO@sub 2@)@sub n@ (n = 0 - 20), onto a silicon surface were studied by measuring the branching fractions of the ICl@sup -@ dissociation and the translational energies of the product anions as functions of n and the collision energy (per ICl@sup -@) of ICl@sup -@(CO@sub 2@)@sub n@ in an apparatus consisting of a tandem time-of-flight mass spectrometer. It was found that the branching fraction of the ICl@sup -@ dissociation did not change with n at the collision energies of 30 - 70 eV. Molecular dynamics simulation showed that the impinging core ion, ICl@sup -@, tends to orient with the molecular axis of the core ion being at the angle of 55 ° with respect to the surface normal, whereas in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ (X = Br, I) collision, the molecular axis of the X@sub 2@@sup -@ core ion being in parallel to the surface plane. This finding together with prominent wedge effect in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ collision leads us to conclude that the CO@sub 2@ molecules do not work as 'wedge' in the ICl@sup -@(CO@sub 2@)@sub n@ collision because of the unfavorable orientation of the incoming cluster anion. No discernible cage effect could also be related to the orientation. The translational energies of the product anions were interpreted in terms of energy redistribution of the collision energy among the degrees of freedom of the cluster anion and the surface atoms involved in the collision. It was also found that the I and Cl product ions reach quasiequilibrium with the surface from the measurement of these translational energy distributions.

10:40am SS2+AS+PS-WeM8 Angle Resolved Measurements of Ions and Neutrals Scattered from HOPG Surfaces upon Hyperthermal Glancing Incidence Irradiation with Large Polyatomic Ions: Charge Changing and Impact Orientation Phenomena, *M. Hillenkamp, J. Pfister, M. Kappes,* University of Karlsruhe, Germany; *R. Webb,* University of Surrey, United Kingdom

We have scattered a series of polyaromatic hydrocarbons and various fullerenes from graphite at hyperthermal kinetic energies (100-5000eV) under glancing incidence (75 degrees with respect to the surface normal). Resulting cations, anions and fast neutrals have been studied with a secondary time-of-flight mass spectrometer/detector rotatable about the scattering plane. The corresponding angular distributions have been compared to those obtained upon irradiation of HOPG with He@super +@ and Xe@super +@ ion beams under otherwise identical conditions. Molecular projectiles were typically studied as either singly or multiply charged parent cations. In addition to dominant neutralization, we also observe the scattering of smaller amounts of both cations and anions (parents and fragments). We discuss the relative yields of charge states in terms of charge transfer rate theories as well as in terms of postcollision decay processes (e.g. delayed electron loss). In comparing the surprisingly narrow (and near Gaussian) angular distributions determined for fast neutrals from fullerene scattering with those recorded for xenon, we find that while Xe is specularly scattered over the full energy range studied, fullerenes are scattered subspecularly - with the deviation from specular angle increasing with increasing collision energy. Molecular dynamics simulations with Brenner potentials suggest that this effect results from a combination of the comparatively long (>300 fesec) "turnaround " time of the molecular projectile and a significant perpendicular deformation of the layered target on the collision time scale. For the topologically much more anisotropic polyaromatic hydrocarbon projectiles we find structured fast neutral angular distributions suggestive of a simple dependence between impact orientation and scattering angle

11:00am SS2+AS+PS-WeM9 Surface Structure Determination by Angle-Resolved Mass Spectroscopy of Recoiled Ions, G.S. Herman, Pacific Northwest National Laboratory

Low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) are powerful techniques for the determination of surface composition and structure. The combination of time-of-flight methods with an electrostatic time focussing analyzer has recently resulted in a new technique - massspectroscopy of recoiled ions (MSRI).@footnote 1@ The MSRI technique has an advantage over LEIS and DRS in that it has much higher massresolution and sensitivities. Results related to the exchange of @super 18@O into samples will be presented to illustrate the high mass-resolution. Furthermore, recent results indicate that in the angle-resolved mode, structural determinations can be performed. Angle-resolved MSRI (AR-

MSRI) results will be presented for CeO@sub 2@(001) and TiO@sub 2@(001)-Anatase films grown on SrTiO@sub 3@(001) substrates by molecular beam epitaxy and chemical vapor deposition, respectively. The experimental data are fit to calculations using the scattering and recoiling imaging code based on the binary collision approximation.@footnote 2@ The ideal CeO@sub 2@(001) surface is polar and predicted to be unstable. However, LEED results indicate that a sharp (1x1) pattern can be obtained. The structural model determined by AR-MSRI consists of an oxygenterminated surface with a half monolayer of oxygen removed. This structure is consistent with a model based on the reduction of the surface dipole moment. The TiO@sub 2@(001)-Anatase surface has only recently been experimentally investigated in much detail. LEED measurements indicate that the surface undergoes a (1x4) reconstruction after a sputter and anneal cycle. A comparison between experiment and theory for several models for this reconstruction will be presented. @FootnoteText@ @footnote 1@ K. Eipers-Smith, K. Waters, and J.A. Schultz, J. Am. Ceram. Soc. 76, 284 (1993). @footnote 2@ V. Bykov, C. Kim, M.M. Sung, K.J. Boyd, S.S. Todorov, and J.W. Rabalais, Nucl. Instr. And Meth. In Phys. Res. B 114, 371 (1996).

11:20am SS2+AS+PS-WeM10 Depth Information in Direct Recoiling Peak Shapes: Simulations from Model Surfaces, *M. Tassotto*, Oregon State University; *P.R. Watson*, Oregon State University, U.S.

Direct recoil spectrometry (DRS) has been used in the past to study adsorbate surface structures, chemisorption processes, and average orientations of molecules at surfaces. In these studies, DRS has experimentally been proven to be very surface sensitive. Information on surface structure and composition is primarily based on the analysis of DR peak intensities from the time-of-flight (TOF) spectra. These DR peaks frequently exhibit long tails to higher TOF which often overlap with neighboring peaks. It is common practice to obtain intensities from TOF spectra by integrating the DR peak areas over narrow time windows. Unfortunately, quantitative analysis is complicated by a lack of accurate background removal and only the use of relative intensity variations is possible. In this study, the MARLOWE computer code has been applied to calculate the trajectories of atoms recoiling from both simple and more complex model surfaces (diamond and alkane polymers, respectively) while the depth from which recoiled particles originated was recorded. The DR peak itself as well as the long TOF tail to lower energies contain depthrelated information. Near the peak maximum recoils originate from mainly the first atomic layer, supporting the high surface sensitivity of DRS. The initial portions of the tail of the peak provide an approximate atomic depth profile but at longer TOF the tail contains recoils that were produced by several mechanisms from a wide variety of depths. The trajectory calculations have been converted to actual TOF spectra which allows comparison with experimental data from the literature. Here it is important to account for varying detector efficiencies as well as broadening of the simulated DR peak due to the finite pulse width of the ion beam. The MARLOWE calculations make DR peak deconvolution possible. This leads to accurate background removal in determining atomic ratios.

11:40am SS2+AS+PS-WeM11 Hyperthermal-energy Ion Scattering on Si(100), C.L. Quinteros, S.I. Tzanev, D.C. Jacobs, University of Notre Dame

Ion-surface scattering experiments on a Si(100) surface are presented, introducing a new gas/surface experimental system with unique capabilities. Using a Colutron type source, an ion beam with energies between 5-300 eV can be generated. The ions are extracted, accelerated, mass-selected by a Wein filter, decelerated and focused on the surface target. Scattered ions and neutral products are mass- and energy-resolved with a fully rotatable, differentially-pumped detector that includes an ionization source for detection of neutrals, a cylindrical electrostatic analyzer for energy selection, and a quadrupole mass spectrometer for mass selection of the energy-filtered particles. Incident angles between 0-90° and scattering angles between 0-150° can be accessed by independent rotation of the sample manipulator and the detector. A complement of surface analysis techniques (LEED, Scanning Auger Electron Spectroscopy, X-Ray Photoelectron Spectroscopy, and a Kelvin Probe) monitor surface modifications resulting from ion-beam exposure. The surface sample can be cooled to 80K through a liquid nitrogen reservoir or resistively heated to 1000K. The hyperthermal energy range spans from thermal energies (<1eV), where chemical interactions produce inelastic scattering events, to the low energy regime (1-5 keV), where predominantly elastic scattering occurs. We present scattering results for a series of different projectiles on Si(100) that bridge these two energy regimes. The charge state and energy distributions of the scattered products are reported as a function of collision energy and scattering angle

Surface Science Division Room 604 - Session SS3+EM-WeM

Surface Electronic Structure

Moderator: G.O. Sitz, The University of Texas, Austin

8:20am SS3+EM-WeM1 Spectroscopic Nonlinear Optical Responses of Clean, H-terminated and Ge-covered (2x1)Si(001), *L. Mantese*, *D. Lim*, *M.C. Downer*, University of Texas, Austin

Nonlinear optical spectroscopies are becoming important in elucidating the electronic structures of surfaces and interfaces. Yet, the accurate theoretical calculation of these spectra remains a difficult challenge. Recently, theoretical models have been developed to predict the nonlinear optical responses of clean and absorbate-covered (2x1)Si(001) surfaces.@footnote 1,2@ Here, we report the second harmonic (SH) responses of clean, H-terminated and Ge-covered (2x1)Si(001) to provide a direct test of predictive models. We have extended the range of previously reported results@footnote 3,4@ further into the IR where tunable IR femtosecond pulses in the range of ~1.15 to 2.5 microns were generated by a commercially available optical parametric amplifier (OPA) system. In this excitation region the SH response is resonantly enhanced by surface states including those from the dangling bonds and reconstruction-induced bonds. In addition, by directly using our oscillator output (700 to 800nm), we measure nonlinear optical responses in the E@sub 1@ region of Si. In this spectral range the SH response is highly sensitive and is altered in contrasting ways to ML coverages of H and Ge on (2x1)Si, originating from a surface electric field related to dimer charge transfer. The two measurement regions are discussed in comparison with theoretical predictions. @FootnoteText@ @footnote 1@B. Mendoza et al., PRL 81 (1998) 3781. @footnote 2@V.I. Gavrilenko et al., PRL submitted (1999). @footnote 3@U. Hofer, Appl. Phys. A 63 (1996) 533;J.I. Dadap et al., PRB 56 (1997) 13367. @footnote 4@P. Parkinson et al., Appl. Phys. B 68 (1999)

8:40am **SS3+EM-WeM2 Si Surface Passivation: Si(111):GaSe versus Si(111):As, A. Bostwick,** S. Meng, B.R. Schroeder, University of Washington; E. Rotenberg, Lawrence Berkeley National Laboratory; F.S. Ohuchi, M.A. Olmstead, University of Washington

Heteroepitaxy on Si(111)7x7 requires removal of the deep reconstruction and accompanying dangling bonds. One way to passivate the Si(111) surface and remove the reconstruction is exposure to As, forming Si(111):As 1x1.@footnote 1@ The initial chemisorption of GeSe on Si(111)7x7 surfaces also results in a nearly ideally terminated 1x1 surface, quite similar to Si(111):As. Ga and Se occupy bulk Si sites, with Ga directly above Si (T1 site) and Se forming three back-bonds to Ga (H3 site). This (1x1) structure is the same as half a bulk GaSe layer, and initiates GaSe heteroepitaxy on Si(111). The very small (less than 0.1 eV) Si 2p core level shift shows the interface silicon to be in a bulk-like environment with minimal charge transfer, in contrast to As terminated silicon (0.75 eV shift). Electron counting arguments predict a lone-pair state on the Si(111):GaSe 1x1 surface, very similar to the As case. We observe such a state with angle-resolved ultraviolet photoemission spectroscopy. It has a similar E(k) dispersion to Si(111):As, though a somewhat larger bandwidth. We find a second surface state between this lone-pair state and the first bulk state. which we attribute to Ga-Se bonds. In addition, the zone-center bulk state, degenerate in bulk Si, is split by about 0.5 eV. This surprising result is not found for Si(111):As. We tentatively attribute the splitting to the Si-Ga interaction. @FootnoteText@ M. A. Olmstead, R. D. Bringans, R. I. G. Urhberg and R. Z. Bachrach, Phys. Rev. B 34, 6401 (1986).

9:00am SS3+EM-WeM3 Electron Excitations and Optical Properties of Semiconductor Surfaces, S.G. Louie, University of California, Berkeley and Lawrence Berkeley National Laboratory INVITED

The presence of electronic surface states and resonances often strongly modifies the structural, chemical, electronic, and optical properties of a surface. Over the past two decades, many sophisticated experimental methods (e.g., photoemission, scanning probes, and optical techniques) have been developed to investigate the spectroscopic properties of surfaces. In this talk, we discuss some of the theoretical developments in studying surface spectroscopic properties. Ab initio quasiparticle calculations can now be used to understand and predict surface-state excitation spectra such as those measured in photoemission and scanning tunneling spectroscopy experiments. A recent advance in treating excitonic effects further allows the first-principles study of surface optical processes. Results on several semiconductor surfaces will be presented. The possibility

of using NMR chemical shifts as a probe of surface states will also be discussed.

9:40am SS3+EM-WeM5 Low Temperature Scanning Tunneling Microscopy and Spectroscopy of the @sr@3x@sr@3 R30° Phase of Sn/Si(111), *L. Ottaviano*, INFM, Italy; *A. Continenza, M. Crivellari, L. Lozzi,* University of L'Aquila and INFM, Italy; *S. Modesti,* University of Trieste and Laboratorio TASC-INFM, Italy; *S. Picozzi, G. Profeta, S. Santucci,* University of L'Aquila and INFM, Italy

In these years there has been a great deal of efforts in the understanding of the low temperature transition from a @sr@3x@sr@3 R30° to a 3x3 phase of Sn(Pb)/Ge(111).@footnote 1@,@footnote 2@ On the other hand, little attention has been devoted to the investigation of iso-electronic interfaces like Sn(Pb)/Si(111) at similarly low temperatures. Among other experimental techniques, STM can provide a deep understanding of the electronic structure of these surfaces by performing measurements at various tunnelling voltages. Theorist who proposed different model interpretations have recently called for STM experiments at low temperatures on such systems.@footnote 3@ We show the first STM atomically resolved images of the low temperature (100 K) 1/3 ML-Sn/Si(111) @sr@3x@sr@3 R30° phase. Correspondingly we have measured tunnelling I-V spectra. Data are compared with all electron ab-initio calculations performed on a slab of Si(111) covered with 1/3 ML-Sn in the @sr@x@sr@3 R30° reconstruction. In particular we compare the ab-initio results with surface and electronic properties as obtained by STM/STS and photo-emission results. @FootnoteText@ @footnote 1@ L.Petaccia, L.Grill, M. Zangrando, and S. Modesti, Phys. Rev. Lett. 82 (1999) 386. @footnote 2@ A. Mascaraque et al., Phys. Rev.Lett. 82 (1999) 2524. @footnote 3@ S. Scandolo, F. Ancilotto, G.L.Chiarotti, G. Santoro, S. Serra, and E.Tosatti, Surf. Sci. 402-404 (1998) 808.

10:00am SS3+EM-WeM6 Electronic Structure of the 3C-SiC(001)-c(4x2) Surface, L. Duda, L.S.O. Johansson, B. Reihl, Universität Dortmund, Germany; H.W. Yeom, University of Tokyo, Japan; S. Hara, S. Yoshida, Electrotechnical Laboratory Tsukuba, Japan

We provide the first investigations of the electronic structure of the Si-rich 3C-SiC(100)-c(4x2) surface using angle-resolved photoemission and synchrotron radiation. The surface is found to be semiconducting. The Fermi level position was determined to be at 1.9 eV above the valenceband maximum. Three surface states are identified within the bulk band gap. We measured the dispersion of these states along the high-symmetry directions of the surface Brillouin zone (SBZ). The upper band at 1 eV binding energy and the third band at 2.6 eV are non-dispersive. The second band is located at 1.5 eV at the center of the SBZ and shows a weak dispersion of 0.3 eV in the @Gamma@-X direction, whereas, it is dispersionless in the other directions. We compare these results to calculated band structures.@footnote 1@ In addition, the comparison with experimental observed band structures of the 2x1 surface@footnote 2@ gives important new insight into the reconstruction behaviour of the SiC surface, supporting the close similarity of both reconstructions. @FootnoteText@ @footnote 1@ W. Lu, P. Krüger, J. Pollmann, Phys. Rev. Lett. 81 (1998) 2292 @footnote 2@ L. Duda, L. S. O. Johansson, B. Reihl, H. W. Yeom, S. Hara, S. Yoshida, submitted to Surface Science (1999).

10:20am SS3+EM-WeM7 Photoemission Spectroscopy of Platinum Overlayers on Silicon Dioxide Films, J.W. Keister, J.E. Rowe, Army Research Office; J.J. Kolodziej, T.E. Madey, Rutgers University

Soft x-ray photoelectron spectroscopy has been used to study ultrathin Pt films on silicon dioxide as model supported-catalyst materials. Using monochromatic synchrotron radiation (NSLS U4A - Brookhaven), platinum and silicon core-level photoelectron peaks were measured as a function of platinum coverage in the range, 0 - 10 monolayers (ML). The bulk Si and SiO@sub 2@ film Si(2p) peaks both show a binding energy drop within the first ~ 0.5 ML of dosing. However, the effect is stronger for the SiO@sub 2@ film Si(2p) peak, indicating an increased screening of the 2p electrons by the metal overlayer. We also observe a monotonic increase of the Pt film workfunction with coverage from 4.52 eV initially to 5.59 eV at ~ 10 ML. The Pt(4f) and valence band spectra display changes with Pt dose which are also consistent with increased screening, from non-metallic below \sim 0.5 ML to metallic as coverage increases. The Pt core level decreases its binding energy from ~ 72.2 eV to ~ 70.9 eV between 0 and 10 ML coverage. The coverage dependence of the Pt lineshape and intensity, and the large saturation coverage for the workfunction change indicate cluster growth (Volmer-Weber growth). The increasingly metallic nature of the Pt overlayer with dose is quantified by numerical lineshape fitting with Gaussian-broadened Doniach-Sunjic functions, as appropriate for varying

amounts of metallic screening. Further quantitative results and interpretation in terms of nucleation and growth of Pt clusters will be discussed.

10:40am SS3+EM-WeM8 The Behavior of Metallic Quantum Well State Dispersions in the Cu/fccCo/Cu(100) System as a Function of Film Thickness, W.K. Siu, R.A. Bartysnki, Rutgers University

The magnetic coupling of ferromagnetic (FM) layers separated by a nonmagnetic (NM) layer has been associated with the formation and behavior of metallic quantum well (MQW) states in the spacer layer. Inverse photoemission has been used to investigate the MQW states in the prototypical Cu/fccCo/Cu(100) system for very thin Cu layers. These studies have shown that their dispersion with parallel momentum can be strongly affected by the electronic structure of the underlying FM material. Specifically, rapidly dispersing MQW states in the NM layer will acquire an uncharacteristically large effective mass when they encounter a projected band gap in the FM material. The experimental result shows the the behavior over severval Cu monolayers. In the Cu/fccCo/Cu(100) case, this occurs near the neck of the Cu Fermi surface and affect the states responsible for the short period coupling in this system. We have investigated how the dispersion of these levels develops as a function of Cu layer thickness and, in particular, how it evolves towards the behavior found for the single crystal Cu(100) surface. These results are explained in terms of a phase accumulation model for the electronic structure of the MQW system. Funded by the National Science Foundation under grant No. NSF-DMR98-01681. and the Petroleum Research Fund under grant No. ACS-PRF-33750-AC6.5.

11:00am SS3+EM-WeM9 Atomic and Electronic Structure of Ag/Ni(110) and Ni/Ag(100), *P.T. Sprunger*, *D.A. Hite*, Louisiana State University

The atomic and electronic structure of Ag on Ni(110) and Ni on Ag(100) has been studied by synchrotron-based angle-resolved photoemission spectroscopy (ARUPS), low energy electron diffraction and scanning tunneling microscopy. These systems are of interest due their high bulk lattice mismatch and immiscibility. STM results of the Ag/Ni(110) system have revealed a novel pseudomorphic, surface-confined alloy phase at a coverage of ~0.5 ML. ARUPS results of this phase show a bulk-like, 3-D Ag electronic structure due to strong hybridization with the Ni bands. However, at a coverage of 1 ML, the Ag "de-alloys" and structurally forms a strained ~ Ag(111) overlayer. The electronic structure of this phase is radically different, namely, the laterally localized Ag d-bands show only kparallel dispersion, that is, 2-D structure. In contrast, ARUPS results of Ni monolayer deposition on Ag(100) reveals no alloy formation below 150 K. However, at deposition temperatures above 400 K, Ni segregates subsurface, resulting in a Ag surface termination. The underlying Ni adopts Ag lattice parameters. ARUPS data from this latter phase reveals 3-D, bulklike electronic structure due to strong mixing of states. The results will be compared and contrasted with theoretical band-structure calculations. This research is funded by DOE through contract DE-FG-02-98ER45712.

11:20am SS3+EM-WeM10 Spin-Orbit-Split Surface States in Clean and Alkali-Metal-Covered W(110)@footnote 1@, E. Rotenberg, Lawrence Berkeley National Laboratory; J.W. Chung, Pohang Institute of Science and Technology, Korea; S.D. Kevan, University of Oregon

The broken symmetry at surfaces can give rise to a non-zero spin-orbit splitting of valence bands, as has recently been observed for the s-p derived surface state on Au(111).@footnote 2@ We now observe such a splitting of the d-derived surface state on W(110) and to a lesser extent, on Mo(110), and follow the evolution of the splitting as monovalent atoms are adsorbed. We find a dramatic increase in the splitting as a function of deposition for H and all alkali metals for coverages up to 1 ML. For Li, which shows the strongest change in splitting, we find a decrease in the splitting at the highest coverages near 1 ML. Our findings show that the spin-orbit splitting is a sensitive probe of the local surface conditions, to the extent that they are sampled by the surface state's wavefunction. The observed evolution is also directly relevant to recent observations of altered orbital magnetic structure vs. adsorbate coverage in magnetic materials. We propose a spin ordering for the associated Fermi contours which has important implications for spin excitations at surfaces. @FootnoteText@ @footnote 1@E. Rotenberg, J. W. Chung, and S. D. Kevan, Phys. Rev. Lett. 82 4066 (1999). @footnote 2@S. LaShell, B. A. McDougall, and E. Jensen, Phys. Rev. Lett., 3419 (1996).

11:40am SS3+EM-WeM11 Resonant Auger Studies of Metallic Systems, I. Coulthard, J.W. Freeland, S.P. Frigo, J.F. Moore, W.S. Calaway, M.J. Pellin, M. Mendelsohn, Argonne National Laboratory; T.K. Sham, S.J. Naftel, University of Western Ontario, Canada; A. Stampfl, Australian Nuclear Science and Technology Organization

Auger electron emission at photon energies near the associated absorption edge which generates the initial core hole is a complex process. Excitation and decay become linked such that the process must be described as a single-step process rather than the classical two step process for Auger emission. This results in the production of discrete lines which are resonantly enhanced at the absorption edge, and whose intensity vanishes far below or above the edge. Another result of utilizing resonant photon energies is that the Auger line width may no longer be limited by the intrinsic lifetime resulting in a narrowing of the Auger spectrum.@footnote 1@ Results will be presented for a variety of systems including, Cu, Co, Al, CuNi alloys, and CuAl alloys. Specific attention will be paid to:probing unoccupied densities of states, very high resolution x-ray absorption spectroscopy utilizing auger yields to produce sub-lifetime narrowed x-ray absorption spectra, and the use of the technique for non-homogeneous sample systems. Work at Argonne is supported by the U.S. Department of Energy, Basic Energy Sciences, under Contract No. W-31-109-Eng-38. @FootnoteText@@footnote 1@T.M. Grehk, W. Drube, R. Treush, and G. Materlik. Phys. Rev. B 57, 6422 (1998).

Plasma Science and Technology Division Room 612 - Session PS+SS-WeA

Ion-Surface Interactions II

Moderator: C.I.H. Ashby, Sandia National Laboratories

2:00pm **PS+SS-WeA1 How Does Ion Bombardment Produce Enhanced Etching?**, *P.G.M. Sebel*¹, *L.J.F. Hermans, H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

Etching of Si by XeF@sub 2@ is enhanced considerably by ion bombardment. The role of the reaction layer in this process is studied in a multiple-beam setup at room temperature. One of the main reaction products, SiF@sub 4@, is formed in this layer. During spontaneous etching a thick reaction layer with a chain-like Si@sub x@F@sub y@ structure is formed.@footnote 1@ From ion pulse experiments on a slow time scale (100 s), it is concluded that this reaction layer is depleted of fluorine by the ion bombardment. This thinner reaction layer leads to a lower spontaneous SiF@sub 4@ formation. The depletion of the reaction layer is supported by model calculations. Despite this lower spontaneous contribution, the release of reaction products on a depleted reaction layer under ion bombardment is enhanced by chemical and physical sputtering. However, to produce more reaction products, more reactants (XeF@sub 2@) have to adsorb. This raises the question: "How does ion bombardment cause XeF@sub 2@ to have an increased sticking probability".@footnote2@ From ion pulse measurements on a fast time scale (1 s) it is concluded that on a depleted reaction layer XeF@sub 2@ mainly sticks on dangling bonds with a sticking probability of 0.71. By contrast, on a thick reaction layer the adsorption probability of XeF@sub 2@ is determined by the much lower sticking probability of 0.08 on SiF@sub 2@ surface species. This explains the enhanced sticking probability under ion bombardment and shows that a depleted reaction layer is a prerequisite for enhanced etching under ion bombardment. @FootnoteText@ @footnote 1@ M.J.M. Vugts, M.F.A. Eurlings, L.J.F. Hermans, and H.C.W. Beijerinck, J. Vac. Sci. Technol. A 14, 2780 (1996) @footnote 2@Y. Tu, T.J. Chang, and H.F. Winters, Phys. Rev. B. 23, 823 (1981)

2:20pm PS+SS-WeA2 Desorption Species from Fluorocarbon Film by Ar@super +@ Ion Beam Bombardment, *M. Hayashi*, *K. Karahashi*, Fujitsu Laboratories Ltd., Japan

Fluorocarbon films are formed on wafers and chamber walls in etching processes with fluorocarbon plasmas.@footnote 1,2@ Desorption species from them during etching have a lot of influences on Si device fabrication, for example, formation of side wall protection films in etched holes and fluctuation of plasma components in the near-surface region of a wafer. We succeeded in detecting the species that are desorbed from fluorocarbon films by ion bombardment. In this study, we constructed a new apparatus in order to investigate desorption species from fluorocarbon films. The measured fluorocarbon films were deposited on a Si wafer by exposing it to a C@sub 2@F@sub 6@ plasma in an inductively coupled plasma (ICP) reactor. The species desorbed by Ar@super +@ ion beam bombardment at a few keV into the films were detected using a quadrupole mass spectrometer (QMS). The film characteristics were evaluated simultaneously by x-ray photoelectron spectroscopy (XPS), and we discuss the correlation between the desorption species and the film characteristics. QMS spectra that were measured during the Ar@super +@ ion beam bombardment of the fluorocarbon films show many sorts of dissociated C@sub x@F@sub y@. CF@sub 3@@super +@ is a dominant QMS peak in the fragment pattern, and this indicates that CF@sub 4@ is a dominant desorption species. Besides, some large desorption species are recognized because of the detected large fragment ions of C@sub 3@F@sub 3@@super +@, C@sub 3@F@sub 5@@super +@, and so on. The ratios among CF, CF@sub 2@, CF@sub 3@, and CF@sub 4@ species, which were measured with the appearance energies, indicate that CF@sub 4@ is a dominant desorption species with the ratio of 80 % among them at the beginning of bombardment. However, continuous ion bombardment causes the CF ratio to increase instead of decrease in the CF@sub 4@ ratio. This demonstrates the change in film characteristics from F-rich to C-rich, which was evaluated by XPS measurement. Moreover, The formation of Crich film also corresponds to a reduction in total amount of desorption species. @FootnoteText@ @footnote 1@K. Takahashi, M. Hori, and T. Goto, J. Vac. Sci. Technol. A 14, 2011 (1996). @footnote 2@T. Shirafuji, W.

W. Stoffels, H. Moriguchi, and K. Tachibana, J. Vac. Sci. Technol. A 15, 209 (1997).

2:40pm PS+SS-WeA3 NH@sub 3@ / Cl@sub 2@ Gas Assisted Etching of Copper with Focused Ion Beams, K. Edinger, University of Maryland

With the implementation of copper instead of aluminum as metallization layer in high performance integrated circuits, the use of gas assisted etching for focused ion beam (FIB) based failure analysis and circuit rewiring becomes increasingly important. In the present study the effects of exposing a copper substrate to a mixture of chlorine (Cl@sub 2@) and anhydrous ammonia (NH@sub 3@) during ion bombardment have been investigated. The exposure of the copper surface to chlorine or to NH@sub 3@-Cl@sub 2@ mixtures leads to the formation of a reaction layer. The thickness of this layer and its texture depends on the FIB parameters such as ion beam dwell time, gas pressure and the NH@sub 3@ to Cl@sub 2@ flux ratio. In addition, the experiments indicate that the formation of the reaction layer is enhanced in areas that have been previously exposed (i.e. damaged) with an ion beam. The etch yield shows a strong dependence on the ion beam dwell time and the gas flux. For short dwell times and low NH@sub 3@ and Cl@sub 2@ flux an up to 10-fold increase over physical sputtering could be achieved. With increasing Cl@sub 2@ flux the etch rate decreased and the maximum in the etch yield shifted to longer dwell times, indicating changes in the adsorption kinetics of the two gases.

3:00pm PS+SS-WeA4 Guided Ion-beam Studies of Low Energy Cu@super +@ and Cu@sub 2@@super +@ Ion Interactions with Mo, S.L. Anderson, A. Lapicki, K.J. Boyd, M. Aizawa, University of Utah

Results of low-energy ion beam deposition of Cu@super +@ and Cu@sub 2@@super +@ on polycrystalline molybdenum at energies from 5 to 220 eV are presented. Thermodynamics in this system favor Cu diffusion to the surface. At low energies, Cu@super +@ is deposited on the surface with a sticking probability of ~0.6. As the energy is increased above 100 eV, stable subplantation of the Cu is observed. This threshold is substantially higher than expected for penetration; it seems likely that penetration occurs at lower energies, however, migration of the subplanted Cu to the surface is efficient. The results for Cu@sub 2@@super +@ are different in that subsurface copper is observed at energies down to 40 eV (20 eV/atom). This counterintuitive result is tentatively explained by the formation of complex defects which stabilize subplanted Cu. Possible defect production mechanisms are explored using variable-angle XPS, XAES and molecular dynamics simulations.

3:20pm **PS+SS-WeA5 Ion Solid Surface Interactions in IMP Cu PVD, X.-Y.** *Liu, M.S. Daw, D.G. Coronell, V. Arunachalam, C.-L. Liu,* Motorola Semiconductor Products Sector; *J.D. Kress, D.E. Hanson, A.F. Voter,* Los Alamos National Laboratory

A thorough understanding of ion-solid surface interactions is important for predictive modeling of ionized mass plasma (IMP) Cu physical vapor deposition (PVD) at feature scales. Besides sticking coefficients and sputter yields, fundamental parameters such as angular distributions of sputtered and reflected particles, and thermal accommodation coefficient are also needed as inputs for the feature scale process simulator. Molecular dynamics (MD) simulations can be used to provide pertinent information and physical insights. In this presentation, we'll demonstrate our recent MD results for Ar+/Cu and Cu+/Cu systems, as a function of hyperthermal ion energies and impact angles. The issue of integrating different sticking coefficients for different surface "roughness" will be addressed, based on ion travel distance analysis. We have found that the sputtered particle distributions are not cosine, but can be described by a simple Gaussian-like formula. Reflection characteristics were also analyzed and compared with simple analytical assumptions. Finally, the existing trends in the MD results from the systems will be discussed in terms of interaction strength, ion energy and impact angle.

