

Surface Science

Room 326 - Session SS1-MoM

Gas-Surface Dynamics

Moderator: K.W. Kolasinski, Queen Mary, University of London, UK

8:20am SS1-MoM1 Angular Distribution of Cl Atom Products from Direct and Precursor-Mediated Hyperthermal Abstractive Chemisorption of Cl₂/Al(111), G.C. Poon, A.C. Kummel, University of California, San Diego

Resonantly Enhanced Multiphoton Ionization (REMPI) and Time-of-Flight Mass Spectroscopy (TOF-MS) have been used to demonstrate that the reaction of Cl@sub 2@ on the low work function Al(111) surface proceeds via a prompt vertical electron harpooning process. Sticking measurements were performed showing that Cl@sub 2@ adsorbs via a direct chemisorption process at either high incident translational energy or high surface temperature. However, at glancing incident angles and low surface temperatures (100 K), a precursor-mediated channel predominates. REMPI studies show that fast abstracted Cl was produced via both channels: direct, remotely-dissociated incident Cl@sub 2@, and indirect, physisorption-mediated Cl@sub 2@. An abstraction reaction results in one Cl atom bound to the surface and one Cl atom ejected back into the gas phase. For incident Cl@sub 2@ of 0.11 and 0.27 eV at 40° incident angle and 100 K surface temperature, only the precursor-mediated channel was observed with atomic Cl abstracted product energies of 0.09 to 0.14 eV. At high surface temperature, 500 K, all incident translational energies and angles yield only the direct channel, with abstracted product energies of 0.19 to 0.26 eV. Currently, angular distributions of the ejected Cl atom products are being determined for both direct and precursor-mediated channels. End-on impinging Cl@sub 2@ on the Al surface is expected to promote harpooning and subsequent abstraction products should be directed along the surface normal. Side-on physisorbed Cl@sub 2@ precursor would yield more broadly distributed abstraction products.

8:40am SS1-MoM2 Photoinduced Electron Transfer Chemistry and Dissociation of Adsorbed CO@sub 2@: Harnessing Å-Scale Molecular Acceleration Towards a Surface, R. Zehr, University of Virginia; T. Wagner, University of Essen, Germany; I. Samanta, I. Harrison, University of Virginia

Activated dissociation of molecules on a metal surface is essential to many catalytic syntheses (e.g. N@sub 2@ dissociation in NH@sub 3@ synthesis) and a firm scientific understanding of this process is important to advancing the field of heterogeneous catalysis. In commercial catalysis, activation energy barriers are invariably surmounted by random thermal energy and not through a more directed use of the energy in light, despite the ubiquitous example of photosynthesis in nature. Potential advantages of using light to overcome a rate-limiting dissociative adsorption step in catalysis include better selectivity towards a chosen reaction pathway, the ability to work at much reduced reaction temperatures, and the opportunity to exploit solar energy. Here, we present evidence that photoinduced electron transfer from a low temperature Pt(111) surface to physically adsorbed CO@sub 2@ leads to rapid acceleration of the newly formed negative ion towards the surface, neutralization, and a high energy collision with the surface that efficiently dissociates (ca. 30%) and desorbs CO@sub 2@. Importantly, this photochemical activation mechanism constitutes an Å-scale molecular accelerator that may be applicable to other hard-to-activate adsorbates. The ability to photochemically induce an adsorbate/surface collision at chemically significant energies (up to ~2.5 eV), after an acceleration over a distance of no more than a few Å from an initial configuration prescribed by the physisorption binding potential, provides novel opportunities to drive energetic dissociation and desorption processes at low temperatures and to examine the reaction dynamics of catalysis.

9:00am SS1-MoM3 Adsorption Dynamics and Desorption Kinetics of Argon and Methane on MgO(100), B.D. Kay, Z. Dohnalek, G.K. Schenter, L.R. Corrales, R.S. Smith, Pacific Northwest National Laboratory INVITED

The adsorption dynamics and desorption kinetics of Ar and CH₄ on MgO(100) are studied using a combination of molecular beam scattering and temperature programmed desorption (TPD). Both Ar and CH₄ exhibit an initial trapping probability that decreases dramatically with increasing kinetic energy and is independent of incident angle indicating adsorption is a barrier-less process obeying total energy scaling. The trapping probability for both adsorbates increases roughly linearly with the increasing coverage in the first layer. Such behavior can be described by a simple model involving constant but different trapping probabilities on clean and

adsorbate covered MgO(100) with fast intra-layer diffusion leading to preferential filling of the bare MgO(100). An alogous behavior is observed for trapping on the second and third layers and indicates layer-by-layer growth of the adsorbate overlayer with layer dependent trapping probabilities. Analysis of the TPD spectra yields desorption energies of 8.5 and 13 kJ/mol for Ar and CH₄, respectively in agreement with previous measurements and theoretical calculations. The total energy scaling observed for the initial trapping of Ar and CH₄ on MgO(100) is in sharp contrast with the normal energy scaling previously observed for these species on Pt(111). These differences indicate that the adsorbate-substrate interaction is laterally smooth on Pt(111) and highly-corrugated on MgO(100). Theoretical scattering calculations based on the classical trajectory method are used to complement and interpret the experimental data. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

9:40am SS1-MoM5 Adsorption of CO on Rutile (1x1)-TiO@sub 2@(110): A Molecular Beam Study, M. Kunač, Ruhr-University in Bochum, Germany; U. Burghaus, North Dakota State University