3:40pm PS+SS-WeA6 Deposition and Etching Using Fluorocarbon Ions: Molecular Dynamics Simulations, *C.F. Abrams*², *D.B. Graves*, University of California, Berkeley

SiO@sub 2@ etch processes use fluorocarbon (FC) plasmas to achieve selectivity to Si, SiN, and photoresist. FC plasmas deposit films which slow the etching of these surfaces compared to SiO@sub 2@. Further etch process optimization hinges on understanding these films. Specifically, the mechanisms of Si etching through the FC overlayer remain matters of speculation. We used molecular dynamics simulations of FC ions impacting Si surfaces to understand this process. We developed a Si-C-F interatomic

² PSTD Coburn-Winters Student Award Finalist

potential as an extension of our C-F potential.@footnote 1@ We simulated ion impacts at normal incidence onto a:Si surfaces up to fluences of 4x10@super 16@ cm@super -2@. We examined the effects of ion composition (CF@sub x@ for x=1,2,3) and incident energy (50 @<=@ E@sub i@ @<=@ 200 eV). At low fluences, all ions deposit FC overlayers with significant Si incorporation. We found that CF ions result in net CF@sub x@ deposition, while CF@sub 3@ ions result in net Si etching with a steady-state overlayer thickness that increased with E@sub i@. For example, for 100 eV CF@sub 3@, we observed deposition of 2 equivalent monolayers of C up to a fluence of 4x10@super 15@ cm@super -2@, followed by Si etching (0.065 Si/ion) through a FC film with a steady thickness of 9.5 Å and F:C of 1.6. For CF@sub 2@, the resulting steadystate, deposition or Si etching, depended on E@sub i@, with deposition being favored at the lower energies. A striking result of the simulations is the dynamic character of the FC film during Si etching. Although the composition and thickness of the layer are unchanging at steady-state, F and C atoms are constantly depositing and then being etched by subsequent ion impacts. This 'recirculation' of F and C through the overlayer appears to play a key role in Si etching. Mechanisms of both initial film deposition and steady-state etching by FC recirculation will be discussed. @FootnoteText@ @footnote 1@ J Tanaka, C F Abrams, D B Graves. Subm, 46th AVS Intl Sym, 1999.

4:00pm PS+SS-WeA7 Comparison of Thin-Film Nucleation and Growth from Ion-Beam and Cluster-Beam Deposition: Atomistic Simulations, T.A. Plaisted, S.B. Sinnott, University of Kentucky

Experimental efforts have examined the formation of diamond-like and tailored polymer films through beam deposition. The results show that strongly adhering hydrocarbon thin films can be generated through the impact of organic ions or small clusters with mica, diamond, or glass surfaces. To study the processes involved in the nucleation and growth of these films we have performed atomistic simulations of beam impacts. Specifically, classical molecular dynamics simulations have been used where the forces are calculated using a many-body, reactive, bond-order potential. Our goal is to better understand the dependence of the film structure the reaction conditions. The simulations show the atomic-scale mechanisms by which the films nucleate and reveal the conditions needed to tailor the structure of the film. They also provide a basis for comparing the nucleation mechanisms and film structures obtained from ion-beam and cluster-beam deposition. @FootnoteText@ This work is supported by the Petroleum Research Fund and the National Science Foundation (CHE-9708049). .

4:20pm PS+SS-WeA8 Understanding Plasma Polymerization by Mass Selected Ions: 25 - 50 eV CF@sub 3@@super +@ vs. C@sub 3@F@sub 5@@super +@ Ion Modification of Polystyrene, *M.B.J. Wijesundara*, *L. Hanley*, University of Illinois, Chicago; *B. Ni, S.B. Sinnott*, University of Kentucky

Mass selected polyatomic ions beams can both create new materials similar to plasma polymers and elucidate polyatomic-surface collision mechanisms that are fundamental to plasma polymerization and etching. The fluorocarbon ions are studied here due to their technological relevance, the large number of previous studies on related systems, and their ability to illuminate several fundamental points in polyatomic ionsurface modification and plasma polymerization. Polystyrene has been chosen because it is a typical polymer surface whose lack of heteroatoms facilitates its surface chemical analysis. Previous experiments with 10 - 100 eV SF@sub 5@@super +@ and C@sub 3@F@sub 5@@super +@ indicated different chemistry with polystyrene surfaces.@footnote 1@ This work is continued here by examination of 25 - 50 eV CF@sub 3@@super +@ vs. C@sub 3@F@sub 5@@super +@ ion reactions with polystyrene surfaces using monochromatic x-ray photoelectron spectroscopy and molecular dynamics simulations. These two fluorocarbon ions display significantly different surface chemistry at these low kinetic energies that cannot be explained simply by eV/atom arguments. @FootnoteText@ @footnote 1@E. T. Ada, O. Kornienko, L. Hanley, J. Phys. Chem. B 102, 3959-3966 (1998).

4:40pm PS+SS-WeA9 Surface Interactions of Plasma-Generated NH@sub 2@ Radicals, E.R. Fisher, J.R.D. Peers, M.L. Steen, Colorado State University Ammonia plasmas are used in the microelectronics industry to deposit amorphous hydrogenated silicon nitride (a-SiN@sub x@:H) films. Thin films of a-SiN@sub x@:H are used as gate dielectrics and barrier coatings in microelectronic devices, capacitors in dynamic random access memory (DRAM) cells, and microfabrication of sensors and actuators. Using the imaging of radicals interacting with surfaces (IRIS) technique, we have performed a comprehensive study of the interactions of NH@sub 2@ with a variety of surfaces during NH@sub 3@ plasma processing. The substrates examined were Si(100), Pt, polyimide, polyethylene, and Teflon. In most cases, NH@sub 2@ scattering from the surface was greater than unity, indicating a production of NH@sub 2@ through surface reaction. Removal of charged species from the plasma molecular beam results in a decrease in the scattered NH@sub 2@ signal, indicating that the presence of ions in the plasma is responsible in large part for radical production at the surface. We have examined the dependence of the scattering signal intensity on applied rf plasma power and substrate temperature for all species. In addition, velocity distributions for NH@sub 2@ radicals scattering off the surfaces were measured. Using Monte Carlo simulation methods and assuming a Maxwell-Boltzmann distribution, we determine the translational temperatures of the scattered species. Species scattering off 300 K Si and Pt substrates have a translational temperature of 400±30 K, significantly higher than the substrate temperature, while the translational temperature of species scattering off the polymeric substrates tends to be closer to the substrate temperature. This suggests that the NH@sub 2@ radicals are coming to equilibrium with the polymeric substrates and not with Si or Pt. The temperature of the radicals in the plasma molecular beam itself is 512±8 K at 25 W applied plasma power, indicating that the radicals are cooling by collisions with the substrate surface.

5:00pm PS+SS-WeA10 FT-IR and XPS Study of Plasma-treated Acrylic Coating Surfaces, *M.K. Shi*, *G.L. Graff*, *M.E. Gross*, *P.A. Mounier*, *M.G. Hall*, Battelle Pacific Northwest National Laboratory

Polymer/metal multilayer structures have many potential optical, display, and packaging applications. A key issue for the successful processing of such multilayer stacks is obtaining good wetting and adhesion at each interface. Low-temperature plasmas have proven to be one of the most efficient technologies for such purposes. Moreover, the effects of plasma treatments are limited typically to the outermost surface layers and the process is fully compatible with the polymer/metal multilayers cluster tools. We studied the interaction of RF (13.56 MHz)plasmas with an acrylic (tripropyleneglycol-diacrylate)coating surface using FT-IR and XPS. The acrylic coating, with thickness varying from 100 Å to 2 µm, was deposited onto an AI metallized PET substrate by vacuum flash evaporation of the acrylic monomer and subsequent UV-curing. FT-IR measurements showed the destruction of initial ester (O-C=O) and ether (C-O-C) groups, and the ablation of H from C-H bonds after plasma treatments. These effects were accompanied by the formation of carbonyl (R-C=O) and/or acid (R-COOH) groups, and the development of graphite-like C-C structures. The spectral features are similar for N@sub 2@and O@sub 2@ plasma-treated surfaces, no N-containing absorption peaks can be identified for the N@sub 2@ plasma-treated surface. XPS measurements confirmed the loss of the ester (O=C-O) and ether (C-O-C) bonds with respect to the C-C (C-H) peak, and the formation of carbonyl groups. The spectra further showed that approximately 10% of atomic N have been incorporated into the surface after N@sub 2@ plasma treatment. These results showed clearly that FT-IR and XPS are complementary techniques for the characterization of plasma-modified polymer surfaces. The possible plasma/acrylic coating interaction mechanisms will be discussed.

Surface Science Division Room 606 - Session SS1+EM-WeA

Semiconductor Surface Science

Moderator: C.T. Campbell, University of Washington

2:00pm SS1+EM-WeA1 Electronic Transport Properties of Silicon Surfaces@footnote 1@, K. Yoo, University of Tennessee; A.P. Baddorf, Oak Ridge National Laboratory; H.H. Weitering, University of Tennessee

Most of our information about surface electronic properties has come from spectroscopic measurements and first principles electronic structure calculations. Direct measurements of transport properties of ultrathin films have revealed interesting physical properties, including quantum size effects. However, to correctly measure the surface or thin film conductivity, the conduction path through the bulk or substrate must be eliminated. We attempt to accomplish this by using crystalline silicon of "silicon on insulator"(SOI) material. Using STM, we have recently shown that 40 nm-thick Si(100) layers on SOI can be prepared with a comparable degree of structural perfection as the surfaces of bulk Si.@footnote 2@ For these SOI films, we also observed that at room temperature, LEED spots drift and gradually disappear during prolonged exposure to the electron beam, indicating that the ultrathin Si top layer is fully depleted of mobile

carriers, i.e. non-conducting. This leaves surface states as the only conduction channel. We have measured the surface conductivity of the Si(100)2x1 reconstruction on SOI as a function of temperature and Si film thickness during exposure to molecular oxygen using a four-point probe technique in ultrahigh vacuum. The oxygen induced conductivity changes strongly depend on the Si film thickness (@DELTA@@sigma@=-1.75x10@super -5@(@ohm@@super -1@) for 40 nm and (@DELTA@@sigma@=-9.219x10@super -6@(@ohm@@super -1@) for 90 nm thick films at room temperature. Differences are also observed in the temperature dependence, with possibly significant surface contributions to total sheet resistance at low temperature. These results indicate a correlation between transport properties and surface states, which will be discussed. @FootnoteText@ @footnote 1@ Work supported by National Science Foundation(DMR-9705246). @footnote 2@ K. C. Lin et al, Appl. Phys. Lett. 72, 2313(1998).@footnote *@ Managed by Lockheed Martin Energy Research Corp.

2:20pm SS1+EM-WeA2 Reinterpretation of the Scanning Tunneling Microscopy Images of Si(100) (2x1) Dimers-Observation on a Defect Free Surface, K. Hata, S. Yasuda, H. Shiqekawa, University of Tsukuba, Japan

In this presentation, we demonstrate that STM images of dimers of Si (100) taken with usual tunneling conditions are seriously characterized by tunneling from surface resonances and bulk states. In some cases, tunneling from these states overwhelm tunneling from the surface states which STM is generally believed to observe. The key point was the success to fabricate an almost defect-free Si(100) clean surface (defect density $\sim 0.1\%$), making observations at a very low bias possible (0.5V). STM images of the dimers at 80K and room temperature taken at such low biases showed several new features. (1) In the empty states, when the surface bias is above ~1.4V, regions between the dimers are observed. (2) At 80K, a bright row similar to that observed at room temperature is obtained, though a bright and dark (2x1) unit align alternatively along the dimer row direction. The brighter units observed at the high bias corresponds to the location of the upper atom. (3) In the filled states, each atoms of the dimers at room temperature when the surface bias is lower than ~-1V. Every time when the bias is increased, the STM images of the dimers would gradually revert to the usual bean-type image of dimers at ~-1V. High resolution CITS measurements and first principle calculations also showed consistent results. We revisit and refine the interpretation of the STM images of the dimers, insisting that tunneling from surface resonances and bulk states are very important. The new interpretation brings results of many experimental and theoretical researches into an unanimous agreement.

2:40pm SS1+EM-WeA3 STM-Study of the Absorption of Molecular Oxygen on GaAs(100), P. Kruse, J.G. McLean, A.C. Kummel, University of California, San Diego

There is currently a strong interest in making GaAs-oxide interfaces with very low defect densities to enable the use of GaAs-based FET technology. The interaction of oxygen with the GaAs surface plays an important role in this process. In this study, high-resolution scanning tunneling microscopy (STM) was used to image the chemisorption sites of molecular oxygen on the three most common reconstructions of the GaAs(100) surface, c(2x8), 6x6 and c(8x2). All studies were performed at room temperature. The sticking probability was greatest on the surfaces with As-As dimer bonds. Even though the molecular oxygen prefers to initially react with the empty dangling bonds of the Ga atoms, after dissociation the oxygen atoms seek to form bridge bonds between an electron rich As atom from an As-As dimer and a second atom, either As or Ga. These dimerized As atoms do not exist in the c(8x2) reconstruction, hence the greater inertness of that surface. This is in contrast to the reaction of these surfaces with halogens which only need to form one bond per halogen atom and equally attack all reconstructions.

3:00pm **SS1+EM-WeA4 Chaotic-like Wavefunction Beating in Thin Silver Films with a Quasiperiodic Superstructure**, *C.-S. Jiang*, *H. Yu*, University of Texas, Austin; *Ph. Ebert*, Forschungszentrum J@um u@lich, Germany; *X.-D. Wang*, *R. Diener*, *Q. Niu*, *C.K. Shih*, University of Texas, Austin

It has been shown that atomically-flat Ag films can be grown on GaAs(110) substrates. These surfaces with (111) orientation exhibit, in addition, a onedimensional quasi-periodic superstructure. Taking such surfaces as a model system, we investigated the effect of quasi-periodic scattering potential on the electronic structure by using spatially resolved scanning tunneling spectroscopy. Quantum well states due to the z-confinement of the 2-D thin film are clearly observed as a function of thickness. In addition, we have observed very intriguing chaotic interference patterns The observation of chaotic interference pattern is found to arise from the quasiperiodic superstructure acting as scattering potential for the 2-D electronic system. Theoretical calculations of the electronic states of quasiperiodic structure are currently underway.

3:20pm SS1+EM-WeA5 3C-SiC(100) c(4x2) Surface and Sub-Surface Probed by Core Level Photoemission Spectroscopy Using Synchrotron Radiation and by Scanning Tunneling Microscopy, V. Derycke, H. Enriquez, P. Fonteneau, V.Yu. Aristov, P.G. Soukiassian, Commissariat à l'Energie Atomique and Université de Paris-Sud/Orsay, France; G. Le Lay, CRMC2 -CNRS and Université de Provence, France; C. Grupp, A. Taleb-Ibrahimi, LURE, Université de Paris-Sud/Orsay, France

We investigate the 3C-SiC(100) c(4x2) reconstruction surface and subsurface regions by Si 2p core level photoemission spectroscopy using synchrotron radiation at various photon energies and by atom resolved scanning tunneling microscopy (STM). The latter experiments are performed by tunneling into the empty and filled electronic states which allows to clearly identify both up- and down dimers (AUDD) [1] of the c(4x2) surface reconstruction. Contrary to earlier core level studies, we identify two surface shifted components at the Si 2p core level having the same intensity. These two Si 2p spectral surface features are clearly related to the up- and down-dimers (AUDD) of the c(4x2) surface reconstruction.@footnote 1@ In addition, two sub-surface shifted components are also found which shows that the sub-surface region is also significantly affected by stress far away from the outer surface, indicating the long range influence of the latter. The results also confirm that the c(4x2) reconstruction is terminated by one Si monolayer as already well established by various quantitative experimental investigations.@footnote 2@ These novel core level photoemission using synchrotron radiation and STM results further support the AUDD model of the 3C-SiC(100) c(4x2) surface reconstruction.@footnote 1@ However, they are clearly inconsistent with predictions of a "missing row asymmetric dimers" model (MRAD) recently proposed on the basis of ab initio pseudopotential calculations and STM image simulations.@footnote 3@ @FootnoteText@ @footnote 1@P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli and C. Joachim, Phys. Rev. Lett. 78, 907 (1997). @footnote 2@see e.g. V.M. Bermudez, Phys. Stat. Sol. (b) 202, 447 (1997); and references therein. @footnote 3@3-W. Lu, P. Krüger and J. Pollmann, Phys. Rev. Lett. 81, 2292 (1998).

3:40pm SS1+EM-WeA6 Mechanistic Studies of SiO@sub 2@ Deposition from TEOS / Ozone, *L.D. Flores, C. Tindall, J.E. Crowell*, University of California, San Diego

The low temperature deposition of SiO@sub 2@ from the reaction of tetraethoxysilane (TEOS) and ozone has been studied in-situ at atmospheric pressures. The studies were performed in a prototypical atmospheric pressure chemical vapor deposition (APCVD) reactor utilizing a commercial injector / vent assembly. The gas phase reactions were followed during deposition at 400°C using gas-phase transmission FTIR spectroscopy. Evolution of gas phase products during TEOS / O@sub 3@ reactions were compared and quite distinct from those observed during reaction of TEOS / O@sub 2@. The primary products produced upon ozonolysis of TEOS are acetic acid, formic acid, formaldehyde, carbon monoxide, carbon dioxide, and water. Mechanistic details of the deposition process were aided by model reaction studies performed in a gas cell using transmission FTIR spectroscopy. The model studies involved reaction of ozone with observed and potential deposition byproducts, such as acetaldehyde. The spectroscopic observations will be discussed with an emphasis on reaction mechanisms and the reactive pathways leading to the production of deposition precursors, and the influence of additives and byproducts on the morphological nature of SiO@sub 2@ film growth.

4:00pm SS1+EM-WeA7 Microcalorimetric Heats of Adsorption of Metals on Metal Oxide and Si(100) Surfaces, *D.E. Starr*, University of Washington; *D.J. Bald*, Intel Corporation; *J.E. Musgrove*, *J.T. Ranney*, *J.H. Larsen*, *C.T. Campbell*, University of Washington

Single crystal adsorption microcalorimetry has been proven to be a powerful method to study the heats of adsorption of gaseous atoms or molecules onto single crystal surfaces. Recently, a microcalorimeter has been built which possesses the capability to measure heats of adsorption of metal atoms onto single crystal surfaces as a function of coverage. A sensitive pyroelectric polymer is used to detect the heat released due to the adsorption of pulses of gaseous metal atoms, each containing ~2% of a monolayer, onto the surface. The microcalorimeter has been employed to study the energetics of film growth from the initial stages of deposition through the multilayer regime for metal on metal and metal on metal oxide

systems. For the metal on oxide systems, an initial heat of adsorption which is much lower than the heat of sublimation of the metal is observed. This provides detailed insight into the thermodynamic driving force for the metal overlayer to form three dimensional islands. Auger electron spectroscopy was used to verify the growth morphology. In addition, the extension of this technique to study the heats of adsorption of metals onto silicon substrates allows the study of many systems important to metalsemiconductor contact technology. In order to accurately quantify the heats of adsorption, the metals sticking probability on the surface must be known. These have also been measured and will be discussed. In addition, via a thermodynamic cycle the adhesion energy of the metal to the substrate is obtained from the measured microcalorimetric heats of adsorption.

4:20pm SS1+EM-WeA8 Nucleation and Growth of Hemispherical Grained Silicon, D. Llera-Rodriguez, E.G. Seebauer, University of Illinois, Urbana

Hemispherical grained silicon (HSG) is a material beginning to find widespread use for electrodes in DRAM applications. HSG is formed by the chemical vapor deposition of amorphous Si, followed by a CVD "seeding" step under slightly different growth conditions to form nuclei for surface crystallization. Subsequent rapid thermal annealing to above 600°C induces the nuclei to grow into 100-nm hemispheres via surface diffusion, yielding an electrode with high surface area that increases the capacitance of the resulting device. In addition to the practical applications, however, HSG formation provides useful insights into the fundamental mechanisms of nucleation and growth in a two-dimensional amorphous-to-crystalline phase transition. For example, we can rationalize our experimental results for nucleation density in terms of a rate-equation-based nucleation theory. Furthermore, through a series of growth studies we show that subsequent growth of the initial nuclei can be well-described by a two-dimensional continuum model based on adatom-vacancy pair formation on the amorphous surface, together with diffusion of the atoms toward the growing hemispheres. The activation energy of 2.5 eV describing growth represents the sum of energies for adatom diffusion and surface vacancy formation on the amorphous surface. Somewhat surprisingly, this value for amorphous Si matches that measured by separate experiments for crystalline Si.

4:40pm SS1+EM-WeA9 Characterization by STM of Interface between Silicon and Silicon Dioxide Layers Fabricated by Highly Concentrated Ozone, H. Itoh, A. Kurokawa, K. Nakamura, S. Ichimura, Electrotechnical Laboratory, Japan

We will show that the silicon dioxide film fabricated by ozone exposure@footnote 1,2@ has smooth and flat interface keeping the original step and terrace feature. Hydrogen-terminated Si(100) wafer was used as a substrate. Flat surface was prepared by additional growth of epitaxial Si layers (thickness; 120 nm) on Si substrate, and atomic hydrogen was adsorbed on the surface for passivation. STM images showed that the prepared surface was atomically flat with wide terraces which is larger than 100nm. A high-concentration ozone generator was used to form ultra thin silicon dioxide film on the surface. The output from ozone generator was the mixture gas of ozone(30 vol%) and oxygen. The substrate was exposed to the gas at room temperature for half an hour to form silicon dioxide film. The thickness of the oxide film formed by the exposure was estimated to be 1 nm, which was analyzed from intensity of XPS Si-2p peaks. After the oxidation, the silicon dioxide fill ! m was carefully removed by rinsing in HF solution to observe the interface structure. Slow etching rate in dilute HF solution(0.1%) was chosen to avoid uneven etching and the thickness was monitored every several minutes by XPS peaks to avoid overetching. The sample was inserted into ultra high vacuum(UHV) chamber and surface and interface was observed by scanning tunneling microscopy. STM images were obtained on the etched surface with monoatomic height resolution. Large terraces and few steps were observed in the STM images and surface roughness is estimated to be below 0.15 nm (rms.). This indicates that the silicon dioxide film was grown keeping the original step and terrace feature. The result suggests that Si was oxidized homogeneously and supports that the film was grown layer-by-layer mode. @FootnoteText@ @footnote 1@ A.Kurokawa et.al., Mater. Res. Symp. Proc.Vol. 513, p38, 1998, @footnote 2@ A.Kurokawa et.al., Mater. Res. Soc. Symp. Proc., 1999, in press

5:00pm SS1+EM-WeA10 Significant Effects of Arsenic Ion Implantation on Si Selective Epitaxy by Ultra-High Vacuum Chemical Vapor Deposition, *T. Furukawa*, *T. Nakahata, S. Maruno, Y. Tokuda, S. Satoh*, Mitsubishi Electric Corporation, Japan

Great attention has been paid on Si selective epitaxial growth for an application into ultra large scale integration. For the practical application, however, surface conditions of a Si substrate, which is affected by preceding process steps such as plasma etching and ion implantation, may have a great influence on growth behaviors. In this work, we have investigated the effect of low energy arsenic ion implantation on the Si selective epitaxy by use of ultra-high vacuum chemical vapor deposition. The substrates were prepared through conventional n-channel MOSFET fabrication sequence. In the arsenic ion implantation, dosage was varied from 0 to 4x10@super 15@cm@super -2@, while acceleration energy was fixed to be 10 keV. Before the Si growth, the wafers were cleaned by chemical wet etching, whereas chemical oxide was removed by diluted HF solution. The epitaxy was performed at nominal temperature of 600°C with a pure Si@sub 2@H@sub 6@ source gas. For a non-implanted wafer, island-like growth occurs. With sufficient dosage of arsenic ions, however, an epitaxial Si layer with excellent surface morphology was successfully grown. X-ray photoelectron spectroscopy measurements reveal that a thin SiO@sub x@ layer is formed below the substrate surface by a preceding plasma etching process. The growth mode change is interpreted in terms of reduction of the SiO@sub x@ layer by means of an additional sputtering effect of the ion implantation.

Surface Science Division Room 607 - Session SS2-WeA

Gas-Surface Dynamics

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

2:00pm SS2-WeA1 Dissociative Sticking of Small Oxidant Molecules on a Simple Metal; NO, O@sub 2@, CO and N@sub 2@ on Al(111), *H. Ternow, I. Zori@aa c@, B. Kasemo,* Chalmers University of Technology, Sweden

Motivated by our combined interest in molecular dissociation mechanisms at surfaces and early stages of surface oxidation, we are studying the dissociative sticking of small oxidizing molecules on Al(111). Hydrogen dissociation on metal surfaces has been clarified in detail by a close interplay between state resolved molecular beam experiments and calculated dynamics of dissociation on multidimensional potential energy surfaces. In contrast, dissociation dynamics of O@sub 2@ on simple metal surfaces, e.g. Al(111) and Ag(110, is not well understood. Molecular beam experiments indicate in both cases activated dissociation, while the calculated PES-s so far do not show such features. We have in this work investigated dissociation of several small molecules on Al(111) surface to elucidate the nature of the activation barrier and to explore these molecules' properties as oxidants for oxide film formation. The observed dissociative sticking for the two isoelectronic molecules, CO and N@sub 2@, is consistent with the presence of a very high activation barrier. In contrast, dissociation of NO and O@sub 2@ shows a rather low apparent activation barrier. Vibrational excitation of the molecules enhances dissociation. In the case of NO dissociation an energy dependent N/O ratio on the metal surface is observed. These features are discussed referring to the known symmetry and spatial extention of the frontier orbitals on the two species. The alternative - or complementary - view of the dissociation event, based on a harpooning mechanism, is also discussed.

2:20pm SS2-WeA2 Chemical Selectivity and Remote Dissociation-ICI/AI(111), K.A. Pettus, A.C. Kummel, University of California, San Diego

We have investigated the chemical selectivity of ICI adsorption onto Si(111)-7x7, a high work function surface, and Al(111), a low work function surface. ICI chemisorbs onto these surfaces by two mechanisms, abstractive chemisorption and dissociative chemisorption. Abstractive chemisorption, in which one halogen atom of ICI bonds to the surface while the other is ejected into the gas phase, is the dominant mechanism for both the ICI/Si(111)-7x7 and the ICI/Al(111) reactions. 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 10:1 for both the ICI/Si(111)-7x7 and ICI/Al(111) reactions. However, the dynamics leading to the chemical selectivity are quite distinct. For the ICI and Si(111)-7x7 reaction, a transition state is formed by the donation of electrons from ICI to an empty dangling bond on the Si(111)-7x7 surface. Since the highest molecular orbital (HOMO) of ICI consists of atomic iodine orbitals, the iodine atom is

the more reactive atom and chemical selectivity occurs. The ICI/Al(111) reaction occurs by a very different mechanism, remote chemisorption. In this process, an electron is harpooned from the aluminum metal surface to the lowest unoccupied molecular orbital (LUMO) of ICI. The adsorption of the electron transforms ICI into an excited repulsive state of the negative ion, ICI-. The LUMO primarily consists of atomic iodine orbitals; therefore, iodine again is the more reactive atom and ICI/ Al(111) abstraction favors the adsorption of iodine.

3:00pm SS2-WeA4 Quantum-State-resolved Studies of Elastic and Inelastic Scattering of H@sub 2@ from Cu and Pd, G.O. Sitz, E. Watts, The University of Texas. Austin

The scattering of H2 from Cu and Pd surfaces was studied using molecular beam techniques and quantum state-specific detection methods. A comparison is made for an unreactive case, H2(v=0)/Cu, and two reactive cases, H2(v=1)/Cu and H2(v=0)/Pd. Rotational excitation was observed in the scattering of H2(v=0) from Pd(111) and Cu(110) and was found to depend on the surface temperature. This rotational excitation occurred even when there was insufficient translational energy to account for the gain in rotational energy, indicating that part of the excitation energy is transferred from the surface to the molecule. The effect of vibrational motion in the H2/Cu system was studied by preparing the incident molecules in the single rovibrational state (v=1, J=1). The absolute survival probability of this state was measured along with the probabilities for rotational excitation and vibrational relaxation. This information is used to estimate the probability of dissociation of the vibrationally excited state. These results are compared with recent quantum dynamical calculations for the scattering of this particular state.

3:20pm SS2-WeA5 Atom Scattering From Atomic Surfactants, G.M. Nathanson, J.A. Morgan, W.R. Ronk, M. Manning, University of Wisconsin, Madison INVITED

Scattering experiments show that the rate of energy transfer between atomic gases and atomic liquids can be controlled by altering only the composition of the outermost surface layer of atoms. In the case of the 0.2% bismuth/99.8% gallium liquid alloy, the surface composition can be varied from a nearly pure Bi monolayer at temperatures near 290 K to 80% surface Ga at 900 K. This Bi surface enrichment is due to the much lower surface tension of pure Bi than of pure Ga. We find that impinging argon and xenon atoms lose nearly the same amount of energy in collisions with pure liquid Bi as with the bismuth-covered Bi/Ga alloy created at low temperatures. With increasing temperature, the rate of collisional energy transfer increases nearly linearly toward the value for pure liquid Ga as the surface Bi atoms are replaced by Ga atoms. These results suggest that the Ga atoms underneath the surface Bi atoms do not play a direct role in controlling the exit energies of the inelastically scattered Ar or Xe atoms; the rate of approach to gas-liquid thermal equilibrium depends only on the composition of the outermost surface layer.

4:00pm SS2-WeA7 Molecular Beam Studies of the Extrinsic Precursor State: Trapping of Alkanes on Alkane-Covered Pt(111), *A.F. Carlsson*, *R.J. Madix*, Stanford University

Adsorbed species can significantly affect probabilities of adsorption of incident molecules. The classic studies of CO adsorption on metals lead to the concept of the extrinsic precursor state, and the analysis of Kisliuk of this process is well known. However, there few systematic studies of the dynamics of this process and the way in which properties of the adsorbed state affect adsorption. Using a liquid helium cryostat to achieve surface temperatures upward from 25 K and molecular beam methods, we have studied the adsorption probabilities of methane and ethane on Pt(111) surfaces presaturated by the adsorption of another alkane from a low pressure ambient. Firstly, methane adsorbs on the clean surface with nearnormal energy scaling. On all covered surfaces, except that saturated by ethane, methane traps with probabilities ranging from 0.8 to 0.9, dependent on incident angle and energy. Generally, the trapping probability depends weakly on incident angle and energy. The weak dependence on incident angle is attributed to surface corrugation produced by the adsorbed alkanes. In the case of methane trapping on an ethane-covered surface a threshold to adsorption is observed. Below 16 kJ/mol the trapping probability remains very small, but above this threshold the trapping probability increases to 0.9. This "activated" molecular adsorption is guite dramatic. Ethane, however, shows distinctly different effects. The differences are attributed to size effects, not binding energy differences. These and other observations will be discussed.

4:20pm SS2-WeA8 Influence of Rotational Energy on Adsorption Probability for a Physisorbed System: C2H4 on Ag(001), *M. Rocca*, *Luca Vattuone*, *U. Valbusa*, University of Genova, INFM, CSFBT-CNR, Italy

We show that the population of the rotational degrees of freedom of gas molecules affects their adsorption probability also for a physisorbed state. The effect, expected to be very general, is demostrated for the case of ethylene interaction with Ag(001) where we observe that the physisorption probability is suppressed for molecules produced with a hot nozzle, characterized by a sustantially larger rotational quantum number. Chemisorption of ethylene is observed for nozzle temperatures above 870 K and occurs in two phases characterized by different vibrational electron energy loss spectra. The barrier to chemisorption is in the vibrational degree of freedom as can be inferred by comparing pure and seeded beam data. At still larger nozzle temperatures fragmentation of ethylene upon adsorption is observed.

4:40pm SS2-WeA9 Vibrational-State-Selected Studies of Gas-Surface Dynamics, A.L. Utz, L.B.F. Juurlink, R.R. Smith, P.R. McCabe, C.L. DiCologero, Tufts University

A recently developed experimental technique uses state-resolved infrared laser excitation to probe dissociative chemisorption dynamics with quantum state resolution. We combine a supersonic molecular beam source, infrared laser excitation of methane molecules in the beam, and UHV surface spectroscopies to quantify the reactivity of gas-phase reagents excited to single, selected vibrational states. This approach permits independent and precise control over the translational and vibrational energy content of gas-phase reactants, as well as the character of their vibrational motion. We report on our use of this approach to unravel the dissociative chemisorption dynamics of methane on Ni(100). We find that methane molecules excited to the v=1 level of the antisymmetric C-H stretching vibration, @nu@@sub 3@, are up to 1600 times more reactive than are molecules in the v=0 level. Over a translational energy range from 16 to 68 kJ/mol, the sticking probability for these molecules increases from 3x10@super -5@ to 2x10@super -2@, which indicates that the @nu@@sub 3@ state is only responsible in part for the reactivity of a thermal distribution of vibrational states. We will also compare the efficacy of @nu@@sub 3@ excitation with other coordinates for energy deposition in the methane/nickel system.

5:00pm SS2-WeA10 Reactive Scattering Dynamics of Fast Atoms with Hydrocarbon Surfaces: Initial and Steady-State Reactions, *T.K. Minton*, *J. Zhang*, *D.J. Garton*, *J.W. Seale*, Montana State University

The interactions of energetic atoms with hydrocarbon surfaces are largely responsible for the degradation of polymeric materials in space and for the outcome of polymer etch processes. Molecular beam-surface scattering experiments show that non-equilibrium processes dominate both the initial and steady-state interactions when a hydrocarbon surface is bombarded with a beam containing fast oxygen atoms. Direct inelastic scattering is the most probable non-reactive interaction. The most likely initial interaction is gas-phase-like H-atom abstraction to form OH. Once formed, the OH may undergo further collisions and reactions with the surface, some of which produce H@sub 2@O. The initial reactive and non-reactive events may be described with a simple kinematic picture that allows us to determine the effective surface mass encountered by an incident O atom, as well as the fraction of the atom-surface collision energy (in the center-of-mass frame) that is converted into internal energy in the surface and in the recoiling gaseous species. During steady-state oxidation, CO and CO@sub 2@ are produced. Formation of these molecules is believed to account for the erosion, or mass loss, of a polymer under O-atom attack. The rate of CO and CO@sub 2@ production from the surface is significantly enhanced when high-energy (>9 eV) Ar atoms collide with a surface that is undergoing continuous oxidation. This observation suggests that collisional processes may be important in material etching.

Surface Science Division

Room 604 - Session SS3+NS-WeA

Islands, Clusters, and Steps

Moderator: J.C. Hamilton, Sandia National Laboratories

2:20pm SS3+NS-WeA2 The Phase Diagram of a Self-Organizing Nano-Array, K. Pohl, J. de la Figuera, M.C. Bartelt, N.C. Bartelt, Sandia National Laboratories; J. Hrbek, Brookhaven National Laboratory; R.Q. Hwang, Sandia National Laboratories

Recent experiments show that in a submonolayer silver film on Ru(0001), a perfectly ordered array of nanometer-sized vacancy islands forms upon exposure to sulfur. By measuring the thermal vibrations of this equilibrium structure the forces responsible for the observed self-organization were identified and the elastic constants of the lattice derived.@footnote 1@ In order to develop a better understanding of the formation and ordering processes of this structure, we have explored the complete phase diagram of the vacancy island lattice. Via scanning tunneling microscopy we follow in real time the assembly of the hole lattice at different temperatures and S-Ag coverages. We find the hole lattice to be very robust against annealing cycles to 500 K. The final periodicity of the vacancy island lattice seems to be independent of the periodicity of the initial dislocation network in the strained silver film. This network only determines the initial etching sites for the S adatoms. The periodicity of the dislocation network in the clean Ag film depends on the Ag coverage. Beyond a threshold S-coverage, the array undergoes a phase transition to a periodic array of stripes. We will present a detailed study of the stability of these various novel equilibrium phases and identify the driving forces behind their formation. This work is supported by the Office of Basic Energy Sciences Division of Materials Sciences of the U.S. DOE (DE-AC04-94AL85000). @FootnoteText@ @footnote 1@K. Pohl et al., Nature 397, 238 (1999)

2:40pm SS3+NS-WeA3 Tunneling on Ag and Au: Surface State Spectroscopy and Magic Molecular Clusters, R. Berndt, RWTH Aachen, Germany INVITED

We use low-temperature scanning tunneling microscopy (STM) to investigate geometric and electronic properties of nanoscale structures. In this presentation, we discuss various aspects of the Ag(111) surface state such as surface state confinement to nanometer-sized islands, its interaction with isolated magnetic impurity atoms, and the first study of lifetimes effects on Shockley surface state electrons using low-temperature STM spectroscopy. Moreover, we report on observations of twodimensional supramolecular clusters and chains which self-assemble upon deposition of 1-nitronaphthalene (NN) onto Au(111). NN molecules become 2D-chiral upon adsorption. Their handedness is determined from from high-resolution STM images and local density calculations. Modeling shows that hydrogen bonds cause the observed self-assembly. Clusters and chains mutually interact via electrostatic repulsion.

3:20pm SS3+NS-WeA5 Step Energetics of Pb(111) Vicinal Surfaces from Facet Shape, H.P. Bonzel, K. Arenhold, A. Emundts, S. Surnev, Forschungszentrum Jülich, Germany; P. Wynblatt, Carnegie Mellon University

The formation energies of steps and kinks, the step stiffness and the step interaction energy of B-steps vicinal to (111) have been derived quantitatively from the equilibrium shape of small three-dimensional Pb crystallites supported on a Ru(001) surface. The crystallites were imaged by scanning tunneling microscopy and show (111) and (100) facets.@footnote 1@,@footnote 2@ The boundary of these facets is well defined in the STM images and was used to determine also the azimuthal dependence of the step free energy for vicinal (111) surfaces by employing an "inverse" Wulff construction. Taking the accepted value for the surface free energy of Pb, absolute step energetic quantities can be quoted for both A- and B-steps. The step stiffness is derived from the step curvature and the step energy. The entropic step interaction energy of B-steps at 440 K is calculated from the step stiffness. Furthermore, by taking into account the curved portion of the vicinal (111) surface normal to the direction of B-steps, which shows a Prokovsky-Talapov behavior,@footnote 2@ the total step interaction energy of B-steps is also obtained. The entropic and total step interaction energies of B-steps at 440 K are thus 2.3 meV/Å@super2@ and 7.9 meV/Å@super2@, respectively.@footnote 3@ The difference is largely attributed to the elastic dipole-dipole interaction. Calculations of the step and elastic step interaction energies using the embedded atom potential of Pb@footnote 4@ are currently underway and will be compared with the experimental data. @FootnoteText@ @footnote 1@ S. Surnev et al., J. Vac. Sci. Technol. A 16(1998)1059. @footnote 2@ K. Arenhold et al., Surf. Sci.

417(1998)L1160. @footnote 3@ K. Arenhold et al., Surf. Sci. 424(1999)271. @footnote 4@ H.S. Lim, C.K. Ong, F. Ercolessi, Surf. Sci. 269/270(1992)1109.

3:40pm SS3+NS-WeA6 Control of Monolayer Island Vacancies on Pt(111) and their Impact on Surface Chemistry, K. Nafisi, J. Samu, J.C. Hemminger, University of California, Irvine

Michely and Comsa@footnote 1@ have demonstrated that argon ion sputtering Pt(111) at elevated temperature will create ordered monolayer deep island vacancies. We show, by varying the surface temperature parameter, that it is possible to control the size of these vacancies over the range of 30Å to 400Å. We have used a variable temperature, scanning tunneling microscope (STM) to quantify the formation of the island vacancies. We have also used the STM to investigate the dehydrogenation of a series of mono-olefins to form carbon particles at 700 K. The carbon particles were formed both on a clean, annealed, and on sputtered Pt(111) surfaces. The carbon particles are randomly distributed over the surface. and show no preference for formation at particular surface features such as step edges. Also, the formation of the carbon particles is not influenced by large monolayer island vacancies. However, on a surface, where smaller island vacancies have been formed, the carbon particles show a preference of forming on the terraces and not inside of the island vacancies. The difference in behavior between large vacancy islands and small vacancy islands (d @<=@ 40Å) can be explained if molecular diffusion across steps is slow and dehydrogenation products initially decorate the walls (steps) of the vacancy islands. We have also studied the impact of sputtering the sample prior to olefin adsorption with the incident ion beam at an angle away from the surface normal. The carbon particles formed on such surfaces are highly spatially aligned. @super *@This work was supported by the US Department of Energy, Office of Basic Energy Sciences. @FootnoteText@ @footnote 1@ T. Michely and G. Comsa, Nucl. Instr. and Meth., B82, 207 (1993).

4:00pm SS3+NS-WeA7 Coalescence Dynamics of Small Pt Clusters on Pt(111) Surfaces: A Molecular Dynamics Study, V. Chirita, E.P. Münger, L. Hultman, Linköping University, Sweden; J.E. Greene, University of Illinois, Champaign-Urbana

The diffusion and coalescence of small clusters are fundamental intralayer mass transport processes, playing a crucial role during the early stages of thin film deposition and crystal growth. We use embedded-atom method molecular dynamics simulations to follow the kinetics characterizing these processes for compact, 2D Pt@sub 5@ and Pt@sub 6@ clusters on Pt(111), at 1000 K. Investigations are carried out for configurations consisting of clusters initially separated by a distance equal to that between second neighbors, in statistically independent runs of 10 ns each. Prior to coalescence, we observe that the intercluster separation distance is reduced via two pathways: net cluster diffusion, involving mechanisms which preserve cluster shape, and repeated cluster reshaping. Cluster diffusion occurs primarily via concerted gliding and reptation, a recently proposed diffusion mechanism for 2D clusters on (111) metallic surfaces. Cluster reshaping involves edge-diffusion and/or concerted dimer/trimer gliding. Our simulations reveal that cluster coalescence is achieved via complex dynamics. Clusters preserving their initial compact shape can coalesce via concerted gliding and form clusters with a high number of intracluster bonds. These larger clusters maximize the number of intracluster bonds in relatively short times, primarily via edge-diffusion. We observe for the first time, that during the fusion process, cluster-cluster interactions can induce cluster translations via sequential atom motion, through fcc/hcp bridge sites, within clusters. For clusters that reshape prior to coalescence, we observe that cluster-cluster interactions induce the transfer of single atoms, from either cluster, to sites neighboring both clusters, and thus create a "bond" between clusters. Once formed, we did not observe dissociation. In this case, the newly formed clusters have elongated shapes with narrow middle sections (1 to 2 atoms thick) and, as a result, the transition toward compactness is achieved over considerably longer times. Moreover, these clusters exhibit a variety of reconfiguration and migration events. Edge-diffusion, reptation and dislocation propagation are the competing diffusion mechanisms observed for clusters in this range.

4:40pm SS3+NS-WeA9 Spontaneous Island Formation on the GaAs(001) 2x4 Reconstructed Surface, P.M. Thibado, V.P. LaBella, M. Anser, Z. Ding, D.W. Bullock, University of Arkansas

Given the growing use of III-V semiconductor materials in wireless and high speed communication devices the preparation of atomically flat single crystal GaAs(001) surfaces was examined, since these devices are primarily

fabricated using epitaxial methods . To achieve this, a state of the art molecular beam epitaxy (MBE) system with a novel temperature measurement system accurate to within ± 2 @super o@C, has been combined, in situ, with a scanning tunneling microscope (STM). Surprisingly, when the GaAs(001) 2x4 reconstructed surface is annealed above a critical temperature (570 @super o@C), under a constant As@sub 4@ flux, it spontaneously forms one monolayer high islands covering one half of the otherwise flat terraces. This process is reversible and when fit to a free energy model yields information about the surface bonding energies. This work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1-1058).

5:00pm SS3+NS-WeA10 TiN(001) Epitaxy: An in-situ Temperature-Dependent STM and Level-Set Modeling Study, S. Kodambaka, P. Desjardins, A. Vailionis, I. Petrov, J.E. Greene, University of Illinois, Urbana; D. Chopp, Northwestern University

We have used in-situ temperature-dependent STM measurements during deposition and post-annealing combined with modeling to provide atomicscale insights into surface morphological evolution during TiN growth. Epitaxial TiN(001) layers were grown by reactive evaporation onto MgO(001) at 700-950 @super o@C. Partial TiN monolayers (0.1-0.4 ML) were then deposited and in-situ high-temperature STM used to follow the coarsening and decay kinetics of single and multiple islands (Ostwald ripening) on flat terraces and in single-atom deep vacancy terraces. From these results, combined with finite-element solutions of the Gibbs-Thompson and diffusion equations, we obtain the activation energy for surface diffusion, the Ehrlich barrier energy, and the island line tension. We have also derived and implemented a level-set method for simulating the dynamics of island decay on time scales not accessible to experiment. Level-set methods are numerical techniques for computing the position of propagating fronts that can easily handle topographical changes as well as singularities including corner and cusp development. Our model includes geometry-dependent surface and edge diffusion, step-edge dynamics, and attachment/detachment rates. We compare our numerical results to in-situ STM time-sequence experiments under the same conditions. The results of the level-set calculations serve as a basis for a robust quantitative and predictive model for both microstructural and surface morphological evolution as a function of deposition conditions during polycrystalline TiN growth.

Surface Science Division Room 4C - Session SS-WeP

Poster Session

SS-WeP1 Strain and Strain Relief in Gadolinium(0001) Thin Films on Mo(112), *T. Komesu, H. Jeong, P.A. Dowben,* University of Nebraska, Lincoln

The electronic structure of strained and unstrained Gd(0001) has been studied with spin-polarized photoemission spectroscopy and spin-polarized inverse photoemission spectroscopy. In this work, we observed that relaxation of the expansively strained crystal in-plane lattice constant, of Gd(0001) on Mo(112), significantly diminishes the differences in the electronic structure from that observed for Gd(0001) grown on W(110). The defects incorporated in Gd films, with increasing film thickness, lead to both lattice relaxation and a loss of net polarization for Gd(0001) grown on Mo(112).

SS-WeP2 Formation process of a Cu-Zn surface alloy on Cu(111) investigated by STM, *M. Sano*, *S. Ishikura*, University of Tsukuba, Japan; *T. Fujitani*, National Institute for Resources and Environment, Japan; *J. Nakamura*, University of Tsukuba, Japan

We had previously shown that a Zn-deposited Cu(111) surface is a good model for methanol synthesis by the hydrogenation of CO@sub 2@, and a Cu-Zn surface alloy is active species for the reaction. Here, we investigated the formation process of the Cu-Zn surface alloy formed on a Zn-deposited Cu(111) surface by STM. The STM measurements were carried out using a UHV-STM apparatus equipped with LEED-AES. Zinc was deposited on Cu(111) by resistively heating a Zn wire. STM image of the surface after the Zn deposition at room temperature showed that the bright atoms were localized in the vicinity of step edges. These blight atoms were considered as Zn atoms substituted for the substrate Cu atoms. The density of Zn atoms decreased with increasing distance from step edges and no Zn atoms were observed on the terrace away from the steps. The migration of Zn atoms over the surface was observed by time resolved STM measurements. The migration rate was determined to be 6.67x10@super -3@ s@super -1@ and the mean residence time was 150 s. These results indicate that the alloying initially occurs around steps and then Zn atoms migrate over the terrace. On the other hand, after annealing the Zndeposited Cu(111) at 523 K, STM images showed that Zn atoms were distributed homogeneously over the Cu(111) surface. The Zn coverage estimated by the STM images was in good agreement with that measured by AES. Pair-correlation analysis of the NN distribution for Zn atoms suggested that Zn atoms were randomly distributed on the terraces, indicating that Zn atoms were randomly substituted for Cu atoms leading to the Cu-Zn surface alloy.

SS-WeP3 Microkinetics of Formate Synthesis on Cu Catalysts, *T. Fujitani*, National Institute for Resources and Environment, Japan; *I. Nakamura*, *H. Nishimura*, *H. Nakano*, *J. Nakamura*, University of Tsukuba, Japan

The kinetics of formate synthesis by hydrogenation of CO@sub 2@ and formate decomposition has been studied on Cu(111) and Cu(110) surfaces using in-situ IRAS and STM apparatuses combined with a reactor (1 atm). It has been found that the formate synthesis does not depend on the surface structure of copper between Cu(111) and Cu(110). The activation energy of formate synthesis on Cu(111) and Cu(110) have been determined to be 68.3 and 69.7 kJ/mol, respectively. The microkinetics of the formate synthesis can be explained by that assuming an Eley-Rideal mechanism. On the other hand, the activation energy and the pre-exponential factor for formate decomposition on Cu(111) were different from those on Cu(110), indicating that the decomposition of formate species depend on the Cu surface structure. Furthermore, the decomposition rate of formate on Cu(111) is very different depending on the preparation method, the synthesis from CO@sub 2@ and H@sub 2@ at atmospheric pressure and the preparation by adsorption of HCOOH in UHV. However, the activation energy of the decomposition for both cases is close to each other, meaning that the frequency factor of the rate constant is different for the two cases. The difference can be explained by the different structures of formate observed by STM. In the presence of atomic hydrogen, the decomposition rate of the formate synthesized from CO@sub 2@ and H@sub 2@ increases and becomes equal to the decomposition rate of the formate prepared by the adsorption of HCOOH. The activation energies and the preexponential factors for both the formate synthesis and the formate decomposition on Cu/SiO@sub 2@ were in good agreement with those on

Cu(111), suggesting that the surface structure of Cu for the Cu/SiO@sub 2@ catalyst is identical with the Cu(111) surface.

SS-WeP4 The Adsorption-Desorption Properties of CO on W(111) Surface, S.-B. Lee, S.-Y. Lee, Y.-D. Kim, T.S. Yang, J.-H. Boo, C.Y. Park, SungKyunKwan University, Korea; H.-T. Kwak, Kook Min University, Korea

The adsorption and desorption properties of CO have been studied on W(111) surface in the temperature range of 300 - 1100 K by LEED, XPS, UPS, and TDS. After CO saturation at 300 K, four adsorption states obtained from TDS experiment were observed at 400, 850, 1000, and 1100 K, called @alpha@, @beta@@sub 1@, @beta@@sub 2@, and @beta@@sub 3@ states, respectively. The desorption temperature of @beta@@sub 3@-CO state shifted to higher temperature with increasing CO exposure signifying an attractive lateral interaction between adsorbed species. Using Bragg-Williams approximation the lateral interaction energy (-5.7 kJ/mol) was calculated and the TD-spectra obtained experimentally were successfully simulated using by quasi-chemical approximation. The desorption kinetic order of the @beta@@sub 3@-CO state is followed by the first order indicating that the adsorbed state of @beta@@sub 3@-CO seems to be a molecular state rather than that of dissociated state. With UPS and XPS, the CO adsorption property (especially the @beta@@sub 3@-CO) on W(111) was clearly confirmed. The adsorption of CO on W(111) at 300 K exhibited only one emission peak at -6.3 eV below Fermi level due to 1@pi@+5@sigma@ molecular orbitals of CO. With heating the adsorbed CO to 1000 K, however, an additional emission peak was also observed at -7.1 eV due to an orbital energy splitting of 1@pi@+5@sigma@. This is strongly supported with a theoretical result calculated by ASED-MO method. Comparing the O state of @beta@@sub 3@-CO with that obtained from the dissociatively adsorbed oxygen species, we can identify that the @beta@@sub 3@-CO is different with that for dissociated CO suggesting a non-dissociated CO species with different geometry. From these results, a lying-down species of adsorbed CO is proposed.

SS-WeP5 Ordered Structures of Oxo Overlayer on Cu(111) Electrode Surface in an Alkaline Electrolyte Revealed by Electrochemical STM, O. Matsuoka, S. Yamamoto, S. Sugiyama, Mitsui Chemicals, Inc., Japan; H. Nozoye, National Institute of Materials and Chemical Research, Japan

Redox behavior of copper surface in aqueous solution is of great interest in many industrial fields, such as energy, catalytic, and microelectronic applications. Many characterization studies on copper electrode surface revealed that surface oxygen is not entirely removed even at the potential corresponding to the onset of hydrogen evolution. This oxo overlayer on surface is considered active for catalytic reactions.@footnote 1@ Information about the structure and behavior of oxo overlayer in aqueous solutions seems to provide a proper understanding of reacting mechanism of copper catalysts. We have investigated the structure of Cu(111) electrode surface that have an oxo overlayer in an 0.01M NaOH aqueous solution by using electrochemical scanning tunneling microscope (EC-STM). Two kinds of periodical structures of bright spots were observed.@footnote 2@ Dimensions of these periodical structures were similar to the unit cell for the (@sr@7 x @sr@7) and (2@sr@7 x 2@sr@7). The periodical structure similar to (@sr@7 x @sr@7) appeared at a cathodic wave at -0.9 V vs. Ag/AgCl on cyclic voltammogram, and this periodical structure was converted into (2@sr@7 x 2@sr@7) at more negative potential. Anodic wave related with the cathodic wave at -0.9 V appeared in anodic sweep. The potential of this anodic wave was different between these two periodical structures. We consider these periodical structures show an alignment of CuOH surface species which created by the reduction of sub-surface oxygen.@footnote 3@ @FootnoteText@ @footnote 1@L.D.Burk, et al., J.Electrochem.Soc., 137,553(1990) @footnote 2@O.Matsuoka, et al., Chem.Lett., 947(1998) @footnote 3@S.Haetinger, et al., J.Electroanal.Chem., 397,335(1995).

SS-WeP6 Structure of MnO@sub x@/Rh(100) studied by STM, H. Nishimura, T. Tashiro, University of Tsukuba, Japan; T. Fujitani, National Institute for Resources and Environment, Japan; J. Nakamura, University of Tsukuba, Japan

A modified Rh/SiO@sub 2@ catalyst with Fe or Mn shows excellent catalytic activity for the hydrogenation of CO into C@sub 2@ oxygenates such as acetic acid, ethanol and acetoaldehyde. The active sites may be located at the interface between Rh and MnO@sub x@ species. We have studied the structure of a MnO@sub x@ deposited Rh(100) surface using an ultra high vacuum scanning tunneling microscope (UHV-STM). The deposition of Mn over a Rh(100) surface was performed by resistively heating a Ta boat and then the Rh sample was annealed in an oxygen atmosphere to prepare the MnO@sub x@ species. The STM images

showed a c(2x2) structure and a characteristic square unit (30 Å x 30 Å), which were tentatively assigned to Mn-Rh surface alloy and MnO@sub x@ species, respectively. A (111) like structure with six-fold symmetry was also assigned to MnO@sub x@ species.

SS-WeP7 Electrochemical Scanning Tunneling Microscopy of Copper Adlayers on Iodine-Covered Au(111) in Sulfuric Acid Solution, A. Martinez-Ruiz, CICESE & Fac. de Ciencias, UABC, MEXICO; J. Valenzuela-Benavides, L. Morales de la Garza, CCMC-UNAM, Mexico; N. Batina, UAM-Iztapalapa, Mexico; F. Castillon, CCMC-UNAM, Mexico

We present structural and electrochemical studies of copper electrodeposition on the Au(111) surface precovered with iodine in a sulfuric acid solution. In situ electrochemical scanning tunneling microscopy (STM) studies reveal different adlayer structures depending on the potential of the gold working electrode. Before initiating the underpotential deposition (UPD) of copper, a (5x@sr@3) structure of the iodine adlayer is observed on wide terraces as reported in a similar study with perchloric acid solution. For more negative potentials, the (5x@sr@3) structure transforms to a (3x3) structure around 320mV (vs a Cu/Cu@super ++@ electrode). Cyclic voltammetry (CV) suggests that not enough copper is depositing at this potential to cause the observed (3x3) structure to form, since only a significant ammount of copper deposition begins at potentials below 250mV. This is in sharp contrast to the reported study performed in perchloric acid solution, where the (3x3) is attributed to the UPD of copper of approximately less than half of a monolayer. At the end of the UPD process a (@sr@3x@sr@3)R30@super o@ structure is observed. All these structures are also observed during the CV anodic cycle, returning to the initial (5x@sr@3) structure of the iodine adlayer, which can be removed at a more positive potential with the iodine atoms diffusing into the solution, leaving a bare Au(111) surface. The above results strongly indicate that the stable iodine layer exist on the top layers of Cu and Au during deposition and stripping of Cu. The presence of anions is discussed which may explain the difference between the CV data and the STM images.

SS-WeP8 Lateral Compression of a Xe Film Physisorbed on the Surface of a Silver Single Crystal, S. Igarashi, A. Tosaka, T. Hirayama, I. Arakawa, Gakushuin University, Japan

The layering transition of a physisorption system on a metal single crystal has been investigated by means of an ellipsometry and an eXtremely-lowcurrent LEED (XLEED). Our XLEED system is operated at the primary electron current of about 1 pA or less, which minimizes the effect of desorption, defect formation, and charging.@footnote 1@ We observed the surface structure of Xe/Ag(111) by XLEED while monitoring the layer growth by the ellipsometry from a submonolayer film to a thick one. An equilibrium between the Xe film and coexisting three-dimensional Xe gas has been maintained throughout the experiment. From a monolayer film to a sufficiently thick film, the Xe overlayer has clear hexagonal structure whose directions of the unit vectors are coincident with those of the substrate. The Xe-Xe spacing in the monolayer film on Ag(111) is known to be a few per cent larger than that of bulk. Our interest is how the Xe-Xe spacing varies in the process of layer growth. We have made a systematic observation of the change of the Xe-Xe spacing in one and two monolayer films at pressures between 10@super -7@ and 10@super -2@ Pa and at temperatures between 50 and 100 K. In the case of isothermal growth at 78.4 K, for example, the Xe-Xe spacing of the monolayer film is 4.53 Å at immediately after the first layer condensation at 1x10@super -5@ Pa and decreases gradually to 4.5 Å with increasing a surrounding pressure up to 1x10@super -3@ Pa. Then the spacing decreases rapidly and reaches almost that of bulk, 4.39 Å, just before the second layer condensation at the pressure of 4x10@super -2@ Pa. @FootnoteText@ @footnote 1@ S. Igarashi, Y. Abe, Y. Irie, T. Hirayama and I. Arakawa, J. Vac. Sci. Technol. A 16, 974 (1998).

SS-WeP9 A Comparative Study for Small Molecule Adsorption onto Stoichiometric and Defective TiO@sub 2@ and SrTiO@sub 3@ Surfaces, *K.F. Ferris, L. Wang,* Pacific Northwest National Laboratories

Interactions of water and HCOOH with stoichiometric and defective TiO@sub 2@(100), TiO@sub 2@(110), and SrTiO@sub 3@(100) surfaces have been studied using electronic structure calculations. This paper presents a comparative study for the relationship between adsorbate interactions and reactivity focusing on the role of surface structure. Preliminary results for formate interaction with SrTiO@sub 3@(100) indicate strong adsorption consistent with experimental results, but in a distinctly different geometric arrangement due to absence of bridging oxygens present for the TiO@sub 2@ surfaces. This absence directly affects the water adsorption and dissociation behavior for SrTiO@sub 3@. Structural differences again modulate the reactivity of defect sites. Further results will be discussed in terms of potential reaction mechanisms and correlations with ongoing experimental studies.

SS-WeP11 Structural and Chemical Investigations on Different Polar ZnO Surfaces, St. Hoevel, Th. Beker, Ch. Boas, U. Burghaus, K. Weiss, M. Wuehn, C. Kolczewski, V. Staemmler, Ch. Woell, Ruhr-Universität Bochum, Germany We report on investigations of the structural and chemical properties of the two differently terminated Zn(0001) surfaces. The clean, oxygen terminated surface was studied with helium atom scattering (HAS) and LEED. The peak-shapes of the He-atom diffraction peaks and the variation of the He-atom reflectivity as a function of He-atom wavelength provide detailed information on the surface morphology (step height distribution, average terrace width, type of defects). As regards the chemical properties of the surface (e.g. presence of acidic sites), we studied the adsorption behaviour of pyridine on the two differently terminated ZnO(0001) surfaces with thermal desorption spectroscopy (TDS), x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (NEXAFS). The interpretation of the latter results is based on precise ab-initio electronic structure calculations for a model compound. The binding energy of pyridine on the O-terminated (000-1)-surface amounts to 57 kJ/mol and the spectroscopic data reveal only small modifications of the pyridine electronic structure, indicating the presence of a physisorbed species. On the Zn-terminated ZnO(0001)-surface the binding is substantially stronger, 112 kJ/mol, and the N1s NEXAFS-data for the pyridine @pi@*-resonance shows a shift of 0.6 eV towards higher binding energies. This observation indicates a substantial interaction between the nitrogen lone pair and the Zn d electrons, as confirmed by the ab-initio calculations.

SS-WeP12 Formation of a Smooth and Pure Chromium Oxide Film on Stainless Steel Surface by Oxidation, *B. Cho, S. Chung,* Pohang University of Science and Technology, South Korea

Oxidation of stainless-steel for annealing temperature of 450 °C in oxygen partial pressures of 10@super -9@ to 10@super -4@ Torr was tested to form a smooth and pure chromium oxide film on the surface. Atomic force microscopy and scanning tunneling microscopy images show that oxidations in low oxygen pressures (10@super -9@ and 10@super -8@ Torr) favor the formation of not only macroscopically but also atomically smooth oxide films, which is almost total chromium oxide, as characterized by X-ray photoelectron spectroscopy. But oxidations in high oxygen pressures (10@super -6@ and 10@super -4@ Torr) prefer the development of very rough oxide films with distinct grains and significant proportion of iron. Considering that rough surfaces usually provide more adsorption sites for impinging molecules than smooth surfaces and pure chromium oxide films block hydrogen diffusion from bulk material more efficiently than inhomogeneous iron-rich oxide films, oxidation with low oxygen pressure may be a promising technique for the fabrication of a stainless steel vacuum chamber with enhanced outgassing characteristics.

SS-WeP13 The Interaction of Water with the Basal Plane of @alpha@-Cr@sub 2@O@sub 3@: Dissociation and Multiply Coordinated Adsorption Sites, M.A. Henderson, S.A. Chambers, C.L. Perkins, Pacific Northwest National Laboratory

We have examined the interaction of water with an @alpha@-Cr@sub 2@O@sub 3@(001) thin film surface using TPD, HREELS and LEED. The @alpha@-Cr@sub 2@O@sub 3@(001) film is the terminus of an 3@/@alpha@-Fe@sub alternating @alpha@-Cr@sub 2@0@sub 2@O@sub 3@ heterostructure grown on an @alpha@-Al@sub 2@O@sub 3@(001) substrate using molecular beam epitaxy. The @alpha@-Cr@sub 2@O@sub 3@ lattice is 2@super o@ expanded inplane due to lattice matching to the @alpha@-Fe@sub 2@O@sub 3@. Water interacts strongly with the @alpha@-Cr@sub 2@O@sub 3@(001) surface, desorbing in two prominent TPD states at 345 and 297 K, both of which exhibit first-order desorption behavior. Weaker binding TPD states are observed at 210 and 185 K. Using a calibrated doser, TPD results indicate that the coverage of water in the 345 and 297 K TPD states is twice that of the surface Cr@super 3+@ coverage suggesting that each surface cation site binds two water molecules. Although no irreversible decomposition is detected by TPD, HREELS (acquired at room temperature to avoid sample charging) shows prominent losses at 3605, 2890 and 915 cm@super -1@. Using D2O, the latter two losses shift to 2645 and 2135 cm@super -1@ and the former is undetected (shifted under the lattice phonon modes). The 3605/2645 cm@super -1@ and 915/(?) cm@super -1@ losses are indicative of the hydroxyl stretching and bending modes, respectively, of a terminal hydroxyl group, whereas the 2890/2135 cm@super -1@ losses are suggestive of a very weak hydrogen-bonding interaction, probably between

the deposited hydrogen/deuterium atom and the terminal OH/OD group. Although this hydrogen-bond is weak, as suggested by its low O-H stretching frequency, the dynamic dipole of its O-H stretch is as strong as that of the terminal OH group. Although HREELS analysis of the 297 K TPD state is in progress, our tentitive model is that each surface Cr@super 3+@ site binds both a molecular and dissociative form of water. The absence of strong coverage dependence in the TPD suggests that these water species are only weakly interacting. The role of lattice expansion will also be discussed, in comparison with studies on an unstrained @alpha@-Cr@sub 2@O@sub 3@(001) film (to be conducted).@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences. Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. The research reported here was performed in the William R. Wiley Environmental Molecular Science Laboratory, a Department of Energy user facility funded by the Office of Biological and Environmental Research.

SS-WeP14 In-situ Study on the Formation of SiC Thin Films on Si(111) Surface with 1,3-disilabutane: Adsorption Properties and Initial Deposition Characteristics, H.G. Yoon, J.-H. Boo, S.-B. Lee, W.L. Liu, SungKyunKwan University, Korea; S.-C. Park, H. Kang, Pohang University of Science and Technology, Korea; Y. Kim, Korea Research Institute of Chemical Technology, Korea

The adsorption properties of 1,3-disilabutane (DSB), SiH@sub 3@-CH@sub 2@-SiH@sub 2@-CH@sub 3@, and an initial deposition characteristics for the formation of SiC thin films on Si(111) surfaces have been studied in the temperature range of 150 - 1200 K in situ by XPS, UPS, TDS, and Cs@super +@ ion reactive scattering methods. After DSB dosing at 300 K, only one adsorbed state was obtained from XPS and UPS. The C 1s and Si 2p XP spectra appeared at ca. 283 and 99.5 eV showed no chemical (binding energy) shifts between RT and 600 K indicating a SiC cluster and/or islands formation. With increasing the surface temperature to 1200 K, however, a gradual binding energy shifts of both Si 2p and C 1s XP peaks to the higher values were observed due to a crystalline SiC thin film deposition. During deposition, moreover, we also identify the intermediate states of the thermal decomposition reaction of DSB on a Si(111) surface with Cs@super +@ ion reactive scattering. Several kinds of intermediates as CsCH@sub 4@Si@super +@, CsC@sub 2@H@sub 8@Si @sub 2@@super +@, CH@sub 4@Si@super +@, and CH@sub 3@Si@super +@ were detected at 150 K. In the case of DSB deposition between 800 K and 950 K, on the other hand, only one intermediate (i.e. CsCH@sub 4@Si@super +@) was observed indicating that most of C@sub 2@H@sub 8@Si@sub 2@ adsorbates have been reacted away at these temperatures, forming either CH@sub 4@Si or SiC thin films on the surface. Based on the experimental results of XPS, UPS, TDS, and Cs@super +@ ion reactive scattering, in this work, we proposed a possible chemisorption geometry and decomposition mechanism of DSB.

SS-WeP15 Real-time VT-STM Studies of Dewetting Processes: Ag/Si(111),

K. Th@um u@rmer, E.D. Williams, J.E. Reutt-Robey, University of Maryland Under typical MBE-conditions thin film morphology is often limited by kinetics. An excellent model system for film growth proceeding far from equilibrium is silver, deposited at room temperature on Si(111) (see review@footnote1@). At a mean film thickness of 1nm, the substrate is completely covered by worm-like structures. Using a variable temperature STM, we have studied the transformation of these metastable structures into equilibrium shaped hexagonal crystallites. By tracking the annealing process in real time, we encounter an astonishing variety of transition shapes. At ~200C the onset of de-wetting exposes substrate areas with a root3 x root3 reconstruction. The higher mobility on these denuded areas acts as a positive feedback, accelerating the decay of adjacent structures. At ~300 C the morphology is dominated by 500 nm wide and 100 nm high crystallites, exhibiting networks of partial dislocations on their (111)-top facets. This work has been supported by the NSF-MRSEC at University of Maryland under grant #DMR-96-32521. @FootnoteText@ @footnote 1@ H.Neddermeyer, Critical Rev. in Solid State and Material Science 16(5),309 (1990) 29, 30, 53-55, 57, 68.

SS-WeP16 Dissociative Reaction of HBO@sub 2@ Molecules on Si(111)-7x7 Surface Studied by Scanning Tunneling Microscopy, K. Miyake, T. Kaikoh, Y.J. Li, H. Shigekawa, University of Tsukuba, Japan

Boron (B) has been attracting considerable attention as a promising c andidate for the formation of atomic-layer doped structure. Atomic-layer dop ing process on Si substrate consists of two parts; adsorption of a monolayer fraction of dopant atoms on Si surface and subsequent Si growth. Therefore, precise control of B atoms on Si surface is essentially important. Recently, HBO@sub 2@ molecules were found as a most appropriate boron source because o f its higher vapor pressure compared to the metal boron cases. However, how HBO@sub 2@ molecules react with the Si surface still remains as an open ques tion. In order to clarify this point, we characterized the chemical reaction process of HBO@sub 2@ molecules on Si(111)-7x7 surface in detail. We succeed ed in confirming two different states of HBO@sub 2@ molecules on the surface . When the substrate temperature during HBO@sub 2@ irradiation was kept at 3 00°C, the adsorbed HBO@sub 2@ molecules remained on the surface witho ut dissociation. On the other hand, when the substrate temperature was kept at 600°C, HBO@sub 2@ molecules were dissociated, and the oxygen- and boron-related adatoms were produced at corner and center adatom sites in 7x7 units, respectively. Taking the difference in the electronegativity between the oxygen and boron atoms into consideration, oxygen and boron atoms in HBO @sub 2@ molecules are expected to react with adatoms and rest atoms, respect ively. Then, as a result of the dissociation of HBO@sub 2@ molecules, oxygen and boron atoms may adsorb at the corner and center adatom sites, respective ly. In order to confirm this reaction process, the sample formed by HBO@sub 2@ irradiation at 300°C was annealed at 600°C for 1min. As exp ected, non-reacted HBO@sub 2@ molecules disappeared and the oxygen- and boro n-related adatoms were observed after annealing. These results indicate high controllability of chemical reaction process of HBO@sub 2@ molecules on Si(1 11)-7x7, and potential exists in this system. @FootnoteText@ high http://dora.ims.tsukuba.ac.jp

SS-WeP17 Investigation of Sulfur-terminated GaAs(001) Surfaces by Selective Atoms Sublimed Method, *S. Tsukamoto, T. Ohno, N. Koguchi,* National Research Institute for Metals, Japan

Recently, a novel S-termination method has been developed by exposure to S vapor in molecular beam epitaxy system, observing not diffused (2x1), commonly reported, but clear (2x6) reconstruction by reflection highenergy electron diffraction and scanning tunneling microscopy(STM).@footnote 1@ Then, we found that the separations, 0.19 - 0.28 nm, between S atoms of S dimers by STM well agreed with the firstprinciples pseudopotential calculated result, 0.237nm, with the condition of one electron transferred from each S dimer.@footnote 2@ However, the (2x6) structure is still not clear. In this paper, we study the detail of this (2x6) by the investigation of the structural change by a selective atoms sublimed method which uses the thermal desorption of selective S-S dimer from the (2x6). The calculated maps of the charge-density contours of the S-S structures show that the center of the charge-density is as same as the poison of the S atom in the case with the transfer of one electron. On the other hand, in the case without the transfer, the center of the chargedensity is about 0.05nm far from the position of the S atom. Therefore, if the charge-density balance is destroied by the thermal desorption, the observed S-S bond length by STM will be drastically changed. The (2x6) structure turns into the (2x3) structure at around 520°C releasing about 20% surface sulfur atoms, which amount consist with the central dimer pairs of the (2x6) structure, however, without interdiffussion and with keeping the same S-S bond length. In addition, the Ga small clusters appeared on this (2x3) surface. It seems that these Ga clusters kept the charge-density balance of the (2x3) structure, keeping the same S-S bond length. @FootnoteText@ @footnote 1@S.Tsukamoto and N.Koguchi, Jpn.J.Appl.Phys., 33 (1994) L1185; Appl.Phys.Lett., 65 (1994) 2199; J.Cryst.Growth., 150 (1995) 33. @footnote 2@S.Tsukamoto, T.Ohno, and N.Koguchi, J.Cryst.Growth., 175/176 (1997) 1303.

SS-WeP18 Dynamical Behavior of Hydrogen Molecule on GaAs(001) Surface, M. Ohashi, M. Ozeki, J. Cui, JRCAT - ATP, Japan

Hydrogen plays important roles as an important reactant and a carrier gas in various surface processes of III-V compound semiconductors. However there are no sufficient data on dynamical behaviors of hydrogen on III-V compounds surface. Supersonic molecular-beam scattering enables us to bring valuable dynamical parameters such as reaction probability, reaction pathway, reaction kinetics, and activation energies of reaction steps. We have been studying in dynamical behaviors of hydrogen on GaAs(001) surface by supersonic molecular beam apparatus. We measured angular distributions of reflected beams, when hydrogen molecule was injected with 110 and -110 directions onto GaAs(001) 2x4 surface. The existence of trapping/desorption channel was clearly discovered and the depth of potential well of hydrogen molecule on GaAs(001) 2x4 surface was estimated 0.4 kcal/mol by the trajectory simulation of trapping probabilities. The angular distribution of reflected hydrogen molecule of

trapping/desorption channels direct scattering was largely affected by the surface corrugation of GaAs(001) 2x4 surface. The experimental result was compared by classical trajectory simulation for this system. The experimental result agreed excellently with classical trajectory simulation. This indicated the important information of the energy exchange from translational to rotational modes was indicated. This work is supported by New Energy and Industrial Technology Development Organization (NEDO).

SS-WeP19 Study on Properties of Defects and Boron at the Si/SiO@sub 2@ Interface using Empirical Interatomic Potential Energy Function, J.-W. Kang, H.-J. Hwang, Chung-Ang University, Korea

Properties of silicon/oxide interface were computed using novel interatomic potential-energy function that was recently developed@footnote 1@ for modeling the interactions between silicon and oxygen atoms. For boron-silicon interaction, we used the Stillinger-Weber (SW)-type interatomic potential with the repulsive part of the twobody term being splined to the Ziegler-Biersack-Littmart (ZBL) universal repulsive potential.@footnote 2@ For boron-oxygen, We used the Born-Mayer-Huggins potential.@footnote 3@ Effects of dangling bonds and oxygen clusters at SiO@sub 2@/Si interface and silicon vacancy and oxygen vacancy in the oxide film were calculated. We have investigated the SiO@sub 2@ evolution on the silicon surface with rich boron and various defects. The evolution of the structure at the Si/SiO@sub 2@ interface according to the presence of boron atom provided an overview of the behavior of boron dynamics at the Si/SiO@sub 2@. @FootnoteText@ @footnote 1@ T. Watanabe et al., Jpn. J. Appl. Phys. Vol.38 Part 2.No. 4A (1999) pp. L366-L369. @footnote 2@ J. W. Kang, E. S. Kang, H. J. Hwang, will be published in May, J. Kor. Phys. Soc. Vol. 34 (1999). @footnote 3@ J. M. Delaye, V. L-Achille, D. Ghaleb, J. Non-Cry. Solids, 210(1997) 234-242.

SS-WeP20 Cesium-induced Structural Transformation from the Si(113)3x2 to the 3x1 Surface, *C.C. Hwang*, Sung Kyun Kwan University, Korea; *K.S. An*, High Energy Accelerator Organization, Japan; *S.H. Kim, C.Y. Park*, Sung Kyun Kwan University, Korea; *A. Kakizaki*, High Energy Accelerator Organization, Japan

Adsorbates such as H, Na, Cs, etc. on the Si(113)3x2 surface are known to induce a structural transformation to the 3x1 surface. The origin, however, seems to be still unclear due to the lack of informations about the adsorption behavior of several adsorbates as well as the structure of the 3x2 surface. To investigate the adsorption behavior of cesium on the Si(113)3x2 surface at room temperature, we measured the change of workfunction, core level (Si 2p, Cs 4d), and valence band spectra with increasing cesium deposition time by using low energy electron diffraction (LEED) and synchrotron radiation photoemission spectroscopy. As previously reported, the adsorption of cesium induced the structural transformation from the Si(113)3x2 to the 3x1 surface. When cesiums adsorbed on the Si(113)3x2 surface, the workfunction decreased to about 3.2 eV and surface states from dangling bonds disappeared gradually with increasing cesium deposition time. These results indicate that cesiums adsorb preferentially on dangling bond sites at the initial stage of adsorption. We also observed that two shoulders at higher and lower binding energy than the bulk peak in Si 2p core level spectrum from the 3x2 surface disappeared by the adsorption of cesium. Rehybridized surface atoms towards sp@super 2@- and s@super 2@p@super 3@-like configurations thus seem to be changed to sp@super 3@-like ones with the structural transformation. Based on these results, we will discuss the possible origin of the cesium-induced structural transformation at room temperature.

SS-WeP21 Investigations of the Effects of P and Ge on the Desorption of D@sub 2@ from Si(100) and Si(111), J.L. Stepnowski, C. Dougherty, G.J. Batinica, M.L. Jacobson, M. Chiu, B.M.H. Ning, J.E. Crowell, University of California, San Diego

The desorption of D@sub 2@ from Si(100) covered with various concentrations of both P and Ge has been investigated using temperature programmed desorption (TPD). Chemical vapor deposition was used to prepare the surfaces. Phosphorus at different concentrations was deposited at 873K using phosphine as the molecular source gas, and separately, various Ge coverages were prepared by exposing the surface to digermane at approximately 160K. After each exposure, the crystal was flashed to 873K to desorb hydrogen. The resulting P and Ge surface coverage was determined by Auger Electron Spectroscopy. The P,Ge modified Si surface was then exposed to D atoms produced by cracking D@sub 2@ gas with a hot tungsten filament and then a TPD spectrum was taken. Previous studies in our laboratory found that addition of phosphorus alone shifts the @beta@1 desorption state to higher temperatures relative

to clean Si(100) while the presence of only submonolayer germanium on the Si surface decreases the @beta@1 peak temperature. This investigation will detail the combined effect of P and Ge on the Si(100) surface. Furthermore, the combined system of P and Ge on Si(111) has been previously examined in our laboratory and a comparison of the effect of these additives on the desorption behavior of Si(100) versus Si(111) will also be presented.

SS-WeP22 Direct Absorption of Thermal H Atoms by Crystalline Silicon: A Narrow Substrate Temperature Window, *J.H. Kang*, Kyung Won University, S. Korea; *S.K. Jo*, Kyung Won University, S. Korea, South Korea; *J. Lee*, Seoul National University, S. Korea; *B. Gong*, *J.M. White*, *J.G. Ekerdt*, University of Texas at Austin

Si(100) surfaces exposed to gas-phase thermal-energy hydrogen atoms, H(g), were studied by temperature-programmed desorption (TPD) together with H/D isotope exchange experiments. We find that direct absorption of H(g) into crystalline bulk of Si(100) substrates occurs within a narrow substrate temperature window of 400 - 600 K. The bulk-absorbed hydrogen evolved out molecularly from Si(100) at a temperature 70 - 120 K higher than that of surface-adsorbed monohydride phase (@beta@@sub 1@) in TPD. This bul k-phase hydrogen (@alpha@) uptake increased with increasing H(g) exposure without saturation within our experimental limits. While pre-adsorbed hydrogen atoms on the surface, H(a), were readily abstracted and replaced by D(g), the amount of pre-absorbed H in the bulk remained unchanged by subsequent D(g) exposures. Our result of extensive H/D isotope mixing suggests that absorbed H atoms remain trapped atomically, rather than molecularly, at interstitial sites. We propose a model, in which the (2x1) surface dimer structure of Si(100) serves as a two-way barrier for both direct H(g) absorption and thermal evolution of molecular hydrogen.

SS-WeP23 Low Energy Electron Damage to Condensed Phase Cyclic Ethers Studied by Electron Stimulated Desorption, *L. Parenteau*, *D. Antic*, *L. Sanche*, University of Sherbrooke, Canada

Low-energy electron (E@sub i@ < 20 eV) damage to condensed molecules prepared under ultra-high vacuum conditions has been the focus of intense study in recent years.@footnote1@ This research has particular relevance to the field of radiation science as it is well known that a large amount of low-energy secondary electrons are produced along the radiation tract following the interaction of ionizing radiation, the majority of which are created with initial kinetic energies well below 20 eV. At these low energies, fragmentation may occur following dissociative electron attachment (DEA) via the formation of negative ion resonances or by dipolar dissociation (DD). These processes are generally monitored in condensed-phase systems by electron stimulated desorption (ESD) which measures the negative ion yield desorbing from the surface. Below the DD threshold negative ion formation arises exclusively via DEA, whereas above this threshold the ESD yield is dominated by anions produced largely via DD. In recent years, there has been a shift in emphasis towards molecular systems of biological relevance, such as DNA bases,@footnote2@ radiosensitizing 5-halo-uracils and homo-oligonucleotides.@footnote3@ We are now studying the chemical consequences of the interaction of low energy electrons with the deoxyribose backbone of DNA and its constituents. Preliminary results on DEA damage to DNA sugar-like backbone analogues, tetrahydrofuran, 3-hydroxy-tetrahydrofuran and tetrahydrofurfuryl alcohol will be presented. In addition to a core excited resonance observed in the H@super -@ ESD yield near 10 eV incident electron energy, we find significant H@super -@ production via DEA to occur above the DD threshold for incident electron energies near 23 eV. @FootnoteText@ @footnote1@L. Sanche, Scanning Microscopy 9, 619 (1995). @footnote2@D.V. Klyachko, M.A. Huels, and L. Sanche, Radiat. Res. 151, 177 (1999). @footnote3@P.C. Dugal, M.A. Huels, and L. Sanche, Radiat. Res. 151, 325 (1999).

SS-WeP24 Electron- and Photon-stimulated Desorption of Alkali Atoms from Silicon Dioxide Surfaces, B.V. Yakshinskiy, T.E. Madey, Rutgers University

As part of a program to probe the mechanisms by which Na and K atoms originate in the atmospheres of the planet Mercury and the Moon, we are studying the electron- and photon-stimulated desorption of Na deposited on model mineral surfaces: amorphous SiO@sub2@ thin films, grown on a Re(0001) substrate. The measurement scheme for electron- stimulated desorption (ESD) of Na atoms includes an efficient pulsed low energy electron source, a highly sensitive detector of Na based on surface ionization, and a time-of-flight technique. For photon-stimulated desorption (PSD), a 500 W Hg arc lamp photon source, a mechanical

chopper, and appropriate filters are used. We find that bombardment of Na / SiO@sub2@ surface by ultraviolet photons or by low energy electrons (E > 4 eV) causes desorption of 'hot' Na atoms with the velocity distribution peak at 1000 m/s. The desorption cross section is ~ 10@super-20@ cm@super2@ at 5 eV excitation energy for both ESD and PSD. The ESD yield demonstrates a resonance-like feature at ~11 eV. We interpret the ESD / PSD of Na as occuring via a substrate mediated charge transfer process, in which ionic Na@super+@ is converted to neutral Na, which desorbs. These data provide evidence that DIET mechanisms (e. g., PSD) may contribute as source processes for Na in tenuous planetary atmospheres. Although there are insufficient electrons in the solar wind to produce the observed lunar sodium atmosphere, there appear to be sufficient UV solar photons to maintain the atmosphere by desorbing Na from the surface.

SS-WeP25 Metastable Surface Structure of KTaO@sub 3@(001) by Helium Atom Scattering@footnote 1@, J.A. Li, T.W. Trelenberg, E.A. Akhadov, J.G. Skofronick, S.A. Safron, Florida State University; L.A. Boatner, Oak Ridge National Laboratory

Helium atom scattering is used for measurements of the surface structure of KTaO@sub 3@ immediately after cleaving in situ in a UHV scattering chamber. Angular distributions (ADs) of this simple perovskite insulator are measured under destructive interference conditions for steps of one-half the unit cell of KTaO@sub 3@(2Å). Initially the specular peak is very small and is flanked on each side by a satellite peak at ±0.043Å@super -1@. Over a period of one to three hours, depending upon the surface temperature, the specular peak grows in intensity while the satellite peaks decrease in intensity until they essentially disappear. The result is what appears to be a typical AD. A model consisting of uniform-width step-up and step-down terraces is presented which agrees with the initial observations. With increasing time, the terrace widths become more nonuniform and the step heights increase to the lattice spacing of the full unit cell(4Å) due to the mass transport. The first of these developments leads to a reduction of the satellite peak intensities and the second leads to an enhanced specular signal because of the constructive interference. @FootnoteText@ @footnote 1@Supported by U. S. Department of Energy grant number DE-FG02-97ER45635.

SS-WeP26 A Calibrated Adsorption and Thermal Desorption System using Glass Capillary Arrays and a Capillary Valve Flow Source, *R.H. Jackson*, *B.G. Frederick*, *D.J. Dwyer*, University of Maine

We demonstrate a calibrated thermal desorption system utilizing a glass capillary array doser as a calibrated beam source. Absolute calibration of the mass spectrometer signal in molecules per second is achieved using both calculated and measured flux distributions from the doser to calibrate the doser flux to the inlet appeture of a differentially pumped thermal desorption mass spectrometer. By a re-parameterization of the formalism of Winkler and Yates,@footnote 1@ we have reduced the order of the necessary integrations from 3 to 2, which simplifies treatment of arbitrarily shaped planar targets. Fourier convolution methods are used to calculate of the flux to a target at any position in a plane parallel to the doser face. These calculations are compared to direct measurements of the doser flux in 3 dimensions. The pressure versus time, measured by a spinning rotor gauge in a gas cell of known volume, determines the flow rate to the doser. The flow closely obeys the simple effusion model after accounting for finite base pressure. A transient molecular flow model is applied to the establishment of the flow from the capillary valve, providing good estimates of the time to steady state for the flow. This Calibrated Thermal Desorption Spectrometer is applied to a study of oxygen on Pd(110) and the coverage results are compared to values from nuclear reaction analysis. @FootnoteText@ @footnote 1@A. Winkler and J. T. Yates Jr. "Capillary array dosing and angular desorption distribution measurements: A general formalism", J. Vac. Sci. Technol. A 6(5), Sep/Oct 1988.

SS-WeP27 Corrosion Inhibition of Aluminum by Self-Assembling Monolayers, S.M. Wetterer, P. Dharia, S. Xie, J.J. Donofrio, Oakite Products, Inc.

Self-assembling monolayers have been evaluated as an alternative to traditional chromium-based treatments for corrosion protection of aluminum surfaces. With good water solubility and long-term solution stability, alkyl phosphonic acids were found to be suitable candidates for the formation of a well-ordered, passivating layer on a series of aluminum alloys. Application process parameters such as immersion time, bath temperature, and anneal time significantly affected the development of the monolayer with implications for the resultant protective benefit of the layer as assessed by humidity and salt-spray corrosion testing. Additional

characterization of monolayer-treated panels by SEM and EDAX has provided information regarding monolayer performance over surface defects and edge sites. Modeling of the mechanisms of corrosion protection and eventual breakdown of phosphonate monolayers will be presented.

SS-WeP28 Structure of the (0001) Surface of Hafnium and Hafnium Diboride and of Epitaxial Thin Films of Hafnium Diboride Grown on Hafnium, *R. Singh, C.L. Perkins, M. Belyansky, M. Trenary,* University of Illinois, Chicago

Scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED) have been used to investigate the surface structure of single crystals of Hf, HfB@sub 2@, and epitaxial thin films of HfB@sub 2@ grown on a Hf substrate through the thermal decomposition of diborane. A comparison of the properties of HfB@sub 2@(0001) and Hf(0001) is of interest because the topmost atomic layer of both surfaces consists of a close-packed two-dimensional array of Hf atoms with lattice constants that differ by only 1.7%. In the bulk structure of HfB@sub 2@, the (0001) Hf atom planes are hexagonal closepacked and are separated by 0.348 nm. A graphite-like honeycomb lattice of boron atoms lies between the Hf planes. A clean well-annealed HfB@sub 2@(0001) surface is found to consist of Hf-terminated terraces separated by 0.35 nm with no boron layers exposed. When the HfB@sub 2@ sample is not well-annealed or when contamination is present, reconstructed surfaces are observed with both LEED and STM, including a (3x3) structure induced by carbon. The Hf(0001) surface consists of flat (0001) terraces separated by monoatomic steps 0.25 nm in height. The high reactivity of the group IV metals is reflected in the difficulty in obtaining contamination free images of the Hf surface. From the determination of the basic structural features of the HfB@sub 2@ and Hf surfaces by STM, patches of Hf and HfB@sub 2@ can be clearly distinguished in STM images acquired during different stages in the growth of epitaxial thin films of HfB@sub 2@ on a Hf substrate. The thin film growth mechanism can thereby be inferred from such images.

SS-WeP29 Molecular-scale Origins of the Surface Memory Effect at a Liquid Crystal - Solid Interface, *D.M. Scott*, *A.J. Brackley*, *J.D. Mougous*, *K.M. Foland*, *D.L. Patrick*, Western Washington University

The surface memory effect (SME) describes the phenomenon in which an initially isotropic surface is rendered anisotropic through contact with anisotropic medium, such as a liquid crystal (LC) fluid. At a LC - solid interface, the SME leads to imprinting of the director orientation onto the surface, which can in turn induce uniform alignment in the bulk LC fluid. The SME is important in LC - based opto-electric devices such as liquid crystal displays. We studied the SME in LC droplets on a polycrystalline graphite substrate using polarized optical and scanning tunneling microscopy (STM). A single crystalline monolayer with macroscopically uniform orientation was prepared by depositing material from the LC droplet in an external magnetic field. The system was found to retain memory of the original bulk orientation, even when the field was removed and the LC was heated beyond its isotropic transition temperature. Loss of the SME coincided with monolayer melting. Comparison of STM images with optical micrographs establish a direct link between molecular alignment in the monolayer adsorbed to the graphite substrate and bulk LC director orientation.

SS-WeP30 Investigation of the Dehalogenation of 1,1-Dichloroethene on Pd(111) Studied by Laser-Induced Thermal Desorption Fourier Transform Spectroscopy (LITD-FTMS), *D.E. Hunka*, *D.P. Land*, *D.C. Herman*, University of California, Davis

The chemistry of chlorinated ethenes on transition metal surfaces is of great interest due to their prevalence as contaminants in groundwater. The decomposition of geminal dichloroethene (g-DCE) on a clean Pd(111) surface is investigated using thermal desorption spectroscopy (TDS) and laser-induced thermal desorption with FT mass spectrometry (LITD-FTMS). Preliminary results of g-DCE decomposition show that HCl is the major reaction product. The TDS studies have been performed as a function of coverage. At very low coverages, only one peak of HCl is seen to desorb in the range of ~600 K - 1000 K. As coverage increases, a significant portion of g-DCE desorbs intact, the HCl peak shifts to lower temperatures and a second HCl peak grows in with a Tp= 450 K, indicating a step-wise decomposition. At these higher coverages of g-DCE, separate TDS experiments monitoring hydrogen evolution from the surface show a sharp peak at 474 K (in between the two HCl traces). Interestingly, the LITD survey experiments reveal decomposition of g-DCE occurs by 150 K with the concomitant appearance of HCl. These results indicate that both C-H

and C-Cl bond cleavage happens at low temperatures, although no chloroacetylene is produced as a second product, which would be indicative of an @alpha@-@beta@ elimination. Further decomposition of the surface intermediates occurs to yield a second formation of HCl which is subsequently liberated from the surface.

SS-WeP31 CV, XPS, SIMS and ISS Examination of Zirconium Passive Film Breakdown in the Presence of Sulfate, *R Schennach*, Lamar University &Texas A&M University; *A. Mamun, N. Kunamneni, D.L. Cocke*, Lamar University

Passive films on zirconia have been prepared by potentiodynamic polarization in the presence of a range of anions and at various pH values. Sulfate has been found to produce unique transpassive peaks that appear to be associated with an amorphous to cyrat alline transitionand subsequent enhanced species transport along the resulting grain boundaries. The passive film breakdown can be qualitatively described by E@sub np@ = E@sub c@ + @eta@ + @PHI@ +E@sub inh@. Where E@sub np@ is the pitting potential, E@sub c@ the corrosion potential in acidified solution, @eta@ the polarization necessary to obtain a current density high enough to maintain acidity inside the pit, @PHI@ the potential drop inside of the pit and E@sub inh@ the contribution to pitting potent ial resulting from inhibitors present. XPS, SIMS and ISS have been used to characterize the films before and after the passive film breakdown. The results of these surface studies along with the variation in CV scans have been used to describe the process and to present a model that involves either IR drop and/or local acidification. The involvement of chemically bound water oxidation and local oxygen evolution are presented as well.

SS-WeP33 Composition and Orientation at the Surface of a Room-Temperature Ionic Liquid Observed by Direct Recoiling Spectrometry, *P.R. Watson*, Oregon State University, U.S.; *T.J. Gannon, G. Law*, Oregon State University; *A.J. Carmichael, K.R. Seddon*, Queen's University, Ireland

Direct recoil spectrometry (DRS) has recently been applied to investigate the structure and orientation at the surface of low vapor-pressure liquids. Room temperature ionic liquids are generating considerable interest as low vapor-pressure clean technology solvents. We report the first measurements of the composition and molecular orientation at the surface of the room temperature ionic liquid - 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF@sub6@]. Recoil spectrometry using rare gas ions on continuously refreshed liquid surfaces in vacuo shows that neither ion is significantly enriched in the surface. The average orientation of the cation is with the plane of the ring vertical. The cation ring is rotated about an axis through its center such that the nitrogen atoms and side chains are deeper in the surface with the surface normal passing between the two nitrogen atoms (with an estimated error of ±30°).

SS-WeP34 Surface Structures of @beta@-(BEDT-TTF)@sub 2@PF@sub 6@ Induced by Its Polar Surface Characteristics, *M. Ishida*, University of Tsukuba, Japan; *T. Mori*, Tokyo Institute of Technology, Japan; *H. Shigekawa*, University of Tsukuba, Japan

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) based organic compounds, one of the low-dimensional conductors, are distinct from the others due to their polar surface characteristics. For @beta@-(BEDT-TTF)@sub 2@PF@sub 6@, an ordered-defect structure was observed on the anion (PF@sub 6@) surface similarly as the typical reconstructions of the inorganic polar surfaces. And characteristic properties such as superstructures and fluctuation of surface structures were observed on the cation (ET) surface. On the other hand, it is well known that @beta@-(BEDT-TTF)@sub 2@PF@sub 6@ undergoes a metal-insulator transition at 297 K, and formation of the 2x|c| superstructure due to 2k@sub F@ CDW is confirmed by X-ray diffraction. However, several superstructures with considerably longer modulations were observed by STM at 285 K instead of the 2x|c| superstructure. From the results of the STM, AFM, XPS studies, and molecular orbital calculations, the observed cation surface structures were concluded to be influenced by charge localization, relaxation of individual molecules, and symmetry breaking in the molecular relaxation. Concerning the modulated CDW phases, susceptibility @chi@(Q) for the surface layers was calculated in order to investigate the origin of the larger modulations, by taking into account the change in the molecular charge on the polar surface. As a result, the observed STM result were in good agreement with the CDW structure derived from the susceptibility calculation.

SS-WeP35 Free Radical Based Amination of Polymeric Interfaces, H. Fairbrother, A. Wagner, K. Han, A. Vaught, Johns Hopkins University The introduction of nitrogen containing functionality into organic surfaces is often used to modify interfacial characteristics, including permeability, wettability, adhesion, friction, wear and biocompatibilty. Compared to wetchemical treatments for surface modification vacuum-based technologies are dry, fast and environmentally benign. Compared to the more traditional ion and plasma based modification treatments, the use of gas phase radicals is a relatively underdeveloped component with considerable promise. For example, nascent radical kinetic energies are typically in the range of 0-5eVs in contrast to the several hundred eVs of energy typically associated with ions. To address this issue a new NH radical source, based upon the thermal pyrolysis of hydrazoic acid (HN3) has been developed and characterized using mass spectrometry. Results from the interaction of NH radicals with thiol-based self-assembled monolayers using mass spectrometry, infrared spectroscopy and X-ray Photoelectron Spectroscopy will also be presented.

SS-WeP36 An Ultra High Vacuum Compatible Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometer, *T.L. Porter*, *S. Hermann*, Northern Arizona University

The emerging technique of matrix assisted laser desorption/ionization (MALDI) time-of-flight mass spectrometry allows for the mass determination of surface bound polymeric materials that suffer from fragmentation effects using conventional MS techniques. Using MALDI, the sample to be analyzed is combined with a strong UV absorbing "matrix", such as 3-hydroxypicolinic acid or 2,5-dihydroxybenzoic acid. Short UV laser pulses desorb the matrix plus sample material from the topmost sample surface, while simultaneously gently ionizing the sample material. The ionized species are then injected into a time-of-flight analyzer for mass determination. The gentle ionization process allows polymers and biomaterials on surfaces that would normally suffer from fragmentation effects to be detected intact. In this paper, we describe an ultra-highvacuum MALDI instrument that has been constructed from primarily offthe-shelf components at minimal cost. This instrument may be used to detect the presence of pico-mole amounts of material with atomic weights from a few hundred to over one hundred thousand.

SS-WeP37 Iodobenzene Reactions and cis-1,2-Dichloroethene Chemistry on Pd(111) Studied by Laser-Induced Thermal Desorption Coupled with Fourier Transform Mass Spectroscopy (LITD-FTMS), *D.M. Jaramillo*, *D.P. Land*, *D.E. Hunka*, University of California, Davis

Halocarbons are important compounds for obtaining alkyl groups on metal surfaces. The thermal and photo dissociation of the carbon-halogen bond allows us to probe the chemistry of hydrocarbon fragments which have shown to be transient intermediates in catalytic processes. In addition, the reactions of halocarbons on metal surfaces relates to the remediation of chlorinated solvents from waste water. Elucidation of the mechanism of halocarbon decomposition will aid in determining better catalysts for remediation. The chemistry of iodobenzene and cis-1,2-dichloroethene have been investigated on Pd(111). Submonolayer iodobenzene adsorption at 90 K results in the formation of phenyl groups and iodine on the surface. The phenyl groups are hydrogenated by subsurface hydrogen to form benzene which desorbs around 500 K. Higher exposures of iodobenzene show iodobenzene desorbing at 200 K and benzene observed only at 140 K. The adsorbed iodine changes the reactivity of iodobenzene. Molecular desorption of cis-1,2-dichloroethene occurs at 160 K for low exposures and at around 200 K for higher exposures. Hydrogen is seen to desorb around 300 K for even the lowest exposure studied. No HCl was observed in TDS or LITD.

SS-WeP38 Energy Transfer in Collisions of Nitric Oxide with Ordered Molecular Adlayers, *M.K. Ainsworth, V. Fiorin, M.R.S. McCoustra, M.A. Chesters*, University of Nottingham, UK

Detailed dynamical measurements have been made of the scattering of nitric oxide from well-characterised and well-ordered monolayers of carbon monoxide (CO) and ethylidyne (CCH@sub 3@) adsorbed on a Pt(111). The scattering dynamics have been probed using a combination of molecular beam and laser spectroscopic techniques for incident NO translational energies in the range 5 to 50 kJ mol@super -1@ at substrate surface temperatures from 100 to 300 K. Time-of-flight measurements were used to determine the translational energy of the scattered NO, while resonance-enhanced multiphoton ionisation was used to recover its rotational quantum state distributions. The results of both types of experiment will be reported. Significant loss of incident NO translational energy is observed and evidence from these measurements suggests that

scattering occurs into both a direct inelastic scattering channel and a trapping-desorption channel. The scattering dynamics from both adlayers are found to be similar, with only slight differences that may be interpreted in terms of different interaction potential strengths.

SS-WeP39 Surface Diffusion of Photogenerated Hydroxyl Radicals as Probed by FTIR, Y. Paz, H. Haick, Technion-IIT, Israel

Titanium Dioxide is a well-known photocatalyst for water and air treatment as well as for catalytic production of gases. For many organic materials, destruction of contaminants occurs through an oxidation mechanism, where hydroxyl radicals formed on the surface of the catalyst attack adsorbed compounds. Structures comprised of photoactive titanium dioxide and inert adsorbents may promote the overall performance of the photocatalyst by concentrating molecules, that usually do not adsorb on TiO@sub 2@, at the vicinity of the photocatalyst. Furthermore, one may consider the modification of the inert domains to achieve selective physisorption of contaminants of interest. This selectivity can be achieved by coating the inert areas with chemisorbed organic molecules, tailored for specific physisorption of the contaminants. The growing interest in such combined structures is strongly coupled with the debate over possible surface diffusion of the oxidizing species (namely OH radicals), which might migrate to the inert domains where they might mineralize the organic templates. The destruction of templates of alkyl-trichlorosilane organized organic monolayers, chemisorbed in the vicinity of TiO@sub 2@ domains, is studied. Based on in-situ FTIR measurements, it is shown that OH radicals, formed on the titanium dioxide micro-domains, are capable of inducing the mineralization of the fixed chemisorbed aliphatic chains. within minutes, even when these chains are located as much as 20 microns away from the titanium dioxide domains. These results, measured as a function of domain size and surface temperature, are now being evaluated in order to deduce surface diffusion parameters.

SS-WeP40 The Interactions of Azomethane and Methyl Radical with Cu(111), *P. Chuang*, National Taiwan University, Taiwan; *Y.L. Chan*, Academia Sinica, Taiwan; *C.H. Chuang*, National Central University, Taiwan; *S.-H. Chian*, T.J. Chuang, National Taiwan University, Taiwan

We have employed TPD, XPS, LEED and HREELS to investigate the interactions of CH@sub 3@ radicals and CH@sub 3@N@sub 2@CH@sub 3@ molecules with Cu(111). The subject is of interest@footnote@ due to the importance of the radical in many heterogeneous reactions involving hydrocarbons. It is found that distinctive adsorption states exist for azomethane on Cu at 90K depending on surface coverage. Molecular desorption is detected at 205K, 145K and 120K corresponding to the first chemisorbed layer, the second layer and the bulk-like multilayer, respectively. Both first-order and zero-order desorption kinetics are observed. Methyl radicals can be chemisorbed on Cu(111) at 300K showing partial decomposition to CH@sub 2@(ads) and H(ads), mediated possibly by defect sites. CH@sub 3@ thermal desorption signals exhibit two channels at about 360K and 440K, corresponding to the second-order and the first-order desorption kinetics. The behavior is closely related to H and CH@sub 3@ coadsorption and reaction during the desorption process. The results of TPD, XPS and HREELS are correlated with each other and compared with previous work. @FootnoteText@ @footnote 1@T.J. Chuang, Y.L. Chan, P. Chuang and R. Klauser, J. Electr. Spectr. Relat. Phenom. 98-99, 149 (1999).

Surface Science Division Room 606 - Session SS1+AS+BI-ThM

Self-Assembled Monolayers

Moderator: N.D. Shinn, Sandia National Laboratories

8:20am SS1+AS+BI-ThM1 Two-Dimensional Phase Transitions in Amphiphile Monolayers, G.E. Poirier, National Institute of Standards and Technology

Recently scientists have explored methods of constructing complex chemically patterned surfaces with the goal of making novel biosensors or of realizing lab-on-a-chip technology. In order to design patterned monolayers it is important to understand how these molecules behave in two dimensions, what is the molecular packing of the surface phases and which phases coexist in thermodynamic equilibrium. The goal of this presentation is to describe the two-dimensional structural phases of decanethiol monolayers. Our studies were conducted using gas-phase transport of decanethiol onto clean Au(111) in an ultrahigh vacuum scanning tunneling microscope. With increasing surface coverage, the monolayer sequentially adopts six discrete structural phases. At low surface coverage, decanethiol exists as a lattice gas. With increasing coverage the molecules sequentially condense into islands of three discrete commensurate crystalline lattices, each characterized by alignment of the molecular axes with the surface plane, but with discretely increasing degrees of out-of-plane interdigitation. Above saturation coverage of the densest surface-aligned phase, the monolayer undergoes an edgemediated melting transition. The c(3x2/3) phase, characterized by alignment of the molecular axes close to the surface normal, nucleates and grows from this liquid. These studies provided a detailed, real-space picture of the coverage-dependent phases and phase transitions of alkanethiol molecular monolayers on Au(111).

8:40am SS1+AS+BI-ThM2 Surface Phase Transitions of Asymmetric Dialkyl Disulfide Self-Assembled Monolayers, *M. Hara*, *K. Kamei*, *T. Araki*, *K. Fujita*, *W. Knoll*, Frontier Research Program, RIKEN, Japan

Adsorption and desorption processes of asymmetric dialkyl disulfide (hexyl octadecyl disulfide: C6-SS-C18) self-assembled monolayers (SAMs) on Au(111) have been investigated by surface plasmon resonance (SPR), mass spectroscopy (MS), thermal desorption spectroscopy (TDS), and scanning tunneling microscopy (STM). Formation of C6-SS-C6 and C18-SS-C18 dimer species in the monolayer and also in the solution through dimerization and exchange processes has been confirmed during the monolayer growth. In the TDS spectra for shorter immersion SAMs, C6 monomer species showed the strong peaks, and gradually C6-SS-C6 dimer and C18 monomer peaks become stronger for longer immersion. Phase-separated domains of pure C6 and pure C18 striped phases have been visualized in the initial growth stage by STM and the area of the C6 domain was larger than that of C18 one. These results suggest that S-S bonds were cleaved when disulfides adsorbed on Au surface followed by the surface diffusion to form phase separation before standing-up SAM formation. After the C6-rich SAM growth, molecules are dimerized and then exchange process starts from the weakly bound C6-SS-C6 dimers toward C18-rich SAM. SPR kinetics studies also showed the double exponential growth which is different from usual Langmuir adsorption isotherm. Following those results, we propose more detailed surface phase transition model of alkanethiol SAM growth through the dimerization and the exchange processes.

9:00am SS1+AS+BI-ThM3 Structure, Bonding and Reactivity of Selfassembled Monolayers, G.J. Leggett, B.D. Beake, N.D. Brewer, UMIST, UK; E. Cooper, Glaxo-Wellcome, UK; D.A. Hutt, University of Loughborough, UK Two approaches to the characterisation of the nature of the sulfur bonding environment in self-assembled monolayers (SAMs) have been explored: sulfur K-edge surface extended X-ray absorption fine structure (SEXAFS) and static secondary ion mass spectrometry (SIMS). S K-edge SEXAFS has proved highly effective for SAMs on Ag and has confirmed that the sulfur adsorbs with threefold coordination during both solution-phase adsorption onto polycrystalline Ag and gas-phase adsorption onto Ag(111) single crystal surfaces. There is no change in the S adsorption site with coverage. Static SIMS has yielded powerful insights into the effect of electron beam bombardment on SAM structure. A complete loss of all gold-molecular fragments from the spectrum is observed after small doses of electrons, indicating a rapid alteration of the sulfur bonding environment, due either to S-C bond scission or, more likely, to oxidation of thiolates to disulfides. Changes in Au-S bonding during the formation of the low coverage phase

of butanethiol on Au have also been studied by static SIMS. Photo- and airoxidation rates are influenced by the adsorbate alkyl chain length; rates of both processes decrease with increasing chain length due to increasing SAM ordering. The nature of the terminal group also affects rates of oxidation, and has a profound influence on the stability of the SAM. Hydrogen bonding between neighbouring terminal groups leads to significant stabilisation. Friction coefficients may be measured for SAMs using friction force microscopy. These decrease with increasing alkyl chain length, and are higher for adsorbates with polar terminal groups. Oxidation of methyl terminated SAMs leads to an increase in the coefficient of friction, interpreted in terms of the collapse of film order following head group oxidation. The rate of increase in the coefficient of friction is faster for short chain SAMs than long-chain SAMs, in agreement with the findings of static SIMS studies.

9:20am SS1+AS+BI-ThM4 Structure of Partially Fluorinated n-alkanethiols on Polycrystalline Gold and Silver Surfaces, *S. Frey*, Universität Heidelberg, Germany; *K. Tamada*, National Institute of Materials and Chemical Research, Japan; *K. Heister, M. Zharnikov, M. Grunze*, Universität Heidelberg, Germany

The physical and chemical properties of self-assembled monolayers (SAM) of alkanethiols (AT) are noticeably affected by partial fluorination of the hydrocarbon chain. We have studied the structure of SAMs formed from partially fluorinated alkanethiols (PFAT) CF@sub 3@(CF@sub 2@)@sub 9@(CH@sub 2@)@sub n@SH with different hydrocarbon chain length (n = 2, 11 and 17) on Au and Ag coated silicon wafers. The objectives of our experiments were (i) to find out whether PFAT form ordered and densely packed SAMs on these substrates, (ii) to determine the individual conformation and orientation of the hydro- and fluorocarbon parts in the molecules, and (iii) to clarify the influence of the headgroup-metal bond (RS-Au or RS-Ag) on the film structure. The PFAT films were characterized by atomic force microscopy, infrared reflection absorption spectroscopy, Xray photoelectron spectroscopy, and angle resolved near edge X-ray absorption fine structure spectroscopy. PFATs were found to form highly ordered and densely packed SAMs on polycrystalline Au and Ag. The hydrocarbon and fluorocarbon chains of the adsorbed PFATs retain the expected planar zigzag and helical conformation of the bulk materials, respectively. The fluorocarbon chains, which are oriented almost perpendicular to the substrates for CF@sub 3@(CF@sub 2@)@sub 9@(CH@sub 2@)@sub 2@SH, assume a more tilted orientation in PFAT SAMs with longer hydrocarbon moieties. As found for the AT on Ag and Au. the hydrocarbon part in the PFAT films exhibits smaller tilt and twist angles on Ag as compared to the Au substrates. Considering the reduced van der Waals interaction between the hydrocarbon chains in PFAT as compared to neat AT SAMs (due to the sterical constraints provided by the fluorocarbon chains), the differences in tilt and twist angle appears to be associated with the different character of the headgroup-substrate bonding on Au and Ag. This work has been supported by the German Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie through grant No. 05 SF8VHA 1.

9:40am SS1+AS+BI-ThM5 Controlling the Placement of Molecules in the Self Assembly and Directed Assembly of Organic Monolayers, *P.S. Weiss, D.L. Allara, L.A. Bumm, J.J. Jackiw,* The Pennsylvania State University INVITED

We manipulate and measure the structures of monolayer films in order to tune their properties. This is accomplished by controlling the defect type and density in the films. We then process the films to insert single molecules, to insert bundles of molecules, or to graft new molecular terraces onto existing domains by using these defects to advantage. The inserted molecules can serve as the anchor points for polymerization; this allows us to choose to produce single polymer dots or isolated polymer brushes. We connect our scanning tunneling microscopy measurements to electron transfer phenomena which are ubiquitous in such areas as biochemistry and electrochemistry by separating the transconductance into components arising from transport through the molecule vs. the tunneling gap outside the film. We show how these components can be measured independently. We prepare films predicted to have many equivalent defect sites so as to provide identical matrix isolation environments for single molecular wire candidates. We also prepare films with well defined interfaces between separated components so that insertion, deposition, or reaction can be directed to these molecularly sharp boundaries.

10:20am SS1+AS+BI-ThM7 Protein Adsorption to Model Surfaces: Probe Adhesion Between Fibrinogen and Patterned SAMs, *L.F. Pardo*, *T.B. Boland*, Clemson University

Interactions between blood and an artificial surface induce a rapid, thrombogenic response believed to be mediated by protein adsorption. In this study, atomic force microscopy (AFM) was used to measure directly non-specific forces between proteins and functionalized surfaces. A protein-modified AFM cantilever tip was used to probe of interactions between a model substrate and a single protein. Model surfaces consisted of both simple and microcontact-printed, -OH, -COOH, and -CH3 terminated self-assembled monolayers (SAMs) of alkanethiols on gold. Fibrinogen was used as the model protein due to its significance in biomaterial-mediated inflammatory responses. It was tethered to the probe tip using a synthetic polypeptide (polyserine). Various approaches were taken to link polyserine to a self-assembled monolayer on a gold substrate. Ellipsometric and vibrational spectroscopic measurements indicated that successive carbodiimide activation of a carboxyl-terminated alkanethiol and polyserine allowed for the successful formation of a polyserine-tethered fibrinogen film. The SAMs, polyserine and fibrinogen films were characterized by ellipsometry and contact angle measurements. Both AFM images and measurements will be presented and discussed. An understanding of how fibrinogen interacts under model conditions will give insight into more complicated real systems.

10:40am SS1+AS+BI-ThM8 Modification of Self-Assembled Monolayers by X-ray, Electron and Thermal Treatments, *H. Fairbrother*, *A. Wagner*, *K. Han*, Johns Hopkins University

Polymer surface modification strategies are widely used to modify interfacial characteristics, including permeability, wettability, adhesion, friction, wear and biocompatibilty. To better understand the detailed nature of these processes thiol-based self-assembled monolayers (SAMs) adsorbed on Au substrates have been used as models for the polymeric interface. In the case of X-ray modification results from X-ray Photoelectron Spectroscopy on fluorinated SAMs show that the degree of cross-linking can be directly correlated with the appearance of CF groups in the organic film. Additional information from Reflection Absorption Spectroscopy and Atomic Force Microscopy on the impact of X-ray, electron, and thermal modification treatments will also be presented, enabling a detailed picture of the chemical and physical modifications that occur during surface treatments to be constructed.

11:00am SS1+AS+BI-ThM9 Electron-induced Damage in Thiofunctionalized Alkanethiol Monolayers, K. Heister, W. Geyer, S. Frey, Universität Heidelberg, Germany; A. Ulman, Polytechnic University; A. Gölzhäuser, M. Zharnikov, Universität Heidelberg, Germany

Potential technological applications of self-assembled monolayers (SAM) of alkanethiols (AT) as lithographic resist require an increased sensitivity of these systems toward ions, X-ray photon or electron irradiation. This effect can be achieved by incorporation of specific molecular groups associated with comparatively weak bonds, such as C-S bond provided by sulfide -Sand sulfone SO@sub 2@- moieties, in the aliphatic chains. We have investigated the damage induced by low-energy electrons in SAMs formed from C@sub 6@H@sub 13@SC@sub 11@H@sub 22@SH (I), C@sub 6@H@sub 13@SO@sub 2@C@sub 11@H@sub 22@SH (II), C@sub 11@H@sub 23@SO@sub 2@C@sub 6@H@sub 12@SH (III), and C@sub 11@H@sub 23@SO@sub 2@C@sub 6@H@sub 4@OC@sub 5@H@sub 10@SH (IV) on polycrystalline Au substrates using angle-resolved near edge X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy. Similar to AT SAMs, an irradiation-induced disordering and a dehydrogenation of the pristine films I - IV as well as the desorption of molecule fragments and the transformation of thiolate molecules in a new irradiation-induced sulfur species were observed. The extent of the irradiation-induced events is, however, affected by the introduction of the sulfide and sulfone moieties. An increased extent of the irradiation-induced desorption processes as compared to AT SAMs was found in I and II, which implies that bond scission events predominately occur in the outermost part of AT SAM. Controversially, an additional dipolar interchain interaction provided by the sulfonic entities has a stabilizing influence on the lower part of SAMs II-IV leading to the conservation of the pristine thiolate species responsible for anchoring of the alkyl chains to the substrate. Considering these controversial effects provided by the sulfonic groups the incorporation of sulfide moiety seems to be a better choice to improve the sensitivity of AT SAMs toward electron irradiation.

11:20am SS1+AS+BI-ThM10 Sensitivity of Alkanethiol Self-assembled Monolayers toward Low-energy Electron Irradiation, *M. Zharnikov, S. Frey, K. Heister, M. Grunze,* Universität Heidelberg, Germany

Potential technological applications of self-assembled monolayers (SAM) as lithographic resist involve their exposure to jons. X-ray photons or electrons. We have investigated the damage induced by low-energy electrons in SAMs of dodecanethiolate (DDT), octadecanethiolate (ODT) and perdeuterated eicosanethiolate (PDET) on gold and of ODT on silver using x-ray photoelectron spectroscopy and angle resolved near edge x-ray absorption fine structure spectroscopy. ODT/Au was taken as a reference system, whereas the other SAMs differed from ODT/Au in the length (DDT/Au) and the isotopic composition (PDET/Au) of the alkyl chains and the strength and character of the thiolate-metal bond (ODT/Ag). All systems studied were found to exhibit a qualitatively similar behavior with respect to low-energy electron irradiation. Both the alkyl chains and the S-Au interface are affected simultaneously through the electron-induced dissociation of C-H, C-C, C-S, and metal-thiolate bonds. The most noticeable processes are the loss of the orientational and conformational order, partial dehydrogenation with C=C double bond formation, desorption of film fragments, decrease of thiolate species, and the appearance of new sulfur species. The cross sections for the individual irradiation-induced processes have been determined. The reactions of the alkyl matrix and the S-metal interface to electron irradiation are essentially independent. The extent and rate of thiolate species reduction and new sulfur species formation are mainly determined by the strength and character of the thiolate-metal bond (Au vs. Ag). At the same time, an extent of irradiationinduced desorption of sulfur-containing fragments depends on the alkyl chain length. Only a slight isotopic variation in the irradiation-induced dehydrogenated process was observed.

Surface Science Division Room 607 - Session SS2+EM+NS-ThM

Nucleation and Growth

Moderator: G.M. Nathanson, University of Wisconsin, Madison

8:20am SS2+EM+NS-ThM1 Evolving Surface Morphology: An In Situ STM Study of 2-20 nm SiGe Quantum Wells Grown on 75 mm Si (100) Wafers, *G.G. Jernigan*, Naval Research Laboratory, US; *P.E. Thompson*, Naval Research Laboratory

Electrical device improvement will come from the understanding and control of interfaces at the atomic level. We have integrated an STM with a commercial Si MBE system for in situ examination of device structures grown on full 75 mm wafers. Our first system of study is the growth of SiGe quantum wells on Si (100). SiGe is being investigated for its use in optoelectronics and high speed circuits. We will present a description of the atomic surface morphology of the initial 100 nm epitaxial Si buffer layer, followed by a Si@sub 0.8@Ge@sub 0.2@ quantum well of thickness up to 20 nm, and a Si capping layer deposited after the quantum well. The Si buffer layer is grown using a 0.08 nm/s Si flux onto a 650 @super o@C substrate. Step-flow growth occurs, but the different adatom sticking probabilities at the S@sub A@ and S@sub B@ steps produces a "wavy" surface which is the result of alternating terraces growing rapidly in different directions rotated by 90@super o@. The deposition of Si@sub 0.8@Ge@sub 0.2@, by co-depositing Ge with a 0.02 nm/s flux and Si, disrupts the "wavy" growth morphology. Ge segregation during deposition produces a "2xn" surface reconstruction that consists of rows which run perpendicular (G@sub A@) and parallel (G@sub B@) to a step edge in a manner analogous to the S@sub A@ and S@sub B@ steps, respectively. The quantum well morphology consists of a mosaic of small terraces containing short rows of G@sub A@ steps and long rows of G@sub B@ steps. The Si capping layer grown on the quantum well reinstates the "wavy" morphology. However, in addition to the S@sub A@ and S@sub B@ step-flow growth, dimer vacancy lines are now observed within the S@sub A@ terraces and are due to Ge segregation from the quantum well. The effects of S@sub A@/S@sub B@ waves, Ge "2xn" terraces, and dimer vacancy lines as a function of growth rate and temperature will be discussed. This work was supported by the ONR.

8:40am SS2+EM+NS-ThM2 Hydrogen-Mediated Surface Morphological Evolution in Si@sub 0.7@Ge@sub 0.3@/Si(001) Layers Grown by Hydride Gas-source Molecular Beam Epitaxy, *T. Spila*, *P. Desjardins*, *H. Kim*, *N. Taylor*, *D.G. Cahill*, *J.E. Greene*, University of Illinois, Urbana; *S. Guillon*, *R.A. Masut*, Ecole Polytechnique de Montréal, Canada

The primary mechanisms for relieving misfit strain @epsilon@ during heteroepitaxy are the formation of misfit dislocations (MD) and straininduced roughening. These mechanisms are initially competing (due to @epsilon@-dependent activation energies) and eventually interacting once relaxation is initiated. Si@sub 0.7@Ge@sub0.3@ layers were grown on Si(001) (miscuts @<=@ 0.1°) to quantitatively investigate the effects of Ge surface segregation and steady-state hydrogen coverage @theta@@sub H@ on mechanisms of surface morphological evolution during GS-MBE from Si@sub 2@H@sub 6@/Ge@sub 2@H@sub 6@. For growth temperatures T@sub s@ > 600 °C where @theta@@sub H@ = 0, layers exhibit (by AFM and XTEM) surface morphologies similar to that observed in solid-source MBE. The islanding process observed at T@sub s@ = 800 °C relieves 45% of the strain (determined from x-ray reciprocal lattice maps) without the introduction of MDs for thicknesses t up to 31 nm. The dominant facet planes evolve from {105}/{113} to {518}/{111}/{011} with increasing t until coalescence (t = 180 nm). Decreasing T@sub s@ < 600 °C to a regime where @theta@@sub H@ > 0 allows an opportunity to probe new hydrogen-mediated surface morphological pathways. The tendency toward strain-induced roughening and faceting decreases with decreasing T@sub s@ as the initial low-thickness strain-relaxation mechanism and corresponding in-plane feature size changes from strain-induced roughening to MD nucleation when T@sub s@ is decreased below 525 °C. We discuss the details of surface morphological evolution in each of the three temperature regimes (< 525, 525-600, and > 600 $^{\circ}$ C) in terms of local precursor adsorption and H-desorption kinetics.

9:00am SS2+EM+NS-ThM3 Interdiffusion During Growth of Ge on Si(100), H. Jonsson, B.P. Uberuaga, M. Leskovar, B.R. Schroeder, S. Meng, M.A. Olmstead, University of Washington

We present both experimental evidence and a theoretical explanation of sub-monolayer Ge epitaxy on Si(100) interdiffusion to the 4th layer of the Si substrate. XPD measurements at both 500 C and 700 C show the presence of Ge atoms in the 4th layer. DFT/GGA calculations of the energetics of a Ge atom in the Si surface, together with a statistical model of Ge occupation of the lattice sites, predict occupation of sub-surface sites, with enhanced occupation in the sites under tensile strain. The calculations indicate that the formation energy of a Ge interstitial near the surface (about 1 eV higher energy than the adatom) is significantly reduced as compared with an interstitial in bulk Si, thus lowering the energy barrier for the interstitial diffusion mechanism near the surface. This work was supported by the National Science Foundation, the University of Washington Royalty Research Fund and the Japanese New Energy and Technology Development Organization.

9:20am SS2+EM+NS-ThM4 Confined Intermixing of Ge and Si, S.-J. Kahng, Seoul National University, Korea; Y.H. Ha, D.W. Moon, Korea Research Institute of Standards and Science, Korea; Y. Kuk, Seoul National University, Korea

In Ge-Si superlattice system, the efficiencies of a possible optoelectric and fast devices can be improved by optimizing the composition at each layer and the abruptness at the interface. It is well- known that intermixing between Ge and Si atoms mainly occurs during the growth process of Si layers on the previously grown Ge layers. Ge atoms tend to segregate toward the surface since the surface free energy of Ge is lower than that of Si. Howerver, with hydrogen adsorbate, the surface free energy of Ge is lower than that of Si, possibly inducing segregation of Si in the Ge overlayer. In this study, Si surface segregation was studied quantitatively for the Ge overlayers grown on Si(100)-(2 x 1) with channeled medium energy ion scattering spectroscopy. The intermixing between Ge and Si presents only at the initial layer in the presence of hydrogen surfactant. Microscopic mechanism for the growth process will be discussed in the view point of kinetics as well as energetics.

9:40am SS2+EM+NS-ThM5 Surface Segregation and Surface Reactivity in Heteroepitaxial Vapor Phase Thin Film Growth: Si@sub 1-x@Ge@sub x@ on Si(111), Y.-J. Zheng, A.M. Lam, J.R. Engstrom, Cornell University

Supersonic molecular beam scattering, x-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectrometry (LEISS) have been employed to examine the heteroepitaxial growth of Si@sub 1-x@Ge@sub x@ thin films on Si(111) surfaces. Molecular beam scattering has been employed to measure the reactivity of Si@sub 2@H@sub 6@ and

GeH@sub 4@ on the Si@sub 1-x@Ge@sub x@ alloy surfaces for a variety of growth conditions (composition and substrate temperature), and these results are compared with results obtained on the clean Si(111) and Ge(111) surfaces. We find that the alloy surfaces are less reactive than both of the pure elemental Si and Ge surfaces. This is in stark contrast to our results for the (100) orientations, where alloy reactivity was always intermediate to that observed on clean Si and Ge. These results reflect the important role played by surface reconstructions on the (111) orientations. XPS and LEISS have been employed in situ to quantify the near-surface Ge concentration of the Si@sub 1-x@Ge@sub x@ epitaxial thin films. Ge segregation is significant, although somewhat less pronounced compared to what we have observed previously on the (100) orientations. Ge segregation, which occurs also in the subsurface layers, has been successfully modeled using both a statistical thermodynamic analytical model, and Monte Carlo simulations.

10:00am SS2+EM+NS-ThM6 The Role of Arsenic Surfactant in the Growth of Germanium Thin Films on Si(100) Surfaces, *C.L. Berrie*, *J. Bright, S.R. Leone*, University of Colorado, Boulder

The role of arsenic surfactant in the growth of germanium films on Si(100) substrates is investigated using laser single photon ionization time of flight mass spectrometry, reflection high energy electron diffraction, and atomic force microscopy. The energetics of arsenic interaction with Si(100) and Ge(100) are investigated by monitoring the temperature dependence of the desorbing fluxes of As@sub 4@, As@sub 2@ and As atoms from the substrate under a constant incident As@sub 4@ flux. These measurements indicate that the As@sub 2@ interactions with Si(100) and Ge(100) differ dramatically. In particular, the As@sub 2@ flux plateaus in the case of the Si(100) substrate from 800 K to 1000 K. In the case of the Ge(100) substrate, the As@sub 2@ flux monotonically increases over this temperature range and a similar plateau is not observed. Measurements of the desorbing As@sub n@ fluxes are also made during Ge growth on a Si(100) surface. The dramatic difference in the arsenic interaction on these two surfaces is evident in these measurements as well. The morphologies of the resulting films are monitored ex-situ using atomic force microscopy to determine the effect of arsenic coverage on the size and density distributions of islands formed. As the arsenic coverage is increases, the observed island size decreases and the density of islands increases dramatically. The mechanisms for the Ge growth and the interaction in the presence of the arsenic surfactant will be considered.

10:20am SS2+EM+NS-ThM7 The Dynamics of the Si(111) (7x7) to (1x1) Phase Transition Investigated by Low Energy Electron Microscopy, J.B. Hannon, Carnegie Mellon University INVITED

We have used low-energy electron microscopy (LEEM) to investigate the dynamics of the (7x7) to (1x1) phase transition on the Si(111) surface. Because the density of the (1x1) surface is 6 percent larger than that of the (7x7) surface, the conversion from (7x7) to (1x1) requires transport of mass to the domain boundary. By measuring the time evolution of complicated configurations of triangular (7x7) domains, and comparing the results to detailed simulations, we are able to quantify the role of mass transport in the dynamics of this phase transition. We find that individual domains decay approximately linearly in time, with a decay rate determined, not by the domain size, but by the local arrangement of neighboring domains. This observation is counter to the simplest picture of phase boundary motion, in which domain walls move with a constant velocity (independent of environment) determined by the free energy difference between the two phases. We have modeled the effect of the mass transport requirement on the observed decay by solving the two-dimensional diffusion equation for the experimentally-observed configuration of 7x7 domains. We find that the (7x7) domain decay is indeed limited by the supply of the additional material to the boundary. Detailed comparison of the diffusion model with experiment suggests the surprising result that the terrace (rather than surface steps) acts as the primary source of the additional atoms required for the (7x7) to (1x1) conversion. This model reproduces the simultaneous decay of all islands in the field of view with only one adjustable parameter.

11:00am SS2+EM+NS-ThM9 The Motion of Atomic Steps on Ultra-Flat Si(111), P. Finnie, Y. Homma, NTT Basic Research Laboratories, Japan

The flattest silicon surfaces are typically made up of terraces of a low index crystal plane connected by atomic steps. We have studied sublimation and growth on ultra-flat Si(111) substrates@footnote 1@ which have (111) terraces of up to 50 microns in width separated by monoatomic steps. The motion of atomic steps is revealed in time lapse movies made by in situ scanning electron microscopy. When samples are heated to high temperatures (about 1000°C) the surface erodes in a step-flow mode: steps

retreat in an orderly fashion, one after the other. Since new terraces are nucleated when step spacings exceed a temperature dependent critical length, the spacing between steps is tunable. Measurements of step velocities as a function of terrace width compare well with theory. The interactions between steps are observed directly by forcing steps to collide@footnote 2@ either destructively, in which opposing steps annihilate, or constructively, in which steps moving in tandem coalesce into double (or triple, or larger) steps. We also studied molecular beam epitaxy in this high temperature regime. Using an electron beam to supply a flux of elemental silicon, desorption is countered and growth occurs in the stepflow mode. Remarkably flat grown surfaces can be obtained in this way since step-flow growth maintains an ultra-flat profile. Monoatomic height island nucleation can also be observed, with circular islands growing to diameters of tens of microns, seamlessly merging with neighboring terraces as the steps collide destructively. @FootnoteText@ @footnote 1@ Y. Homma, H. Hibino, T. Ogino, and N. Aizawa, Phys. Rev. B 55 (1997) R10237 @footnote 2@ P. Finnie and Y. Homma, Phys. Rev. Lett. 82 (1999) 2737.

11:20am SS2+EM+NS-ThM10 Novel Growth Behavior of Ge on Pb Covered Si(111) Surface, *I.S. Huang*, Academia Sinica, ROC; *T.C. Chang*, Academia Sinica, ROC, Republic of China; *T. Tsong*, Academia Sinica, ROC

A surfactant can modify the growth behavior of a system to our advantages. We report discovery of a novel growth behavior in a Pb-layer promoted growth of Ge on Si(111). For this system, not only can Ge atoms grow on Si(111) surface layer by layer for many layers, but the growth behavior is contrary to traditional nucleation and growth theory and most experimental results in epitaxy. This growth is not governed by the reaction-limited-aggregation (RLA) process at low temperature as has been found in traditional epitaxy. The most interesting feature we find is that a compact-to-fractal island shape transition occurs when the sample temperature is increased, or the deposition flux is decreased. In traditional epitaxy, fractal growth occurs by diffusion-limited-aggregation (DLA) at low temperatures, thus fractal growth will disappear as the sample temperature is raised to the extent that step edge diffusion can occur. Our observation demonstrates that fractal islands can also be grown by RLA, and the importance of reactions in aggregation of Ge atoms in this system. Earlier theories neglect the reaction processes which may be acceptable for metal-on-metal systems, but are not good enough for other systems. Our result points to a need to develop a more complete nucleation theory where both diffusion and reaction are properly taken into account.

11:40am SS2+EM+NS-ThM11 The Growth of High Density, Small Ag Islands at the Si(111)7x7 Surfaces with Adatom Defects, *H. Hirayama*, *H. Okamoto*, *K. Takayanagi*, Tokyo Institute of Technology, Japan

We studied the growth of Ag islands on the Si(111)7x7 surfaces with missing adatoms. The missing adatoms were created by 0.5keV Ar ion bombardment. Ag atoms were deposited on the surfaces at room temperature. The growths were observed by using scanning tunneling microscope (STM). At the Si(111)7x7 surface of no missing adatoms, several half unit triangular cells of the 7x7 reconstruction changed their contrast to be bright in the initial stage of the Ag deposition . Then, at the coverage above 0.03 monolayer (ML), each bright triangular cell changed to a bright spot. With the coverage, the number of bright spots increased, and occasionally two spots in neighboring cells kissed. At 0.8ML, the surface was covered by the two-dimensional (2D) percolating network of kissing spots. On the network, three-dimensional (3D) Ag islands grew. Meanwhile, at the Si(111)7x7 surfaces with missing adatoms, the bight spots appeared at the very early stage of the Ag deposition. The spots appeared as to avoid missing adatom sites. This resulted in an imperfect 2D network; the connection of kissing spots were cut into pieces here and there. On the imperfect 2D network, 3D islands grew above 0.7ML. At the stage of the 3D island growth, the missing adatom sites of the underlying 2D network was never filled up. However, we found strong dependence of the size and density of the 3D islands on the number of missing adatoms at the starting surfaces. With an increase of missing adatoms, the size of the islands decreased, while the density increased dramatically. The effects of the missing adatoms on the 3D Ag islands growth were attributed to the substantial increase of the super saturation and the decrease of the diffusion constant of Ag atoms on the imperfect 2D network.

Surface Science Division Room 604 - Session SS3+AS+NS-ThM

Novel Surface Probes & Technique Enhancement Moderator: B.E. Koel, University of Southern California

8:20am SS3+AS+NS-ThM1 Determination of Sticking Probability and Transition State Energy by Line-of-Sight Detection: Halocarbons on Cu(111), A.S.Y. Chan, C.A. Clifford, R.G. Jones, University of Nottingham, UK We have used a new technique, Line-of-Sight Sticking Probability (LOSSP) to study the reactions of chloroform and 1-bromo-2-chloroethane (BCE) on Cu(111). The sticking probability measurements were made by applying a thermally randomised pressure of the halocarbon above the surface and detecting the reflected flux as a narrow beam of molecules flying in line-ofsight from the centre of the sample surface to the mass spectrometer.@footnote 1@ The general reaction undergone by both halocarbons on the copper surface is: M(gas) -> M(phys) [1] M(phys) -> M(gas) [2] M(phys) -> chemisorbed halogens + gas phase product [3]. By measuring the sticking probability as a function of temperature, we are able to obtain the energies of the transition state M(phys) towards decomposition, which for the non-activated adsorption system of BCE on Cu(111) is ~13 kJ/mol below zero, and for the activated adsorption of chloroform on Cu(111) is ~4 kJ/mol above zero. (Zero energy is defined as the energy of the molecule at an infinite distance from the surface. @FootnoteText@ @footnote 1@ R G Jones and C J Fisher; Surface Science 424 (1999)127.

8:40am SS3+AS+NS-ThM2 Demonstration of Angle Resolved Augerphotoelectron Coincidence Spectroscopy from a Solid: First Results from the Cu(111) Surface, D.A. Arena, R.A. Bartynski, Rutgers University; D. Cvetko, L. Floreano, A. Morgante, F. Tommasini, Laboratorio Nazionale TASC-INFM, Italy; A. Attili, A. Ruocco, G. Stefani, Universita' di Roma, Italy; L. Marassi, P. Luches, Universita' di Modena, Italy; S. Iacobucci, CNR-IMAI, Montelibretti, Italy

We report the first successful angle-resolved Auger-photoelectron coincidence spectroscopy (AR-APECS) measurements from a solid. These measurements were made at the ALOISA beamline at the ELETTRA synchrotron radiation center in Trieste, Italy. This novel analysis chamber is equipped with seven hemispherical electron energy analyzers mounted on two independent rotatable frames; the arrangement allows for the efficient exploration of different kinematical conditions for the emitted pair of electrons. We measured the angular distribution of Cu L@sub3@VV Auger electrons from the Cu(111) surface in coincidence with Cu 2p@sub 3/2@ photoelectrons emitted at selected angles; these angles correspond to maxima and minima in the photoelectron diffraction (PED) pattern. When the 2p@sub 3/2@ core level is at a PED maximum, the Auger pattern is indistinguishable (within statistics) from the noncoincidence distribution. In contrast, if the 2p@sub 3/2@ photoelectrons are at a PED minimum, the coincidence Auger angular distribution shows additional structure as compared to the noncoincidence pattern. This observation may arise because the two coincidence conditions access different intermediate states. The effects of the lattice may be more pronounced in the Auger angular pattern collected in coincidence with photoelectrons on the PED maximum while the Auger angular distribution acquired in coincidence with the photoelectrons on the PED minimum may exhibit more "atomic-like" behavior. Alternatively, the difference may be a consequence of different probing depths on and off the PED maximum, and hence the sampling of different scattering sites. Experiments to discriminate between these possibilities are currently underway. This work is supported by NSF-DMR 98-01681 and NATO-CRG 97-0175.

9:00am SS3+AS+NS-ThM3 Multiple Atom Resonant Photoemission: A New Tool for Determining Near-Neighbor Atomic Identities and Bonding, A.W. Kay, UC Davis and LBNL; E. Arenholz, LBNL and UC Berkeley; B.S. Mun, UC Davis and LBNL; J. Garcia de Abajo, LBNL; C.S. Fadley, UC Davis and LBNL; R. Denecke, Z. Hussain, M.A. Van Hove, LBNL

A newly discovered resonance photoemission process between neighboring atoms in multielement samples will be presented. Experimental evidence for the effect and possible applications will be considered. In several metal oxides, including MnO, Fe2O3, and La0.7Sr0.3MnO3, we have observed an enhancement in the core-level photoelectron peak intensity associated with one element in the sample (e.g. O 1s) while the excitation energy is tuned through an energetically deeper absorption edge of a second element (e.g. Mn 2p or Fe 2p or La 3d). At the edges of this second element, a 40-100% enhancement in the peak intensity (as an area above inelastic background) of the first element is

observed. Furthermore, this peak intensity enhancement exhibits a dependence upon photon energy that closely, but not identically, follows the x-ray absorption coefficient of the second atom. This is evidence of an interatomic or multi-atom resonance photoemission (MARPE) process, that is related to but distinctly different from the much-studied intraatomic or single-atom resonance photoemission (SARPE). Theoretical calculations based on extensions of previous intratomic resonance models have yielded encouraging agreement with our experimental results. The MARPE effect is expected to provide a direct method for determining the atomic identities (atomic numbers) of near-neighbor atoms to the excited atom, as well as providing a new technique for studying bonding and magnetism in molecules, at surfaces, buried interfaces, and perhaps bulk materials provided that secondary fluorescence detection of the resonance can be utilized.@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the U.S. Department of Energy, Office of Energy Research, Basic Energy Sciences Division, Materials Science Division, and the Miller Institute (Berkeley).

9:20am SS3+AS+NS-ThM4 Incident Beam Diffraction in Electron Stimulated Desorption, *M.T. Sieger, G.K. Schenter, T.M. Orlando,* Pacific Northwest National Laboratory

The use of electron beams to remove surface-bound atoms and molecules (electron-stimulated desorption, or ESD) is a topic of interest for many disciplines, from semiconductor device processing to astrophysics. We have been studying the role of scattering and diffraction of the incident electron in the initial state of the desorption process. We report calculations and experiments demonstrating that total ESD yields show fine-structure with incident electron direction, consistent with quantum-mechanical scattering and interference of the electron in the initial state of the desorption process. In a time-independent picture interference of the incident plane wave with waves scattered from the crystalline lattice forms an electron standing wave (ESW), having spatially localized maxima and minima in the incident electron density. Whether a particular point on a surface experiences a maximum or minimum depends on the wavelength of the electron, the direction of incidence relative to the crystal axes, and the locations of nearest neighbor atoms. Since the probability of excitation is proportional to the incident electron density at or near the site of the "absorber" atom (the site of the inelastic scattering event), the total ESD rate should depend upon the local atomic structure and the k-vector of the incident wave. The total desorption yield, when measured as a function of incident direction at constant energy, shows oscillations with the symmetry of the absorber bonding site. Since every inequivalent atomic bonding site has a unique pattern of oscillation electron standing wave stimulated desorption (ESWSD) measurements can in principle uniquely determine the bonding geometry of the absorber. We present experimental measurements for chlorinated Si surfaces.

9:40am SS3+AS+NS-ThM5 Direct Atomistic Observation of Structural Dynamics in Surfaces and Interfaces by Time-Resolved High-Resolution Transmission Electron Microscopy, *T. Kizuka*, Nagoya University and Japan Science and Technology Corporation, Japan INVITED

Atomic processes of mechanical interaction and gas-phase epitaxial growth were directly observed in situ by time-resolved high-resolution transmission electron microscopy at spatial resolution of 0.1 nm and time resolution of 1/60 s. Nanometer-sized tips of gold and silicon approached, and were contacted, bonded, deformed and fractured inside a 200 kV electron microscope using a piezo-driving. Contact boundaries of a few atomic columns width in gold, silicon/silicon-oxide/silicon tunnel junctions, and quantum dots of silicon/gold-cluster/silicon were produced.@footnote 1@ A few layers near the surfaces and contact-boundaries were responsible for the bonding and separation processes. Atomic scale contact or non-contact type surface-scanning similar to that in scanning probe microscopy was performed by the same method.@footnote 2@ The mechanical removal of one atomic layer was also demonstrated.@footnote 3@ New kinds of atomic scale mechanical tests, such as friction test, compressing, tensile and shear deformation tests were proposed. Gold was vacuum-deposited on (001) surfaces of magnesium oxide inside the electron microscope. Atomic process of epitaxial growth was in-situ observed cross-sectionally. Various types of growth phenomena, such as 'embryo' formation, structural fluctuation, repeated process of truncation and construction of a corner in one gold cluster, secondary nucleation and coalescence, were analyzed in real-space.@footnote 4@ @FootnoteText@ @footnote 1@T. Kizuka, Phys. Rev. Lett., 81 (1998) 4448. @footnote 2@T. Kizuka et al., Phys. Rev., B55 (1997) R7398. @footnote 3@T. Kizuka, Phys. Rev. B57 (1998) 11158. @footnote 4@T. Kizuka et al., Phys. Rev. B56 (1997) R10079

10:20am **SS3+AS+NS-ThM7** Ionization Mechanisms of Water in High Interfacial Electric Fields, *D.L. Scovell*^A, University of Washington, U.S.A; *V.K. Medvedev, C.J. Rothfuss, E.M. Stuve,* University of Washington

High surface fields (Ã1 V/Å) drive many important processes, such as electrochemistry and field emission. The behavior of water in these fields is important because water is the primary component in electrochemical processes and a major contaminant in the vacuum surrounding field emitter arrays in flat panel displays. It is usually assumed that water amplifies the field at the electrode surfaces, but little is known about how water affects the electric field distribution. Field emitter tips lend themselves to the study of the dielectric properties of water because they produce fields as high as 5 V/Å. To better understand the effect of high electric fields on water, numerical analyses have been conducted to model the electric field distribution around a water-covered emitter tip. The calculations include the field-dependence of the relative permittivity of the water adlayer. The model predicts that the dominant field occurs at the vacuum interface in thin water layers and at the metal surface in thick layers. In very thick layers the field at the tip surface is predicted to be greater than the applied electric field. This response is analogous to that assumed for a traditional electrode/electrolyte interface. Experiments have been conducted to verify the predicted trends for thin water layers. In these experiments water was adsorbed onto a platinum field emitter tip under field-free conditions in ultrahigh vacuum. Ionization was examined by isothermal ramped field desorption (RFD) performed as a function of temperature and water layer thickness. The experimental results are consistent with the predicted trends. This work was supported by the Office of Naval Research.

10:40am SS3+AS+NS-ThM8 Free Electron Laser Nanospectroscopy Interface Applications, G. Margaritondo, Ecole Polytecnique Fédérale, Switzerland; A. Cricenti, Consiglio Nazionale delle Ricerche, Italy; N.H. Tolk, Vanderbilt University; R. Generosi, P. Perfetti, Consiglio Nazionale delle Ricerche, Italy; I.D. Aggarwal, U.S. Naval Research Laboratory

We present the first result of a major effort to investigate the lateral fluctuations of properties of solid interfaces on a microscopic scale. The key elements were the use of a small-tip optics fiber and its coupling with a scanning module; in this way, we achieved and verified the condition of near-field microscopy -- including a lateral resolution much below the wavelength value. Our discussion includes a presentation of the first scanning near-field optical microscopy images obtained with a free electron laser infrared sources and data on small and microscopic-scale fluctuations of semiconductor interface barriers.

11:00am SS3+AS+NS-ThM9 Imaging and Charge Transport Measurements using Dual-Probe Scanning Tunneling Microscopy, *H. Grube*, *J.J. Boland*, University of North Carolina

Scanning tunneling microscopy has evolved into a valuable tool for the study of semiconductor and metal surfaces. However, the single probe geometry of STM limits its application to local and static measurements of the local density of states.@footnote 1@ Incorporation of a second electrically and mechanically independent STM tip within nanometers of the first enables measurements of surface properties that conventional STM cannot perform.@footnote 2,3,4@ Our DP-STM has been characterized by placing both tips in close proximity on a sample surface and obtaining images from each tip showing its local surface environment and the other probe. We discuss the challenges encountered of DPSTM and the feasibility of charge transport measurements on a variety of systems including carbon nanotubes. @FootnoteText@ @footnote 1@ G. Binnig et al., Phys. Rev. Lett., 49 (1), 57 (1982)@footnote 2@ Q. Niu, M. C. Chang and C. K. Shih, Phys. Rev., B 51 (8), 5502 (1995)@footnote 3@ J. M. Beyers and M. E. Flatte, Phys. Rev. Lett., 74 (2), 306 (1995)@footnote 4@ J. M. Beyers and M. E. Flatte, J. Phys. Chem. Solids., 56 (12), 1701 (1995)

11:20am SS3+AS+NS-ThM10 The Miniature Cylindrical Mirror Analyzer: A New Tool For Surface Analysis, *K. Grzelakowski*, Focus Polska Sp. Z o.o., Poland; *M.S. Altman*, Hong Kong University of Science and Technology, P.R. China

The design and performance of a new miniature cylindrical mirror analyzer (CMA) are presented. The CMA comprises outer and inner cylinders, integral on-axis electron gun, and detector system consisting of ring aperture and channeltron, all mounted on a 2.75" flange. Entrance angle, sample-to-detector distance, and polar cone angle were chosen, in consideration of second order focussing effects, that optimized analyzer transparency and resolution. Fringe field correction at the ends of the CMA

¹ Morton S. Traum Award Finalist

8:20 AM

is made by means of six rings precisely separated by sapphire insulators. The electron gun is a one-lens electrostatic system equipped with XYdeflector for beam adjustment and scanning. A CeB6 low temperature cathode operating at up to -2.0keV delivers emission current up to 100 mA. The energy range of analyzed electrons can be varied between 0 eV to 2.0 keV. The flange mounting also incorporates a high precision Z-motion for optimization of the working distance. The control electronics and software permit operation of the instrument in pulse and phase sensitive detection modes. Results obtained for a W(001) surface with this new miniature CMA demonstrate an energy resolution of 0.08%, which is comparable to larger 6" and 8" flange mounted instruments. The very small size of the mini-CMA permits its use in small or crowded ultra high vacuum chambers or where only 2.75" ports are available, thereby increasing flexibility in surface analysis.

11:40am SS3+AS+NS-ThM11 Investigations of Surface Reactions on Thin Film-Supported Catalysts Using Microhotplate Arrays, R. Walton, R. Cavicchi, S. Semancik, M. Class, J. Allen, J. Suehle, National Institute of Standards and Technology

This presentation describes the use of microhotplate arrays and electrical measurements for efficiently investigating surface reactions on supported metal catalysts under varied temperature and gas exposure conditions. Each ~100 μm x 100 μm microhotplate platform used in our work includes functionality for rapid control and measurement of film temperature (thermal time constant ~ 1 ms) and for probing of gas-induced changes in a film's electrical properties. Arrays of individually addressable microhotplates are well suited for directly comparing catalytic layers of different composition, loading, and degree of dispersion. The results we present are relevant to both gas sensing and catalysis. Specifically, fourelement arrays were used to evaluate reactions on Pt, Pd, and Cu catalyst particles (formed by annealing 25-100 Å layers) supported on tin oxide. Electrical conductivity was used to monitor changes in the electron density of the thin film catalysts caused by surface reactions in air of H@sub 2@, CO and CH@sub 3@OH, respectively, at film temperatures ranging from 20 to 500 °C. Each of the catalysts interacts with these reactants in air to produce changes in film conductivity that we relate to factors including surface oxygen concentration, reaction rates, catalyst loading, and catalyst fouling. As a further example of this approach, we also illustrate the use of microhotplates to explore the conditions of thermal cycling and partial pressures under which CO oxidation oscillations occur on Pt particles supported on SnO@sub 2@.

Surface Science Division Room 606 - Session SS1+EM+NS-ThA

Metal/Metal Growth

Moderator: R.Q. Hwang, Sandia National Laboratories

2:00pm SS1+EM+NS-ThA1 Dislocation Structures of Submonolayer Films near the Commensurate-Incommensurate Phase Transition: Ag on Pt(111), J.C. Hamilton, R. Stumpf, Sandia National Laboratories; K. Bromann, M. Giovannini, K. Kern, H. Brune, EPF Lausaane, Switzerland

provide a theoretical explanation@footnote 1@ for unusual experimental observations@footnote 2@ of submonolayer Ag film growth on Pt(111). These films exhibit parallel partial dislocations with narrow hcp regions separated by much wider fcc domains. Using a 2D Frenkel-Kontorova (FK) model we show that this unusually large difference is primarily due to proximity to the commensurate-incommensurate phase transition, and only secondarily to stacking fault energies. We next consider the relationship between island energy, island dislocation structure, and island shape. Using the FK model we calculate the stability of islands with no dislocations, a single dislocation pair across the island, two parallel dislocation pairs across the island, and a "Y" shaped dislocation structure. The model is in excellent agreement with experiment in predicting the onset of dislocation structures in growing islands. It also suggests that the dislocations have little or no effect on the equilibrium island shape. Finally we discuss the relationship between these calculations and related experiments@footnote 3@ on the structure of the clean Pt(111) surface which reconstructs above 65% of the melting point. @FootnoteText@ @footnote 1@ J. C. Hamilton, R. Stumpf, Karsten Bromann, Marcella Giovannini, Klaus Kern and Harald Brune, Phys. Rev. Lett., in press@footnote 2@ Karsten Bromann, Harald Brune, Marcella Giovannini, and Klaus Kern, Surf. Sci. V388, L1107 (1997). @footnote 3@ A. R. Sandy, S.G.J. Mochrie, D.M. Zehner, G. Grubel, K.G. Huang and Doon Gibbs, Phys. Rev. Lett. 68, 2192 (1992).

2:20pm SS1+EM+NS-ThA2 Non Capillarity Driven Grain Growth in a Strained Cu Ultrathin Film, A.K. Schmid, T. Giessel, N.C. Bartelt, J. de la Figuera, R.Q. Hwang, Sandia National Laboratories

Properties of metal films are crucially influenced by details of their grain structure. To determine basic mechanisms of grain evolution we have investigated a prototypical granular thin film using LEEM and STM. In two monolayer thick films of Cu on Ru(0001) a uniaxial relaxation relieves the misfit strain (5.5%) with the substrate, leading to a two-dimensional grain structure consisting of three orientationally different domain types. We observed in-situ grain growth using LEEM in dark field imaging mode and took STM snap shots at several stages of the grain evolution. While on large scale of both time and area the total length of grain boundary decreases in order to reduce the free energy of the system an increase of boundary length has been observed locally and on smaller time scale. The observed behavior can not be described within the framework of a Q-state Potts model which has been widely used for the description of grain growth. We show that the long-ranged lateral interactions between the surface atoms in the strained Cu film which are not considered in Potts model are responsible for the observed behavior.

2:40pm SS1+EM+NS-ThA3 Exchange Processes in Metal on Metal Growth Studied with High-resolution STM, *M. Schmid*, Technische Universitaet Wien, Austria INVITED

In the early 1990's, after the first atomic-scale studies by field ion microscopy and related simulation calculations it became apparent that many processes in growth of thin films involve exchange of substrate and deposited atoms. It was concluded that interlayer diffusion at steps, the key process determining the growth mode, often occurs by replacing a substrate atom with a deposited atom, pushing the substrate atom onto the lower terrace. A new way to study such phenomena is scanning tunneling microscopy (STM) with atomic resolution and chemical contrast@footnote 1@. We have deposited a small amount of Co on a Pt(111) surface with a high density of steps. In the resulting structure, we can distinguish between substrate (Pt) and deposited material (Co) on an atom-by-atom basis. An analysis of the STM data shows that Co atoms do not descend Pt steps by diffusing over the step, but descend from the upper terrace to the lower by an exchange diffusion process at the step edge with the Pt atoms. The Co atoms descend a Pt step edge by this process neither at straight A nor at B steps, but rather at the corners or kinks of the vacancy islands. These results are in qualitative agreement with simulations based on embedded atom method (EAM) potentials. Other examples of exchange processes can lead to subsurface growth of the deposited material, with substrate atoms floating on top of it. Such phenomena were observed to occur already at or near room temperature when Co was deposited on the Pt(111) and Pt(110) surfaces. @FootnoteText@@footnote 1@ E. Lundgren, B. Stanka, G. Leonardelli, M. Schmid, and P. Varga, Phys. Rev. Lett., accepted.

3:20pm SS1+EM+NS-ThA5 Self-diffusion on Pt(110)-1x2: Ab-initio Barriers vs. Experiment@footnote 1@, P.J. Feibelman, Sandia National Laboratories

Because it requires breaking more bonds, dimer diffusion by dissociation and recombination on clean Pt(110)-1x2 should cost more energy than the recently discovered@footnote 2@ "leapfrog" mechanism. Since cohesion per bond decreases with increasing coordination, the leapfrog mode should also have a lower barrier than monomer diffusion. Though firstprinciples calculations confirm these deductions, they are at odds with experiment, possibly signalling the influence of low-level surface contamination. @FootnoteText@ @footnote 1@ Work supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy @footnote 2@ T.R. Linderoth, et al., Phys. Rev. Lett. 82, 1494(1999); F. Montalenti and R. Ferrando, Phys. Rev. Lett. 82, 1498(1999).

3:40pm SS1+EM+NS-ThA6 Novel Temperature Dependence of the Morphology of Deposited Multilayer Ag/Ag(100) Films, C.R. Stoldt, A.R. Layson, C.J. Jenks, Iowa State University; M.C. Bartelt, Sandia National Laboratories; K. Caspersen, J.W. Evans, P.A. Thiel, Iowa State University Metal(100) homoepitaxy provides a natural testing ground for recently developed ideas on kinetic roughening and "mound formation" due to step-edge barriers. Non-monotonic variation of roughness with deposition temperature (T) has been predicted,@footnote 1@ but not observed. Here, we report comprehensive VT-STM studies for growth of Ag/Ag(100) films between 130K and 300K which reveal this behavior. Roughness of 25ML Ag/Ag(100) films at first increases "classically" below 300K due to inhibited downward transport, but then decreases below 220K, achieving a low plateau value below 170K. Unlike Pt/Pt(111) and Rh/Rh(111) growth, non-monotonic behavior is not associated with a dramatic change in 2D island morphology, but rather with enhanced downward funneling from (the more prevalent) step edges at lower T. We also characterize the mound morphology, noting the steepness of the mound sides and small lateral dimension at lower T. A breakdown of kinematic scattering behavior of the intensities observed in our HRLEED studies of these films is attributed to this feature. Monte Carlo simulations of a realistic model for growth@footnote 1@ are consistent with and elucidate observed behavior. @FootnoteText@ @footnote 1@M.C. Bartelt and J.W. Evans, Surf. Sci. 423 (98) 189; Phys. Rev. Lett. 75 (95) 4250.

4:00pm SS1+EM+NS-ThA7 Edge Diffusion During Growth: Kink Ehrlich-Schwoebel Effect and Resulting Instabilities@footnote 1@, O. Pierre-Louis, Univ. J. Fourier (CNRS), France; T.L. Einstein, University of Maryland In addition to the usual step Ehrlich-Schwoebel effect (SESE) on typical metal and semiconductor surfaces, there can also be a kink Ehrlich-Schwoebel effect (KESE), associated with asymmetries in barriers at kinks/corners encountered by atoms during transport along step edges.@footnote 2@ We take into account both phenomena to study the evolution of arbitrarily oriented surfaces during molecular beam epitaxy. We find that the heretofore rarely discussed@footnote 3@ KESE has a profound effect on growth morphology. Under the usual growth conditions, KESE induces a new instability of vicinal surfaces, supplanting the familiar Bales-Zangwill instability@footnote 4@ due exclusively to SESE. The possibility of stable kink flow growth is analyzed; fluctuations can shift the stability threshold. For some orientations, KESE can stabilize steps. KESE can also induce mound formation. @FootnoteText@ @footnote 1@Work supported by NSF MRSEC grant DMR 96-32521. @footnote 2@ O. Pierre-Louis, M. R. D'Orsogna, and T. L. Einstein, Phys. Rev. Lett. 82 (1999) 3661; note also M. V. Ramana Murty and B. H. Cooper, preprint. @footnote 3@ See, however, I. L. Aleiner and R. A. Suris, Sov. Phys. Solid State 34 (1992) 809; Z. Zhang and M. G. Lagally, Science 276 (1997) 377; J. G. Amar, Bull. Am. Phys. Soc. 43 (1998) 851 and to be published. @footnote 4@ G.S. Bales and A. Zangwill, Phys. Rev. B 41 (1990) 5500.

4:20pm SS1+EM+NS-ThA8 Atom-by-Atom Growth: Bonding and Rebonding on Metal Surfaces, A. Bogicevic, Sandia National Laboratories The bond-order--bond-length concept put forth by Pauling almost 70 years ago has greatly added to our intuitive understanding of atomic-scale bonding in molecules. The basic idea is that the more bonds an atom makes, the weaker and longer each becomes [rebonding]. This concept has been extensively tested, and is routinely used in molecular chemistry today, so one would assume that a similar model for the gas-surface interface would prove useful. In an early first-principles study of Al/Al(100). strong and observable rebonding effects were predicted. Unfortunately, these results are an artifact of some severe modelling compromises imposed by computational limitations. New, fully converged (160-180 atom unit-cells, 36 k-points), first-principles density-functional calculations for a wide variety of homogeneous and heterogeneous metal systems show that, contrary to rebonding theory, addimers (adsorbed atom pairs) do not have longer surface bonds than adatoms, do not reside farther above the surface, and do not meet the rebonding arguments for augmented mobility. Rebonding does contribute to destabilize addimers, but does not explain inherently weak adatom-adatom interactions. I explain the absence of rebonding effects in terms of elastic and electronic contributions to the rebonding energy, and present an alternative explanation for the adatomadatom bond weakness based on bond frustration. Implications for nucleation and growth of metals will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Work at Sandia National Laboratories is supported by the U.S. Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

4:40pm SS1+EM+NS-ThA9 Diffusion of Lead on the Au(111) Surface Studied by Scanning Tunneling Microscopy and Embedded-Atom Method Molecular Dynamics, *M.C. Robinson*, Trent University and Queen's University, Canada; *K. De'Bell*, University of New Brunswick in Saint John, Canada; *A.J. Slavin*, Trent University and Queen's University, Canada

Low coverages of Pb deposited on the reconstructed Au(111) surface have been studied with STM and show that the reconstruction strongly influences diffusion and film morphology. Nucleation sites for Pb adatoms are found at the kinks of the reconstruction. For higher coverages, Pb atoms concentrate in the fcc and hcp regions; the elevated transition regions are much less populated. The reconstruction is lifted for some coverage between 0.05 and 0.3 monolayers (ML). For comparison, the Embedded Atom Method-Molecular Dynamics (EAM-MD) method has been used to study diffusion of Pb on both the unreconstructed (flat) and reconstructed surfaces. EAM-MD simulations show that diffusion is complicated by the reconstruction. Using both static and dynamic methods, the diffusion energies have been determined. They show that, for an adatom moving perpendicular to the compression direction, the energy barrier is 1.7 times greater than for motion in the parallel direction. Diffusion is slowed on the fcc part of the reconstructed surface, as compared to the unreconstructed, by a factor of about 2. No greater coverage than 0.07 ML could be forced onto the EAM-modelled reconstructed surface. However, the flat surface could be fully covered, suggesting that the reconstruction is not energetically stable at higher coverages, as has been observed experimentally.

5:00pm SS1+EM+NS-ThA10 Low Energy Electron Microscope Investigation of Pb Overlayers on Cu(100), G.L. Kellogg, Sandia National Laboratories

Pb overlayers on Cu substrates provide a model system for investigating epitaxial films exhibiting large lattice misfits and for studying twodimensional phase transitions (e.g., disordering and surface melting). On Cu(100), room-temperature deposition of Pb follows classical Stranski-Krastanov growth with three well-defined overlayer structures forming at submonolayer coverages.@footnote 1@ In this investigation, low energy electron microscopy (LEEM) is used to (1) characterize the changes that occur to these structures resulting from annealing to various temperatures and (2) monitor the subsequent growth of 3-D islands. The low-coverage c(4x4) and high-coverage c(5@sr@2x@sr@2)R45 phases, both of which consist of rotationally inequivalent domains, are observed to disorder at temperatures of 270C and 215C, respectively. By forming images using selected low energy electron diffraction beams (i.e., dark-field LEEM), the domain structure that forms upon cooling from above the transition temperature is imaged directly with a spatial resolution of ~10 nm. Darkfield LEEM is also used to characterize the c(4x4) - c(2x2) co-existence structure that forms upon desorption of excess Pb from the high-coverage phase. The growth of three-dimensional Pb islands on top of the highcoverage phase and the coarsening of these structures at temperatures

from 100-150C are measured to derive fundamental energetic parameters involved in the melting of 3-D Pb clusters. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. DOE under Contract DE-AC04-94AL85000 @FootnoteText@ @footnote 1@ J. Henrion and G. E. Rhead, Surface Sci. 29(1972)20.

Surface Science Division Room 607 - Session SS2-ThA

Adsorption at Surfaces

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

2:00pm SS2-ThA1 Dissociative Adsorption of H@sub 2@ on Si(001): Reaction Channels and Structure Sensitivity, *M.B. Raschke*, *M. Dürr*, *U. Höfer*, Max-Planck-Institut für Quantenoptik, Germany

Making use of the high adsorbate sensitivity of second-harmonic generation (SHG) the dissociative adsorption of H@sub 2@ on Si(001) could be detected in previous experiments.@footnote 1@ The extremely small sticking coefficients were found to exhibit a pronounced dependence on surface temperature, which indicates the importance of dynamic lattice distortions. In the present investigations, by preadsorbing atomic hydrogen, configurations are realized where, e.g., one of the two danglingbonds per dimer becomes hydrogen terminated. In contrast to the dissociation on the initially clean Si(001) surface this preparation scheme facilitates two additional inter-dimer reaction pathways occuring with either a neighboring identical half-hydrogen-terminated dimer in the cisconfiguration or a clean Si-dimer. Studying the dependence of the reactivities with kinetic energy of the H@sub 2@ molecules using molecular beam techniques, in the first case the dissociation was found to be non-activated, whereas a barrier of 0.2 eV was determined for the second. Together with the barrier of 0.8 eV found for dissociation on the clean surface this corresponds to differences in reactivity up to seven orders of magnitude for a surface temperature of 400 K. Comparing the activation with surface temperature with the dependence on H@sub 2@ beam energy a complementarity between exciting surface and molecular degrees of freedom was found. These results are particularly remarkable because of the geometric similarities of the different configurations of the Si-atoms involved. This together with the results of the recent study of the dissociation at D@sub B@-steps on Si(001)@footnote 2@ provide a systematic understanding of the parameter governing the H@sub 2@/Si(001) interaction. @FootnoteText@ @footnote 1@P. Bratu, K.-L. Kompa, and U. Höfer, Chem. Phys. Lett. 251 (1996) 1. @footnote 2@P. Kratzer, E. Pehlke, M. Scheffler, M. B. Raschke, and U. Höfer, Phys. Rev. Lett. 81 (1998) 5596.

2:20pm SS2-ThA2 Adsorption of Molecular Hydrogen on the Si(100)-2x1 Surface, J.J. Boland, E.J. Buehler, University of North Carolina

The mechanism of molecular hydrogen adsorption on the Si(100)-2x1 surface was studied using variable temperature scanning tunneling microscopy. The measured desorption barrier of ~2.5eV and the bond energies of Si--H (3.5eV) and H--H (4.5eV) predict a tiny barrier to adsorption. This agrees with data showing that desorbing molecules have no excess translational energy as they leave the surface. The magnitude of the room temperature sticking coefficient (<10@super -10@), however, shows that there is actually a large barrier to adsorption, suggesting a violation of detailed balance. We show that the origin of this discrepancy lies in the motion of the atoms of the Si dimers. The dimers of the clean Si(100)-2x1 surface are constantly tilting at room temperature. We have prepared a surface that contains clean Si--Si dimers that are frozen in a relatively untilted configuration. The room temperature sticking coefficient of molecular hydrogen at these sites is six orders of magnitude greater than that on a clean Si(100)-2x1 surface. The implications for hydrogen adsorption and detailed balance are discussed.

2:40pm SS2-ThA3 Molecular Beam Study of the Adsorption and Desorption of Hydrogen Sulfide on Au(100), *St.J. Dixon-Warren,* Washington State University

The adsorption and desorption of hydrogen sulfide on clean reconstructed Au(100)-(5x20) and sulfided gold, denoted Au(100)-(1x1)-SH, has been studied with a combination of temperature programmed desorption (TPD), low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and molecular beam methods. Precursor adsorption kinetics were observed for the adsorption of H@sub 2@S on the Au(100)-(5x20) between 80 and 100 K. The H@sub 2@S adsorbs reversibly into a weakly bound physisorbed state, which desorbs at ~107 K. At 110 K reversible Langmuir

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adsorption was observed for H@sub 2@S on the Au(100)-(5x20). The Au(100)-(1x1)-SH was prepared by electron irradiation of H@sub 2@S adsorbed on the Au(100)-(5x20) substrate. The adsorption kinetics for H@sub 2@S on the Au(100)-(1x1)-SH exhibited Langmuir adsorption kinetics at 80 K, in sharp contrast with the precursor adsorption kinetics observed on the clean Au(100)-(5x20) surface. The TPD of H@sub 2@S from Au(100)-(1x1)-SH and H@sub 2@S adsorbed on Au(100)-(1x1)-SH showed additional features at higher temperatures which are probably associated with the disproportionation of chemisorbed HS(ad). Finally, we have identified a further sulfided gold surface, denoted Au(100)-(2x2)-S which is prepared by annealing the Au(100)-(1x1)-SH to remove adsorbed hydrogen.

3:00pm SS2-ThA4 Decomposition of Nickelocene on Single Crystal Surfaces, D.L. Pugmire, C.M. Woodbridge, M.A. Langell, University of Nebraska, Lincoln

The decomposition mechanisms of nickelocene on several surfaces of varying reactivity have been elucidated by use of high resolution electron energy loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). Exposure of nickelocene to the reactive Ni(100) surface at 135 K results in its decomposition into fragments containing C-C triple bonds. When this substrate is warmed to 273 K, carbide contamination is observed. Exposure of nickelocene to NiO(100) at 135 K also yields decomposition, but with different products than those observed on Ni(100). There is no evidence for the formation of species containing C-C triple bonds on NiO(100). Instead, species with C-C double bonds result upon adsorption at 135 K and as the NiO(100) substrate is warmed to 273 K, all carbon-containing species desorb. In contrast to the reactive nature of Ni(100) and NiO(100), Ag(100) molecularly adsorbs nickelocene at 135 K with its molecular axis perpendicular to the substrate surface. When this substrate is heated, nickelocene desorbs molecularly at approximately 210 K, leaving a surface free of residual carbon. Mechanisms of nickelocene decomposition on the reactive surfaces are proposed based on the HREELS, XPS and TPD results.

3:20pm SS2-ThA5 New Opportunities in Surface Studies using High Brilliance Synchrotron Radiation, N. Mårtensson, Uppsala University, Sweden INVITED

Synchrotron radiation is a most powerful source for electromagnetic radiation with wide applications in a variety of research areas. With synchrotron radiation one can span in a continuous manner a large photon energy range. The radiation is intense and stronly polarized, linearly or circularly. The third generation synchrotron radiation sources which are now coming into operation are optimized for the utilization of insertion devices, i.e. undulators and wigglers, in the straight sections of the storage rings. The utilization of resonant spectroscopies will be discussed. The element specificity at core level thresholds can be used to focus on specific elements or even chemically different species of the same element in complex environments, e.g. at buried interfaces or in adsorbed molecules. The utilization of such techniques will be discussed in different regimes of the electronic structure. The characterization of the electronic states in CuNi systems will be discussed. Resonant photoemission, autoionization or resonant x-ray scattering also allow one to study dynamic properties of the excited states, e.g. probing charge transfer processes between weakly adsorbed molecules and surfaces. It is also shown how X-ray photoelectron spectroscopy at a resolution of 50 meV of adsorbed molecules make it possible to resolve vibrational fine-structure, thereby enhancing the information contents in the spectra considerably. The new way of studying chemical bonding at surfaces using x-ray emission spectroscopy will also discussed

4:00pm SS2-ThA7 The Surface Chemistry of Iron Pentacarbonyl on Palladium (111), M.N. Rocklein, D.P. Land, University of California, Davis

The interaction of organometallic compounds with surfaces can lead to catalytically-active surface moieties or to metal deposition. This is important to industries concerned with supported metal catalysts, magnetic storage, and microelectronics. Depending of the exposure, iron pentacarbonyl desorbs from the close-packed palladium surface in ultrahigh vacuum at 153 and 170 K. This corresponds to multilayer and saturation coverage desorption. However, approximately 30% of the first saturation layer decomposes on the surface during the temperature programmed desorption (TPD) experiment. This implies that some reaction was initiated below 170 K. Laser-induced thermal desorption Fourier transform mass spectrometry (LITD-FTMS) is capable of showing time-resolved changes in molecular surface composition. Interestingly, LITD shows that submonolayer coverages react at 150 K with further

decomposition near 200 K. This study represents the first LITD-FTMS temperature survey of an organometallic/substrate system. TPD further shows evolution of carbon monoxide by a reaction-limited process near 260 K. The simplest explanation of this behavior involves a stepwise decarbonylation and the existence of surface intermediates up to at least 260 K. The proposed mechanism is further supported using reflection-absorption infrared spectroscopy (RAIRS).

4:20pm SS2-ThA8 Adsorption Driven Displacement of N@sub 2@ from Pt(111), G.A. Kimmel, K.P. Stevenson, B.D. Kay, Pacific Northwest National Laboratory

Pt(111) with beam reflection measurements and temperature programmed desorption (TPD). The interaction of weakly adsorbed species on surfaces is of fundamental interest since these systems provide a benchmark for more complicated systems. Our experiments involve the preparation of monolayer or sub-monolayer coverages of N@sub 2@ on Pt(111) followed by the adsorption of another species (e.g. CH@sub 4@, Kr and H@sub 2@O). Both species are monitored throughout the experiments, allowing for quantitative measurements of the coverages and sticking coefficients versus time. In all cases, N@sub 2@ is displaced from direct contact with the Pt(111) by the adsorbates which have higher binding energies. The fate of the displaced N@sub 2@ molecules is governed by the surface temperature and its interaction energy with the co-adsorbate. At higher temperatures, the N@sub 2@ desorbs as soon as it is displaced from the first layer. As the temperature is lowered, the N@sub 2@ desorbs when it is displaced from successively higher layers. This behavior results from the successively lower binding energy of N@sub 2@ to increasingly thick coadsorbate layers. At "high" temperatures (~38 K), the N@sub 2@ desorption rate is approximately constant during the adsorption of the first monolayer of CH@sub 4@, falling abruptly to zero with its completion. This suggests that the mobility of the adsorbed CH@sub 4@ is high allowing it to rapidly find and displace N@sub 2@. The CH@sub 4@ sticking coefficient increases linearly with time as the surface layer is converted from N@sub 2@ to CH@sub 4@. TPD subsequent to the CH@sub 4@ exposure shows that the entire N@sub 2@ monolayer was displaced and desorbed during the CH@sub 4@ adsorption. At lower temperatures, lower diffusion rates lead to departures from zero-order desorption kinetics. The displacement of N@sub 2@ by H@sub 2@O is qualitatively similar, but quantitative comparisons are complicated by details of the N@sub 2@/H@sub 2@O interaction.

4:40pm SS2-ThA9 The Vibrational Spectra of Adsorbed Alkoxies on Cu(100) and W(110): Experimental Data and ab initio Calculations, *P. Uvdal*, *R. Ásmundsson*, Lund University, Sweden; *A.D. McKerell*, *Jr.*, University of Maryland

Using surface FTIR spectroscopy we have measured the vibrational spectra of different alkoxies adsorbed on single crystal surfaces of Cu(100) and W(110). It is demonstrated how modification of the alkyl chain and the associated changes in the experimental vibrational spectra can be calculated with a high degree of accuracy using ab initio electronic structure calculations of an alkoxy-metal complex as the model. Analysis of the symmetry properties of the calculated normal modes allows for a determination of the geometry of the adsorbed species.

5:00pm SS2-ThA10 Probing the Metal Sites of a V-oxide/Pd(111) "Inverse Catalyst": Adsorption of CO, F.P. Leisenberger, G. Koller, S. Surnev, M.G. Ramsey, F.P. Netzer, Karl-Franzens-Universität Graz, Austria

A vanadium oxide / Pd(111) "inverse catalyst" system, consisting of V-oxide island structures and bare Pd(111) patches in between, has been prepared by reactive evaporation of V onto Pd(111) at submonolayer to monolayer coverages and has been characterised by STM and high-resolution core level photoelectron spectroscopy. Here we report a study of the adsorption of CO on these "inverse" V@sub 2@O@sub 3@/ Pd(111) catalyst. Since CO does not adsorb on V-oxide at room temperature, this allows to probe the adsorption properties of free Pd(111) sites in the presence of the V-oxide phase boundary. The adsorption of CO has been followed by monitoring the C 1s core level signals as a function of the V-oxide coverage and the CO exposure at room temperature, using high-resolution XPS with synchrotron radiation. The amount of adsorbed CO, as determined quantitatively from the C 1s peak areas, decreases with the V-oxide coverage as a result of the blocking of Pd adsorption sites. The concomitant decrease of the CO saturation exposure, i.e. the CO exposure necessary to reach CO saturation of the various surfaces, indicates, however, that a precursor state exists on the V-oxide surface, from which CO can diffuse over the metal-oxide boundary on to Pd sites. This spill-over effect is also corroborated by the dependence of the initial sticking probability of CO on the V-oxide surface

coverage. The difference of the C 1s binding energies of CO adsorbed on pristine and oxide covered Pd(111) suggests that Pd adsorption sites are electronically influenced by the presence of a V-oxide phase boundary. Supported by the Austrian Science Foundation.

Surface Science Division Room 613/614 - Session SS3+BI-ThA

Biological Surface Science

Moderator: B. Kasemo, Chalmers Univ. of Tech. and Göteborg Univ.

2:40pm SS3+BI-ThA3 Thia(Ethylene Oxide) Alkanes: Tuning the Structure of a Supported Biomimetic Membrane via Spacer Length and Packing Density, D.J. Vanderah, C.W. Meuse, T. Petralli-Mallow, A.L. Plant, National Institute of Standards and Technology INVITED Interest in reconstituting transmembrane proteins in supported cell membrane mimics of phospholipid/alkanethiol hybrid bilayers has led to development of novel tethering molecules. In an attempt to introduce a disordered, hydrophilic region at the proximal side of the supported lipid bilayer, ethylene oxide moieties have been used as spacers between the sulfur and the alkane chain of alkanethiols. We have observed by infrared spectroscopy, neutron reflectivity, and electrochemistry that such ethyleneoxide moieties are not necessarily hydrated or disordered. The ethylene oxide of thiahexa(ethylene oxide) alkanes (HS(EO)@sub 6@alkanes) form a highly ordered arrangement of 7/2 helices when allowed to self-assemble at gold from an ethanolic solution. This highly ordered conformation is apparently not driven by order in the alkane chains, since the helical structure occurs in both HS(EO)@sub 6@-decane and HS(EO)6octadecane. The conformation is, however, determined in part by molecular density. Infrared analysis of mixed monolayers of HS(EO)@sub 6@-alkanes and phospholipids transferred from the air-water interface indicates that at low packing densities the EO region is disordered, but it assumes the helical structure at higher packing densities. Infrared spectroscopy and sum frequency generation suggest that the conformation of the EO region may be controlled by its length. For a series of selfassembled monolayers of HS(EO)@sub n@-decanes, the EO segment is an extended all-trains chain when n=4, a 7/2 helix when n=5-7, and a less ordered conformer when n=8. This effect of spacer length and packing may provide a means of tuning the molecular order of biomimetic matrices.

3:20pm SS3+BI-ThA5 Quantitative Analyses of Biological Interactions using Surface-Biofunctionalized Surface Plasmon Resonance Devices, C.T. Campbell, L.S. Jung, J. Shumaker-Parry, K.E. Nelson, P.S. Stayton, M.S. Boeckl, M.H. Gelb, S.S. Yee, T. Sasaki, R. Aebersold, University of Washington INVITED

The adsorption of molecules from liquid solutions onto solid surfaces can be monitored with high sensitivity and fast time response by following changes in the angle or wavelength at which the surface plasmon resonance (SPR) of a thin metal film is optically excited. Simple methods convert these measured changes into adsorbate concentrations. We report here the adsorption and desorption kinetics and equilibrium coverages of a variety of species on well-characterized surfaces as determined by SPR techniques. When the diffusion constant of the adsorbing species is known in the liquid phase, the intrinsic rate constants can be determined from the kinetic results. A new method will be described for converting intrinsic adsorption rate constants into sticking probabilities (i.e., the probability that adsorption occurs, given a collision of the molecule with the surface). Several applications of gold-thin-film SPR sensors in quantifying biological interactions will be described. A gold surface containing a few biotin headgroups in a self assembled alkylthiol monolayer of mainly oligo(ethylene glycol) headgroups has been used to assess the effects of protein mutations on the strength of biotinstreptavidin binding. With wild-type streptavidin, the free biotin sites in the resulting streptavidin monolayer have been used as strong linker sites for further attachment of intact, biotinylated lipid vesicles and biotinylated, double-stranded oligonucleotides to the surface. These complex biological films then provide a surface template that can be used to probe the kinetics and equilibrium binding constants for: (1) peripheral membrane proteins binding to vesicle walls, and (2) the binding of DNA-binding proteins to select oligonucleotide sequences.

4:00pm SS3+BI-ThA7 Adsorption and Reactions in Enzymes and on Surfaces: Similarities And Differences, A. Logadottir, T.H. Rod, Technical University of Denmark; J.K. Nørskov, Technical University of Denmark, Denmark INVITED

There are a number of cases where surfaces and biomolecules adsorb the same molecules and catalyze the same reactions. This makes it possible to make comparisons and to see if the concepts of surface science can be transferred to biomolecules. As a specific example, the adsorption of N@sub 2@ and the ammonia synthesis reaction on metal surfaces and in the enzyme nitrogenase will be compared in detail. The comparisons are largely based on density functional calculations which provide a detailed description of the extensive database of experiments for the nitrogen activation process on Fe and Ru surfaces, and which can be used to give the first hint of a mechanism in the enzyme process.

4:40pm SS3+BI-ThA9 The Role of Hydrogen Bonding in Chemisorbed Aminoacids, N.V. Richardson, University of St Andrews, UK INVITED Glycine and its derivatives such as phenyl glycine and alanine form wellordered monolayers of the corresponding anion on Cu(110). The unit cells reflect both the strong adsorbate-substrate interaction and the hydrogen bonding interactions between adsorbed species. In the case of the chiral amino acids studied, this leads to ordered domains of the two isomers which are distinguishable. Glycine undergoes several orientational changes during the build up of the ordered monolayer and is then able to form a stable bilayer. Such a bilayer is not formed in the case of phenyl glycine or alanine demonstrating the importance of optimal hydrogen bonding in stabilising the bilayer. Adsorption of water on the glycine covered copper surface drives a re-orientation of the molecule which we also relate to the importance of hydrogen bonding between the co-adsorbed species.

Surface Science Division Room 606 - Session SS1+AS+BI-FrM

Organic Films/Self-Assembled Monolayers

Moderator: G.E. Poirier, National Institute of Standards and Technology

8:20am SS1+AS+BI-FrM1 Simple Viscosity Model Analysis of Hydronium Ion Motion in Nanometer Organic Films, K. Wu, M.J. ledema, J.P. Cowin, Pacific Northwest National Laboratory

Nanometer organic films such as methylcyclohexane and 3-methylpentane were vapor-deposited at 30 K on Pt(111) with a molecular beam. Pure hydronium ions were soft-landed on top of the films at a kinetic energy less than 1.2 eV. The voltage change and desorption of the organic films were simultaneously monitored by a Kelvin probe and a mass spectrometer. Ion dosing on the organic films was a capacitive charging process, therefore the film voltage change actually reflected the ion motion in the organic films, assuming the dielectric constants of the organic films do not change much with temperature. When the films were warmed, ions gradually moved into the films. The experimental results were analyzed by a simple viscosity model. To a large extent, the temperature (or time) evolution of the film voltage could be well predicted by the model. The film voltage fall-off temperature width from the theory was, however, about half of that from the experiment. Further experimental evidence showed that the ion selfgenerated electric field strength had a strong effect on the ion motion. For example, when the electric field strength was higher than 0.05 V/Angstrom, the theoretical prediction seriously deviated from the experimental result, indicating that a high electric field might trigger nonlinear ion motion and made the Stokes-Einstein equation not accurate. When films were prepared at higher temperatures, methylcyclohexane could crystallize on Pt(111), making ions more difficult to transport in the crystalline films. But, 3-methylpentane never crystallized before ion motion in it completed, indicating that it's a good glass material. With this general approach, we could attack many important issues such as ion motion across liquid-liquid interfaces, hydration of ions and so on.

8:40am SS1+AS+BI-FrM2 Direct Observation of Topological Defect Evolution and Domain Motion in Ultrathin Films of PS-b-PMMA Diblock Copolymers Using Atomic Force Microscopy, J. Hahm¹, W.A. Lopes, H.M. Jaeger, S.J. Sibener, The University of Chicago

We report the tracking of individual topological defects in the microdomain patterns of cylinder-forming polystyrene-block-polymethylmethacrylate (PS-b-PMMA) films. These films undergo vertical and lateral phase separation when they are thermally annealed. The vertical phase separation results in thickness quantization where each layer exhibits its own topology and dynamics. The lateral phase separation provides height contrast between the two components of the diblock in single-cylinderlayer thick films. In the atomic force microscopy (AFM) topographic images, the PMMA is higher by approximately 1nm as compared to the PS blocks. 50nm thick films, containing a single layer of cylinders aligned parallel to the film plane, were repeatedly and non-destructively probed with AFM in an attempt to elucidate the evolution of the diblock domain topology between annealing treatments. We show explicitly that the evolution of topological defects takes place through relinking, joining, clustering and annihilation of defects. Such processes form the basis for predicting structural changes in polymer thin films. We also have used time-lapse AFM imaging to observe directly the kinetics of domain mobility responsible for topological evolution. Domains of different thicknesses were monitored as a function of annealing temperature and time. The higher mobility and lower activation energy associated with thicker domain mobility are accounted for by the essentially negligible substrate interactions where polymer-polymer rather than polymer-substrate interactions govern the dynamics. Our hope is that the combined understanding of topological changes, such as those reported in this talk, when combined with mobility kinetics, will give us a predictive understanding of the thermally activated structural changes that occur within thin polymer films. @FootnoteText@ Supported by the NSF-MRSEC at the University of Chicago and AFOSR.

9:00am SS1+AS+BI-FrM3 Properties of Self-Assembled Monolayers of Biphenyl-Based Thiols, *T. Felgenhauer*, *H.-T. Rong, M. Buck, M. Grunze*, University of Heidelberg, Germany

Despite their versatility to modify surface properties, self-assembled monolayers (SAM) based on alkane thiols have limitations concerning conformational stability or structural perfection. In search for more rigid molecules, thiols based on aromatic moieties offer an alternative. However, in contrast to SAMs consisting of alkane thiols experiments on aromatic thiols are relatively scarce. Our experiments focus on thiol SAMs consisting of 4,4'-substituted biphenyls (BP). To allow systematic investigations the number of methylene units between the biphenyl moiety and the thiol group was varied between zero and six. The electrochemical behavior of BP-SAMs turns out to be very different from alkane thiols. In general, the charge permeability of BP-SAMs is higher by orders of magnitude even though the electrochemical stability of BP-SAMs is dependent on the methylene spacer. Exposure to an etching solution reveals a stability significantly higher compared to alkane thiols and suggests an improved structural perfection of BP-SAMs. Spectroscopic characterization of the BP-SAMs yields an orientation of the biphenyl units alternating with the methylene chain length. Comparison of BP-SAMs on Au with those on Ag shows a reversal of the odd-even effect and demonstrates that the sulphur-substrate bond is crucial for the molecular orientation of the biphenyl-SAMs.

9:20am SS1+AS+BI-FrM4 Structure of Self-assembled Monolayers of Alkanethiols and Disulfides on Au(111), *H. Nozoye*, National Institute of Materials and Chemical Research, Japan; *C. Kodama*, *T. Hayashi*, University of Tsukuba, Japan

Self-assembled monolayer (SAM) films of alkanethiols and alkyldisulfides have been attracting an increasing interest. However, we do not have a concrete picture of SAM, e.g. is the SH bond broken on the surface ? , is the SS bond formed on the surface ?, or where is the adsorption site of S ?. We studied these problems by means of STM, HREELS, high-sensitivity LEED, and TPD. Alkanethiols (C1-C10) and alkyldisulfides (C2-C12) were adsorbed on a Au(111) single crystal surface at room temperature or at around 120 K. Dersorption of H2, parent alkanethiol, alkylthiolate radical, and alkyldisulfide were observed in TPD and a vibration peak assigned to a SS bond was missing in HREEL spectra. We clearly concluded that the SH bond of alkylthiols breaks at low temperature forming alkylthiolates on the surface. Furthermore, the SS bond of alkyldisulfides was shown to be broken on the surface, forming alkylthiolate. The Au-S bond of alkylthiolates on the surface gave a relatively strong peak in HREEL spectra. We will discuss the formation process and the relation between the local structure and the long-range order of SAM.

9:40am SS1+AS+BI-FrM5 Toward Vapor Deposition of Polycyanurates: The Surface Chemistry of Phenyl Cyanate and Phenol on Al(111), *B. Bartlett, J.M. Valdisera, J.N. Russell, Jr.*, Naval Research Laboratory

Polycyanurates, formed by polymerization of monomers containing two cyanate groups, show promise as vapor depositable, low dielectric parameter materials for microelectronics applications. Consequently, we are examining the chemistry of a model system, phenyl cyanate on Al(111) surface, with temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). (Aluminum was chosen as a substrate because it is used for interconnects in microelectronics.) For submonolayer coverages, XPS shows that the phenyl cyanate undergoes O-CN bond cleavage between 150 and 200 K, leaving phenoxide and cyanide groups on the surface. Benzene and hydrogen decomposition desorption products were observed at 620 K, and between 500 and 800 K, respectively. This is analogous to the reaction of phenol on Al(111). Deuterium labeling was used to determine the sequence of C-H bond scission on the phenoxy species. XPS and AES reveal the formation of aluminum oxide, nitride and carbide on the surface above ~ 400 K. After multilayer exposures, the formation of the phenyl cyanate trimer, triphenoxytriazine, was observed with XPS between 160 and 200 K. The trimerized multilayer was stable up to ~ 500 K before it decomposed. This data suggests that at high coverages, a dicyanate functionalized molecule may chemically attach to aluminum by cleavage of an O-CN bond, while the other cvanate group is available for trimerization, thus anchoring a polycyanurate film to the surface. The surface chemistry of a dicyanate functionalized molecule, 1,1-bis(diphenylcyanato)ethane, is currently under investigation to confirm this hypothesis.

10:00am SS1+AS+BI-FrM6 Formation of Organic Layers by Cycloaddition Reactions at Germanium Surfaces, S.W. Lee, University of Missouri, Columbia; J.S. Hovis, R.J. Hamers, University of Wisconsin, Madison; C.M. Greenlief, University of Missouri, Columbia

The formation of ordered organic layers on Ge(001) substrates is explored. Ge substrates are prepared by a novel method and exposed to a variety of cyclic hydrocarbons, including cyclopentene and cyclohexene. The subsequent surface interactions are followed by a variety of surface sensitive techniques. Bonding configurations are determined by photoelectron spectroscopy and scanning tunneling microscopy. The strength of surface interactions are also monitored by temperature programmed desorption. Cyclopentene and cyclohexene react with Ge dimer bonds via a [2+2] cycloaddition reaction. This reaction generates rows of the surface, which is easily observed by scanning tunneling microscopy. Experiments using other cyclic hydrocarbons and attempts at further surface modification will be discussed.

10:20am SS1+AS+BI-FrM7 Multilayer Phases in Self-Assembled Monolayers Based on Silane Coupling Agents, B.C. Bunker, R.W. Carpick, M. Hankins, M.L. Thomas, R. Assink, M. DeBoer, Sandia National Laboratories

Thin films prepared using silane coupling agents are used extensively to chemically modify surfaces. In micromachines, such films are used to control stiction, friction, and adhesion of moving parts. The films are commonly depicted as self-assembled monolayers, in which each silane molecule forms extensive Si-O-Si linkages to the surface and to other molecules. However, many workers report that it is difficult to produce self-assembled monolayers on a reproducible basis, especially for films having fluorinated hydrocarbon chains. In this paper, atomic force microscopy studies are used to show that irreproducible film formation is associated with the fact that silane coupling agents can self-assemble into a range of structures described in common surfactant phase diagrams. Evidence is presented suggesting that hydrocarbon and fluorocarbon silanes form lamellar and inverse micelle structures on silica and silicon nitride surfaces. In some instances, multilayer structures are produced during fabrication. Films which start out as monolayers can also reorganize into multilayer phases after deposition. Factors influencing the phases observed include surface pretreatment, the solvent, silane and water concentrations in the deposition solution, and environmental parameters such as temperature and relative humidity. Mechanisms for the evolution of the observed range of self-assembled structures vs. reaction conditions are described.

10:40am SS1+AS+BI-FrM8 Self-assembled Monolayers on Silicon Surfaces: The Opposite to Siloxane Chemistry, J.A. Mulder, R.P. Hsung, X.-Y. Zhu, University of Minnesota

Self-assembled monolayers (SAMs) on silicon surfaces are of interest for a number of reasons: they may be used as monolayer resists in high resolution lithography, as dielectric layers, as active components in hybrid sensor devices, as passivation and lubrication layers in MEMS, and as a new platform for biochips. SAMs on silicon are traditionally formed via siloxane chemistry on oxidized surfaces from organosilicon derivatives, such as alkyltrichlorosilane. The problems with siloxane SAMs are well known: they are difficult to prepare and suffer from poor reproducibility; the contradiction between cross-linking and close-packing is inherent; the presence of the amorphous and insulating oxide layer is not desirable in some applications. There is much incen tive to develop simple processes for the formation of stable molecular layers directly on the silicon surface. We present a novel approach which, in essence, is the opposite to the siloxane SAM process. The assembly processes are based on the reaction bet ween R-OH or R-NH2 with chlorinated silicon surfaces, leading to molecular assembly via Si-O or Si-N linkages. These reactions are not only efficient but also sufficiently versatile for the assembly of a wide variety of functional organic molecules. A par ticular advantage of this new assembly chemistry is that it is compatible with both vacuum and solution phases and can be carried out under very benign experimental conditions. We characterize these SAMs using a variety of techniques, such as multiple-int ernal reflection FTIR, X-ray photoelectron spectroscopy, contact angle measurements, and scanning probe microscopy. We address structural and stability of these SAMs and their dependence on molecular structure, such as alkyls and aromatics. We also discuss immediate and future applications.

11:00am SS1+AS+BI-FrM9 The Photochemistry of Model Organosulfur Compounds Adsorbed on GaAs (110): Energy-Resolved Photofragment Angular Distributions, *N. Camillone III*, *K. Adib*, *R.M. Osgood*, *Jr.*, Columbia University

Self-assembled monolayers of organothiols and related compounds hold promise for use in the semiconductor industry as ultrathin electron beam resists and precursors for the growth of II-VI materials, as well as for the growth of passivating gallium sulfide films on GaAs. An understanding of the structure and photon and electron chemistry of organothiols and related compounds is relevant to the development of these technologies. We report on our studies of the photoinduced chemistry of three model organosulfur compounds. CH@sub 3@SH. (CH@sub 3@S)@sub 2@ and CH@sub 3@SCH@sub 3@, on the (110) surface of GaAs. We find that the cross sections for the photoinduced reactions of these molecules in the adsorbed monolayers follows the trend CH@sub 3@SH > CH@sub 3@SCH@sub 3@ > (CH@sub 3@S)@sub 2@. Comparison of these measurements to photoinduced chemistry in the multilayer regime gives insight into the degree to which close proximity to the semiconductor surface perturbs the photochemistry. In addition, the structure and molecular orientation of these molecules is discussed in light of the results of energy-resolved photofragment angular distributions and low energy electron diffraction measurements. The post-irradiation chemistry of the trapped photofragments will also be discussed.

Surface Science Division Room 607 - Session SS2-FrM

Adsorption on Metals and Silicon

Moderator: A.A. Baski, Virginia Commonwealth University

8:20am SS2-FrM1 Quantitative Determination of Adsorbate Interactions on an Iron Surface, L. Österlund, M.O. Pedersen, I. Stensgaard, E. Laegsgaard, F. Besenbacher, University of Aarhus, Denmark

We introduce a new concept of Configuration Distribution Analysis (CDA) to extract quantitative values of the adsorbate-adsorbate interaction potential from Scanning Tunneling Microscopy (STM) data. By analyzing atomically resolved nitrogen islands on a Fe(100) surface, we show that the propensity of small, compact c(2x2) islands is due to a many-body effect in combination with elastic interactions. It is shown that the nearest and nextnearest neighbour interactions are strongly repulsive and weakly attractive, respectively, where the latter is modulated by the nearest neighbour coordination. Accurate determination of adsorbate-adsorbate interactions are essential to understand a variety of surface phenomena, and until now, there has been a lack of reliable experimental results. The results presented here promise to provide a new tool to bridge this gap.

8:40am SS2-FrM2 CO Adsorption on Mn Films on Cu(100), *M. Grüne*, Universität Bonn, Germany; *G. Boishin*, Bulgarian Academy of Sciences, Bulgaria; *R.-J. Linden*, *T. Pelster*, *J. Breitbach*, *A. Frey*, *C. Becker*, *K. Wandelt*, Universität Bonn, Germany

The adsorption of carbon monoxide on Mn films on Cu(100) at 100 K was studied by means of UPS, HREELS, LEED, TDS, and work function change measurements. On the c(8x2) Mn monolayer, two stages of adsorption can be separated. The first type of molecularly adsorbed CO increases the work function by 0.9 eV. HREEL spectra resolve at least 4 different adsorption states, which cannot be separated by dosing or annealing. We assign these to side-on CO, step sites, and different kinds of bridge-bonded sites. The substrate superstructure remains intact in this low-coverage range. No adsorbate-induced LEED spots can be observed. Further CO adsorption beyond a critical exposure leads to a destruction of the Mn film order accompanied by a change of the CO-metal interaction as revealed by UPS and a decrease of the work function by 0.16 eV. In HREELS an additional CO state can be identified, presumably ontop-CO. At submonolayer Mn coverages, CO adsorbs simultaneously on both Cu and Mn patches. A thick polycrystalline Mn film exhibits molecular adsorption preferably in the side-on geometry. Annealing of CO-covered monolayer films leads to a restructuring of the surface around 220 K, subsequent dissociation of CO around 300 K, accompanied by desorption with a maximum at 350 K. It is not possible to re-establish the ordered film structure by annealing. At submonolayer Mn coverages, an additional desorption maximum at 420 K can be attributed to CO desorption from the Mn island edges. If the surface has not been saturated with CO, molecules change from Cu to Mn sites upon annealing to 160 K. Annealing a CO-covered thick polycrystalline Mn film leads to complete CO dissociation around 210 K.

9:00am SS2-FrM3 STM Tip Induced 1D Chains on H-covered Ni(100) Surface, T. Komeda, M. Kawai, The Institute of Physical and Chemical Research (RIKEN), Japan

The adsorption of H on metal surfaces is considered as a weak chemisorption in general, based on its low desorption temperature. Due to its weak bonding, the surface reconstruction on H adsorption is observed only for very open surface, such as (110) surface of fcc transition metal. It has been shown that the H saturated Ni(110) surface at room temperature shows streaky (1x2) superstructure, on which high resolution STM observation showed added and missing rows as the origin of its structure. In this paper, we show STM tip can create very characteristic 1D chains of protrusion and depletion on H-saturated Ni(100) surface: Ni(100) surface is believed to be stable for H adsorption and forms no reconstruction. The 1D structure is apparently similar to the added and missing row structure on H saturated Ni(110) surface. Experimentally clean Ni(100) surface was exposed to 10 L(1L=10-6 torr s) of H2 at 100 K and observed with low temperature STM which is cooled with liquid nitrogen. When the surface is scanned with a very small gap between the tip and the sample (scanning condition such as -1 mV biased on the sample and tunneling current of 4nA), straight protruded rows accompanying depleted rows besides them appear. The height of the protruded row is 0.3-0.5 A, and the high resolution image shows it is composed of a chain of single atoms spaced with 2x1 periodicity. The characteristic 1D structure is similar to the added and missing row structure formed on H saturated Ni(110) surface, and apparently slight touch of the STM tip on the substrate can dig a single row and the released NiH species form added row. As can be seen in the apparent low height of 0.3-0.5 A for the added row on the terrace, the added row and the missing row shows strong bias dependence in the STM image, which indicates very characteristic electronic structures appeared on this quasi 1D structure.

9:20am SS2-FrM4 Morphology and Electronic Structure of 1D Ca-induced Rows on the Si(111) Surface, M.S. Turner, K.M. Jones, A.A. Baski, J.A. Carlisle, Virginia Commonwealth University

Deposition of highly reactive alkaline-earth adsorbates (Ca, Sr, Ba) onto semiconductor substrates leads to reconstructions which are row-like in nature. The Ca/Si(111) system has been studied using RHEED, STM and synchrotron radiation photoemission. For Ca coverages less than 0.5 ML, a series of odd-order nx1 (n=3,5,7...)reconstructions have been observed. The most stable of these is a (3x1) phase that occurs at 0.33 ML. Various models have been proposed for the general metal/Si(111)-(3x1) system, and we discuss the accuracy of these models as they apply to this system.@footnote 1@ In particular, we discuss how well the models can be altered to account for the higher-order reconstructions that are observed at higher Ca coverages, and for commonly observed defect structures in the (3x1) phase. These objectives are accomplished through comparison between the surface morphologies observed in STM images and the electronic structure of the different surface phases observed in highresolution core-level and valence-band photoemission. @FootnoteText@ @footnote 1@S.C. Erwin and H.H. Weitering, Phys. Rev. Lett. 81, 2296 (1998).

9:40am SS2-FrM5 STM Study of Metal Row Growth on Si(5 5 12), K.M. Saoud, I. Samanta, K.M. Jones, A.A. Baski, Virginia Commonwealth University

The high-index Si(5 5 12)-2x1 surface has recently gained interest as a template for overlayer growth, primarily because of its highly anisotropic row reconstruction. Our recent STM studies have shown that a noble metal such as Ag forms well-ordered overlayer rows on this surface.@footnote 1@ At coverages below 0.25 ML and moderate annealing temperatures (450°C). Ag forms monatomic rows with an inter-row spacing of ~5 nm. These Ag rows nucleate along the more reactive tetramer rows of the surface reconstruction, and are separated by isolated @pi@-chains remaining from the clean surface. At higher temperatures and coverages (>500°C, >0.25 ML), these @pi@-chains are removed and the Ag rows become wider with a strong 3x periodicity. We now have preliminary studies of more reactive metals such as Au and Ca on Si(5 5 12). At moderate annealing temperatures, both metals form overlayer rows that still preferentially nucleate along the tetramers. However, these rows are less well-ordered and are shorter at a given coverage, indicating the enhanced reactivity of these adsorbates. As expected, both metals change their growth behavior at higher annealing temperatures. The Au grows in 3x rows that become substantially more ordered and longer at a given coverage, whereas Ca rearranges the surface into a more complicated undulating row-like structure. In both cases, no remaining structures from the underlying reconstruction are visible. This work clearly demonstrates

the utility of the Si(5 5 12) surface as a template for the 1D growth of a variety of metals. @FootnoteText@ @footnote 1@ H.H. Song, K.M. Jones, and A.A. Baski, J. Vac. Sci. Technol. A Jul/Aug 1999.

10:00am SS2-FrM6 Chemisorption and Dissociation of O@sub 2@ on Pd(111) Studied by STM, M.K. Rose, Lawrence Berkeley National Laboratory; A. Borg, Norwegian University of Science and Technology, Norway; F. Besenbacher, University of Aarhus, Denmark; D.F. Ogletree, M. Salmeron, Lawrence Berkeley National Laboratory

A variable temperature STM study of chemisorption and dissociation of O@sub 2@ on Pd(111) is presented. Adsorption of O@sub 2@ on Pd(111) at 30K in the submonolayer range causes formation of a superoxo like and peroxo like molecular oxygen species. These two species image differently in STM, the superoxide appears to have weaker corrugation as compared to the peroxide. The superoxide is the more mobile species of the two at 30K. The peroxide display (2x2) structure in ordered areas, which grow in size upon annealing to 100K. Induced by the STM tip, individual O@sub 2@ molecules dissociate into pairs with a preferred separation of 2 lattice spacings, which is the equilibrium spacing in the (2x2)-O structure on Pd(111). Thermal O@sub 2@ dissociation is observed at about 150K. Our data show that the oxygen molecules evaporate from the peroxide island periphery onto the terrace before dissociation. Similar atomic oxygen pair spacings are observed in this case, but the distribution of oxygen on the surface is influenced by subsurface species present in the Pd(111).

10:20am SS2-FrM7 The Oxidation and Reduction of Pd(111), G. Zheng, E.I. Altman, Yale University

Palladium is a promising catalyst for oxidation reactions. Therefore, the oxidation of Pd(111) was characterized using STM, TPD, and LEED. Exposure of Pd(111) to O@sub 2@ resulted in a (2x2) structure, that saturated after exposure to 30 L. To increase the oxygen coverage, NO@sub 2@ was used. Initial exposure of Pd(111) to NO@sub 2@ also produced the (2x2) structure. Further exposure, however, resulted in additional diffraction spots, which persisted until the oxygen coverage reached approximately 1.0 ML. At oxygen coverages between 1.0 - 2.0 ML, a complicated LEED pattern was observed. This pattern could be explained as the superposition of two surface structures, one with a square surface lattice rotated 15° with respect to the Pd(111) substrate, the other with a rectangular surface lattice rotated 30° with respect to the Pd(111) substrate. In STM images, ad-islands and peninsulas were observed in this oxygen coverage regime. The rectangular structure was found on the original Pd(111) terraces, while the square structure was observed on the islands and peninsulas. A Moiré pattern due to lattice mismatch with underlying layers was also observed on the islands and peninsulas. The lattice constant for the square structure was 0.679 nm; and the two lattice constants for the rectangular structure were 0.394 nm and 0.638 nm, respectively, consistent with LEED observations. After further increasing the oxygen coverage, the complicated LEED patterns became faint. At the same time, a low temperature shoulder associated with bulk PdO developed in TPD traces. These results indicate that oxygen can exist in five different states on the Pd(111) surface. The reactivity of these states towards reduction is being characterized by monitoring the rate of disappearance of the different surface oxygen phases by recording STM movies during reduction by CO, H@sub 2@, and CH@sub 3@OH.

10:40am SS2-FrM8 Experimental and Theoretical STM Imaging of Molecules on Metal Surfaces@footnote 1@, D.N. Futaba, University of California, Davis; C.A. Pearson, University of Michigan; A. Loui, S. Chiang, D.M. Jaramillo, D.P. Land, University of California, Davis

We have imaged the surface structure of benzene coadsorbed with carbon monoxide (CO) on the Pd(111) surface in ultrahigh vacuum using a low temperature (90K) scanning tunneling microscope (STM). In conjunction with low-energy electron diffraction, three distinct overlayer structures have been observed to form as a function of various dosing conditions: two hexagonal structures when predosed with CO, (2@sr@3x2@sr@3)R30° and (3x3), and one rectangular structure. We are currently studying the mechanism by which one hexagonal layer transforms into the other as the benzene coverage increases. Our models of the structure give an overall molecular coverage of 1/3 for both hexagonal structures, suggesting molecular place exchange. We have performed laser induced thermal desorption and thermal desorption spectroscopy measurements to calibrate relative amounts of CO and benzene for the different structures. We also use a simple computational method, based on extended Hückel theory, to calculate STM images expected for the dehydrogenation of cyclohexene to benzene on Pd(111). Based on the proposed bonding geometry by Hunka et al.,@footnote 2@ we expect to see significant

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differences between the chemisorbed cyclohexene molecules and the resultant benzene molecules. Our calculated images of paraxylene and metaxylene on Rh(111) showed good agreement with existing experimental STM data by Cernota et al.@footnote 3@ Therefore, we expect good agreement between our calculations of orthoxylene on Pd(111) and our experiments in progress. @FootnoteText@ @footnote 1@ Funded by NSF (CHE-95-20366) and CLC Program of Univ. of California. @footnote 2@ D.E. Hunka, T. Picciotto, D.M. Jaramillo, D.P. Land, Surf. Sci., 421, L166 (1999). @footnote 3@ P.D. Cernota, H.A. Yoon, M. Salmeron, G.A. Somorjai, Surf. Sci., 415, 3511 (1998).

11:00am SS2-FrM9 In-Situ Soft X-ray Studies of Acetylene Oxidation on the Pt(111) Surface, *D.J. Burnett, A.M. Gabelnick,* University of Michigan; *D.A. Fischer,* National Institute of Standards and Technology; *J.L. Gland,* University of Michigan

In-situ studies of acetylene oxidation have been performed using Fluorescence Yield Soft X-ray methods for temperatures up to 600 K and pressures up to 0.01 torr. Absolute carbon coverages have been determined in steady-state and dynamic conditions on the Pt(111) surface over an extended pressure and temperature range using in-situ soft X-ray methods. Transient surface concentration measurements were used during these in-situ studies to provide direct measurement of surface reaction rates. Temperature-programmed oxidation of preadsorbed acetylene monolayers (TP-FYNES) on the Pt(111) surface was conducted in oxygen pressures up to 0.01 torr. Acetylene remains on the surface until skeletal oxidation occurs around 350 K, depending on the oxygen pressure. The onset temperature for skeletal oxidation decreased slightly with increasing oxygen pressures. Transient experiments with both acetylene and oxygen in the gas phase were performed over a wide range of pressures and temperatures. Further, detailed mechanistic studies were performed vielding a substantial amount of high quality kinetic rate data. These kinetic studies, coupled with the TP-FYNES results suggest a mechanism limited by C-H bond activation. In addition to the transient studies above, detailed spectroscopy was accomplished via in-situ, soft X-ray fluorescence yield methods to identify the dominant oxidation intermediates. Both acetylene and ethylene oxidation appear to involve the same surface intermediates since both processes are limited by the same rate-determining step. In both instances, oxidation intermediates have been identified and characterized using in-situ fluorescence yield methods.

11:20am SS2-FrM10 The Adsorption and Decomposition of Trimethylamine on Pt(111), D.-H. Kang, M. Trenary, University of Illinois, Chicago

Reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction spectroscopy (TPRS) have been used to study the adsorption and decomposition of trimethylamine on Pt(111). In a series of previous RAIRS studies, it was shown that several different molecules containing CN bonds all rearranged on Pt(111) to form the same stable intermediate, aminomethylidyne, CNH@sub 2@. Aminomethylidyne was formed following the initial adsorption of azomethane, methylamine. hydrogen cyanide, and from the hydrogenation of surface CN that was produced from the dissociative adsorption of cyanogen. Furthermore, the hydrogenation of undissociated cyanogen was found to form the H@sub 2@NCCNH@sub 2@ species, which contains the same aminocarbyne functionality as in aminomethylidyne. This suggests that aminocarbynes of the general formula CNRR', where R and R' can be H or an alkyl group, may be common intermediates in surface chemical reactions involving CNcontaining molecules. Dimethylaminocarbyne (CN(CH@sub 3@)@sub 2@) is a well-known ligand in the organometallic literature. It could be formed on the Pt(111) surface through the removal of the three H atoms from one of the methyl groups of trimethylamine. The RAIRS and TPRS data obtained so far support the formation of dimethylaminocarbyne as a stable intermediate species formed from the partial dehydrogenation of trimethylamine on Pt(111). A key spectroscopic feature of CN(CH@sub 3@)@sub 2@ is an intense RAIRS band at 1471 cm@super -1@, which is characteristic of the CN stretch in aminocarbynes.

11:40am SS2-FrM11 Investigation of the Adsorption and Reactions of Thiophene on Sulfided Cu, Mo and Rh Catalysts, *M.E. Bussell*, *P. Mills*, *D.C. Phillips*, *B.P. Woodruff*, *R. Main*, Western Washington University

Infrared (IR) spectroscopy and temperature programmed desorption (TPD) have been used to investigate the adsorption and reactions of thiophene on alumina-supported sulfided Cu, Mo and Rh catalysts over wide ranges of temperature (130-700 K) and pressure (10 @super-9@ - 10 @super3@ Torr). Following adsorption at 130 K, thiophene adsorbs on sulfided Mo and Rh catalysts in an @eta@@super 1@(S) geometry; it has not been

possible to determine the adsorption geometry of thiophene on Cu sites of the sulfided Cu catalyst due to low coverage. The coverage of thiophene on sites in the supported metal sulfide particles is observed to increase in the order Cu < Mo < Rh, in agreement with CO chemisorption measurements. Little or no reactivity is observed when the different catalysts are heated in thiophene vapor alone at temperatures up to 700 K. In thiophene/H@sub 2@ mixtures, hydrogenated species are observed to form on sulfided Rh catalysts by 350 K, and by 550 K on sulfided Mo catalysts. Following evacuation to UHV pressures, TPD shows the major products to be butadiene, butenes and butane. The results of these experiments are in good agreement with flow reactor studies of thiophene hydrodesulfurization over these same catalysts.

Surface Science Division Room 604 - Session SS3+EM-FrM

Reactions on Semiconductors

Moderator: S.F. Bent, Stanford University

8:20am SS3+EM-FrM1 A Comparative Study of [2+2] Cycloaddition Reactions of Organic Alkenes on Group IV Semiconductor Surfaces, R.J. Hamers, J.S. Hovis, S.C. Coulter, University of Wisconsin, Madison; C.M. Greenlief, University of Missouri, Columbia

Organic alkenes such as cyclopentene can bond to Si(001) and Ge(001) surfaces to produce monolayer organic films that are chemically homogeneous and structurally ordered. The bonding of these molecules to the dimerized Si, Ge, and C (diamond) surfaces is analogous to a class of ring-forming reactions known in organic chemistry as [2+2] cycloaddition reactions. While the bulk reactions involve the reaction of two alkene groups to form a four-member ring, the surface reactions involves two electrons from the organic alkene and two electrons from the ? orbital of the surface Si=Si, Ge=Ge, or C=C dimers. Solution-phase reactions of organic compounds via [2+2] processes are forbidden by orbital symmetry considerations and are therefore extremely slow. In order to better understand the nature of the analogous surface reactions, we have used infrared spectroscopy, scanning tunneling microscopy, X-ray photoelectron spectroscopy, and quantum chemistry methods to investigate the adsorption of cyclopentene and other simple alkenes on Si and Ge(001) semiconductor surfaces. Our results show that reactions of simple alkenes on Si(001) and Ge(001) surfaces are facile, producing ordered monolayers. Ab initio calculations for Si, Ge, and C clusters indicate that the reactions on Si and Ge surfaces are facile because of the ability of these surface dimers to tilt, facilitating a low-energy, low-symmetry pathway to adsorption on these surfaces. This talk will summarize our recent experimental and computational studies aimed at understanding the nature of cycloaddition reactions of organic alkenes on Group IV semiconductor surfaces. @FootnoteText@ This work was supported in part by the U.S. Office of Naval Research and the National Science Foundation.

8:40am SS3+EM-FrM2 Novel Organic Monolayer Films on Si(100): Theoretical Studies of Cylocaddition Chemistry, J.A. Barriocanal, D.J. Doren, University of Delaware

A class of cycloaddition reactions will be described that can be used to attach monolayer organic films to Si(100). These reactions, known as 1,3-dipolar additions, can be performed with organic molecules containing a wide variety of organic functional groups. Examples include nitro compounds (R-NOO), azides (R-NNN) and their sulfur and phosporous analogs. Density functional theory calculations for prototypical cases show that the molecules chemisorb with negligible activation barrier. As in traditional organic synthesis, having a variety of functional groups that react in a similar way allows some control over the final product by proper choice of the reagent. A complication, in many cases, is that the product of the initial reaction is not the thermodynamic product, and rearrangements, based on density functional theory calculations, will be discussed. Potential applications and comparisons to available experimental work will also be described.

9:00am SS3+EM-FrM3 Formation of Si/Thiophene Hybrid System in UHV by a Hetero Diels-Alder Cycloaddition Surface Synthetic Strategy, Y. Cao, G.Q. Xu, National University of Singapore, Singapore

The formation of organic monolayer on semiconductor surfaces has great device applications in biosensors, field effect transistors as templates for the epitaxial layer growth on semiconductors. In this work, the covalent coupling of thiophene monolayer on a semiconductor surface has been

attained by a facile way at room temperature in UHV. We demonstrate here a hetero Diels-Alder cycloaddition reaction strategy for chemical modification of a well-defined Si(111)-7x7 surface with thiophene molecules. The concerted [4+2] cycloaddition reaction of thiophene with adjacent rest atom-adatom pair, resulting the formation of a 2,5dihydrothiophenelike cycloadduct on Si(111)-7x7, has been clearly demonstrated by combined STM and HREELS spectroscopic studies. Documented as the least reactive diene in Deils-Alder cycloaddition reaction due to its high aromaticity, however, the cycloaddition reaction of thiophene on Si(111)-7x7 is facile even under UHV conditions. In addition, the reactivity of thiophene toward the rest atom-adatom pairs on Si(111)-7x7 can be theoretically explained by correlation of the the HOMO and LUMO energy of thiophene molecule and the surface band level for the empty and filled states on Si(111)-7x7. The feasibility of such procedure provides a better understanding of the chemical reactions proceed through semiconductor surfaces, more significantly, offers a potential new methodology for functionalization the semiconductor surfaces with desired control.

9:20am SS3+EM-FrM4 Kinetics of Abstraction of Monohydride and Dihydride D from Si(100) Surfaces, A. Dinger, C. Lutterloh, J. Küppers, Universität Bayreuth, Germany

The interaction of H(D) atoms with Si(100) surfaces and the abstraction of D adsorbed in the monohydride and dihydride phases on Si(100) by H was studied with thermal desorption spectroscopy and direct product rate measurements. H/D atoms were produced in W tube sources heated at 2000 K. H/D atom exposure to clean Si(100) surfaces at 380 K and 640 K lead to the formation of dihydride and monohydride phases with the characteristic desorption peaks at 690 K and 810 K. In addition, after application of high atom fluences, H@sub 2@ (D@sub 2@) peaks were seen at 910 K which are interpreted as a consequence of etching. Etch products were monitored in desorption and during reaction. H atom exposure to monohydride D covered surfaces at 640 K revealed HD and D@sub 2@ as gaseous products. At a saturated monohydride surface about 6% of the adsorbed D occurred in D@sub 2@ products. The kinetics of HD formation is not in accordance with the operation of an Eley-Rideal mechanism. This is most clearly apparent at small D coverages since then the HD rate is constant at decreasing D coverage. Abstraction of D from dihydride phases at 380 K exhibit an Eley-Rideal phenomenology in the HD rates, however a small contribution of D@sub 2@ products (<1%) illustrate that another mechanism also acts in abstraction of D from the dihydride. The results can be explained by the operation of hot-atom mechanisms, in which the probabilities of hot-atom sticking and reaction determine the kinetics of gaseous products formation.

9:40am SS3+EM-FrM5 The Adsorption and Thermal Decomposition of Dimethylamine Adsorbed on Si(100), S.M. Casey, C.P.A. Mulcahy, A.J. Dennis, University of Nevada, Reno

Dimethylamine (DMA) adsorption on the Si(100)-(2x1) surface has been studied using Auger electron spectroscopy (AES), low-energy electron diffraction, and temperature-programmed reaction spectroscopy (TPRS). It is shown that at room temperature DMA chemisorbs on this surface with a saturation coverage of about 0.5 monolayers. These experiments also show evidence for multilayer formation in this adsorbate system. For doses above the saturation dose level, intact DMA molecules begin to adsorb on top of the surface-bound adsorbate layer. TPRS data show that the decomposition of DMA adsorbed on the Si(100) surface proceeds via two different mechanisms in the monolayer vs. multilayer coverage regimes. The adsorbates directly bound to the surface are shown to decompose via reactions that form gaseous hydrogen and hydrogen cyanide products, while the intact multilayer DMA species decompose to form hydrogen and imine dehydrogenation products. Evidence for formation of both the cyclic ethylenimine species and the straight-chained N-methylmethanimine species in this multilayer regime is presented. Kinetic analysis of the TPRS data shows that the heats of desorption for the two products of the surface-bound adsorbate decomposition (hydrogen and hydrogen cyanide) are much higher than the heats of desorption for the products of multilayer decomposition. AES results show that repeated decomposition of DMA on Si(100) leads to the slow deposition of carbon- and nitrogen-based films, although the thermal deposition efficiency is relatively low and the overall stoichiometry of the resulting films could not be clearly established.

10:00am SS3+EM-FrM6 Reactivity of Diamond (100) towards Cycloaddition Chemistry, *G.T. Wang, S.F. Bent,* Stanford University; *J.S. Hovis, R.J. Hamers,* University of Wisconsin, Madison; *J.N. Russell, Jr., J.E. Butler,* Naval Research Laboratory; *M.P. D'Evelyn,* General Electric

Diamond has a number of extreme material properties that make it an ideal candidate for a wide range of applications, including electronic devices, electron emitters, multispectral windows, and heat sinks. Similar to Si(100) and Ge(100), the diamond (100) surface undergoes a 2x1 reconstruction in which pairs of atoms are bonded into dimers via a strong sigma bond and a partial pi bond. Recent studies on 2x1 reconstructed Si(100) and Ge(100) have shown that the pi bond of the surface dimers can react with unsaturated hydrocarbons via [2+2] and [4+2] (Diels-Alder) cycloaddition reactions, forming covalently attached ring structures. In this study we investigate the viability of the diamond (100) surface to undergo cycloaddition reactions with cyclopentene and 1,3-butadiene using multiple internal reflection infrared spectroscopy and ab initio quantum chemistry calculations. While cyclopentene can react with the surface only via a [2+2] cycloaddition (which is formally forbidden for concerted reactions by symmetry considerations), 1,3-butadiene can potentially react via a [2+2] or [4+2] cycloaddition due to its conjugated double bond. It was found that both cyclopentene and 1,3-butadiene reacted with the diamond (100) surface at room temperature, although significantly larger exposures of cyclopentene were required. The greater reactivity of 1,3-butadiene versus cyclopentene may be attributable to 1,3-butadiene bonding via a lower-barrier [4+2] pathway not available to cyclopentene. Comparison of cycloaddition reactivity on diamond (100) versus Si(100) and Ge(100) provides insight into the mechanism of these reactions on semiconductor surfaces. These results also demonstrate the viability of organic synthetic routes for modifying the diamond surface.

10:20am SS3+EM-FrM7 Surface Infrared Spectroscopy of CH@sub x@ Adsorbates during GaAs OMVPE, J.R. Creighton, K.C. Baucom, Sandia National Laboratories

We have used surface infrared spectroscopy (SIRS) to identify the adsorbates present on GaAs(001) during organometallic vapor phase epitaxy (OMVPE) and atomic layer epitaxy (ALE). The key advantage of SIRS, as compared to reflectance-difference spectroscopy (RDS) and related UVvis reflectance techniques, is that the interpretation of infrared spectra is much more straightforward and less ambiguous. One example of the rich spectral information derived with SIRS is seen during the trimethylgallium (TMGa) ALE cycle. During the initial stages of TMGa exposure, methyl groups (CH@sub 3@) bonded to both gallium and arsenic can be detected and differentiated. With time, the methyl-arsenic species disappear and methylene (CH@sub 2@) species (the precursors to carbon incorporation) begin to cover the surface. During low-temperature OMVPE we also detect a significant methyl group coverage, and these results will be compared to the other in-situ optical measurements, e.g. RDS, at similar growth conditions. (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.).

10:40am SS3+EM-FrM8 Ab initio Study of Adsorption and Decomposition of NH@sub 3@ on Si(100)-(2x1), Y. Widjaja, M. Mysinger, C. Musgrave, Stanford University

Deposition of silicon nitride thin films has become a key technology in the microelectronics industry. In silicon nitride deposition, NH@sub 3@ is typically used as the nitriding agent because of its high sticking coefficient and reactivity. In this study, we investigate the atomistic mechanisms for NH@sub 3@ adsorption and initial decomposition on the (2x1) reconstructed Si(100) surface using B3LYP density functional theory (DFT) and by utilizing the cluster model. We present a detailed investigation of the effects of cluster size on the reaction energetics. We find that the Si@sub 9@H@sub 12@ (1-dimer) cluster model does not describe the NH@sub 3@(a) adsorption state well due to the delocalized nature of the electron transfer in forming the NH@sub 3@(a) dative bond. We find that the Si@sub 21@H@sub 20@ (3-dimer) cluster is necessary to fully capture these non-local effects. The 3-dimer model is able to satisfactorily reproduce the results of larger cluster models. We then use the 3-dimer cluster model to study the adsorption and decomposition reactions of NH@sub 3@ on the Si(100)-(2x1) surface. Ammonia is found to adsorb on the down atom of buckled silicon dimers with no activation barrier. This adsorption is exothermic with an adsorption energy of 29 kcal/mol. This adsorption is then followed by dissociation to form NH@sub 2@(a) + H(a) with a low activation energy. Our calculated recombination desorption energy of 51 kcal/mol is found to be in good agreement with the TPD experimental result of 47 kcal/mol. In addition, we also calculate the

vibrational spectra of the dissociated species. We find our results to be in good agreement with the experimental HREELS spectra.

11:00am SS3+EM-FrM9 Reactions of Substituted Aromatic Hydrocarbons with the Si(001) Crystal Surface, S.C. Coulter, J.S. Hovis, M.D. Ellison, R.J. Hamers, University of Wisconsin, Madison

The surface chemistry of small aromatic molecular systems chemisorbed on the single domain Si(001)-(2x1) face has been investigated using Infrared and X-ray Photoelectron Spectroscopy. Both the [2+2] and the [4+2] Diels-Alder cycloaddition processes are possible. Substitued aromatic hydrocarbons, including toluene, benzonitrile and ortho-, meta- and paraxylene, have been studied to provide clues as to their possible steering effects into a favored bonding geometry. Our data indicates that these reactions are complex and, in some cases, involve multiple bonding configurations. Detailed analysis of the infrared spectra and comparisons with known compounds have been used to help identify the surface products and to provide new understanding of substituent effects during molecular bonding at silicon surfaces.

11:20am SS3+EM-FrM10 Thermal Hydrogen Reactions with Boron-doped Si(100) Surface, B. Gong, The University of Texas at Austin; S.K. Jo, Kyung Won University, South Korea; J.G. Ekerdt, The University of Texas at Austin The reactions of hydrogen with boron-doped Si(100) have been studied with temperature programmed desorption, high resolution electron energy loss spectroscopy and low energy electron diffraction. Recent studies by our group have illustrated that in the boron concentration range from 0.002 to 0.1 monolayer (ML), SiH@sub 2@ (@beta@@sub 2@) formation is greatly suppressed at 400 K. This inability of the H-passivated Si(100) to undergo the 3x1 reconstruction is associated with the subsurface boroninduced bond strain and silicon dimer vacancy defects. At higher boron coverages (0.2-0.5 ML), H@sub 2@ desorption data show a new, broad desorption peak (@beta@@sub 3@) at ~ 400 K in addition to SiH (@beta@@sub 1@) and SiH@sub 2@ states. The @beta@@sub 1@ and @beta@@sub 2@ desorption energies are unchanged by boron. The new H@sub 2@ desorption peak is related to trihydride formation (SiH@sub 3@) on silicon sites that are associated with second layer boron atoms. Both SiH@sub 3@ and @beta@@sub 3@-H@sub 2@ desorption increase with increasing boron coverage. We propose that the enhanced silicon growth rate found during in situ boron doping is related to the new H@sub 2@ desorption channel that has its origin with SiH@sub 3@ formation. Extensive H-induced surface etching is also seen on intrinsic Si(100) surfaces at 180 K. SiH@sub 4@ desorption at ~600 K has been used as an indicator of H-induced etching, where SiH@sub 3@ forms as a result of H atoms breaking Si-Si back bonds; SiH@sub 2@ formation precedes the formation of the SiH@sub 3@ etch product. This surface etching is sharply reduced on lightly boron-doped Si(100) surfaces, which is in good agreement with the result that low coverage boron prevents SiH@sub 2@ formation on Si(100).

11:40am SS3+EM-FrM11 Impact of Surface Structure on the Arsine Adsorption Kinetics on GaAs and InP (001), *Q. Fu*, *L. Li*, *C. Li*, *D. Law*, *R.F. Hicks*, University of California, Los Angeles

Arsine adsorption on the gallium-rich GaAs (001) (4x2) reconstruction and on the indium-rich InP (001) (2x4) reconstruction has been studied by internal-reflection infrared spectroscopy and scanning tunneling microscopy. It was found that AsH@sub 3@ adsorption on the (4x2) follows an autocatalytic mechanism, with the rate proportional to the fraction of occupied and vacant sites. By contrast, AsH@sub 3@ adsorption on the (2x4) follows a Langmuir adsorption mechanism, with the rate depending only on the fraction of vacant sites. We attribute these differences in the reaction kinetics to the impact of the semiconductor surface structure on the adsorption mechanism. The GaAs (4x2) reconstruction is terminated with 3 gallium dimers per unit cell, while the InP (2x4) contains one In-P heterodimer, and 4 In dimers per unit cell. An arsine molecule dissociatively adsorbs onto the group III dimers and transfers hydrogen to a group V dimer site. On the GaAs (4x2), only a few of these latter sites are present, and more are created by adsorption, so the reaction is autocatalytic. Conversely, on the InP (2x4), the latter sites are readily available, and Langmuir adsorption occurs. The decomposition mechanisms of arsine on these surfaces will be discussed in detail at the meeting.

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