Presented are initial, S@sub 0@, and coverage dependent, S(Θ@), adsorption probability measurements, respectively, of CO on the rutile (1x1)-TiO@sub 2@(110) surface obtained along both high symmetry azimuth directions (i.e. along the [1-10] and [100] azimuth) and parametric in the impact energy, E@sub i@, the angle of incidence, and the surface temperature, T@sub s@. Whereas along the [001] azimuth approx. a Kisliuk shape of S(Θ@) has been observed, for glancing angle of incidence and E@sub i@ @>= 0.52 eV a turnover from the Kisliuk shape of S(Θ@) to an auto-catalytic adsorption (increase in S with Θ@) could be detected along the [1-10] direction. Along both azimuth directions S@sub 0@ obeys for E@sub i@ @>= 0.52 eV normal energy scaling and below that impact energy total energy scaling. The effect of an intrinsic precursor state is tentatively concluded. A decrease in the heat of adsorption with coverage indicates repulsive lateral interactions of the CO. The results will be discussed in comparison with Monte Carlo Simulations.

10:00am SS1-MoM6 Ultra-Low Coverage Spontaneous Etching and Hyperthermal Desorption of Aluminum Chlorides from Cl@sub 2@ on Al(111), T.G. Grassman, G.C. Poon, A.C. Kummel, University of California, San Diego

Non-resonant multiphoton ionization (MPI) and time-of-flight mass spectrometry (TOF-MS) have been used to monitor the desorption of aluminum chloride (Al@sub x@Cl@sub y@) etch products from the Al(111) surface at 100 K and 500 K during low-coverage (<5% monolayer) monoenergetic Cl@sub 2@ dosing. Three pulsed molecular beams of Cl@sub 2@ were prepared with translational energies ranging from 0.11 eV to 0.65 eV. The desorption products showed predominantly hyperthermal exit velocities under all dosing conditions, regardless of etch product species assignment (AlCl, AlCl@sub 3@, or Al@sub 2@Cl@sub 6@). For example, with an incident beam of Cl@sub 2@ seeded in neon (0.27 eV) at normal incidence dosing and normal detection, the etch product was found to have a most probable velocity of 532 ± 29 m/s at an Al(111) surface temperature of 100 K. This corresponds to nearly 7 times the expected thermal kinetic energy even if one assumes that the etch product is AlCl, and 30 times expected if one considers the more likely etch product, Al@sub 2@Cl@sub 6@. Sticking probability and transient etch rate profile measurements show etching even at Cl@sub 2@ coverages of less than 5% monolayer at all surface temperatures. High-temperature (500 K) etch rate profiles reach steady-state etching at equally small doses. These experimental results seem to indicate a combination of fast-time-scale surface agglomeration of the adsorbed chlorine to form aluminum chlorides, and the presence of activated aluminum chloride chemisorption states having potential energies above the vacuum level. Density functional theory calculations yield results that are consistent with both our experimental findings and mechanistic descriptions.

10:20am SS1-MoM7 Probing the Vibrational State-Resolved Gas-Surface Dynamics of Polyatomic Molecules Without the Laser, D. Killelea, D. DelSesto, R. Smith, A.L. Utz, Tufts University

We describe an experimental approach that yields vibrational-state-resolved reaction probabilities for polyatomic molecules without the need for selective laser excitation of the target state. The method relies on a detailed knowledge of the vibrational structure of the molecule under study and its vibrational energy transfer dynamics in a supersonic expansion. In the case of methane, non-equilibrium cooling of vibrational states within polyads leads to the population of a single vibrationally

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excited state under easily obtained expansion conditions, even though several excited vibrational states would contain significant population under the nominal thermal conditions of the nozzle source. We apply this approach to extract state-resolved reaction probabilities for methane in its ground vibrational state ($v=0$) and $n=4$ vibrational fundamental incident on clean, low-index nickel surfaces. State-resolved reaction probabilities obtained in this way are free from the vibrational-state averaging that clouds interpretation of beam-surface reactivity measurements and permit a more direct test of theoretical models of gas-surface reactivity.

10:40am SS1-MoM8 Kinetics of H Atom Adsorption on Si(100) at 325 - 600 K, A. Kutana, B. Makarenko, I.L. Bolotin, J.W. Rabalais, University of Houston

The kinetics of atomic hydrogen isothermal adsorption on a Si(100) surface has been studied by the time-of-flight scattering and recoiling spectrometry (TOF-SARS) technique. A continuous decrease in saturation coverage with temperature under constant atomic hydrogen exposure has been observed for temperatures in the range 325 - 650 K. It is suggested that the obtained coverages are a result of a kinetic equilibrium between competing adsorption, abstraction, and migration reactions occurring at the surface. This approach explains how the coverages corresponding to the well-known phases of hydrogen on Si(100) at different temperatures are obtained. Introducing two types of adsorption sites into the model for the Si sticking probability, the coverage decrease is shown to be due to depletion of the surface concentration of atoms in the secondary adsorption sites. For lower temperatures, there is a significant concentration of hydrogen atoms in the precursor states that saturate the monohydride dangling bonds after hydrogen source shut-off and discontinuation of Eley-Rideal abstraction. The time for this transition is on the order of $\frac{1}{k_{\text{sat}}}$, where k_{sat} is the saturation coverage for a given temperature. Increasing the temperature leads to an increase in the migration rate from secondary to primary sites, where more efficient Eley-Rideal abstraction causes a decrease in total concentration. The migration constant k_{m} obeys the Arrhenius equation with a low activation energy of 0.29 eV. It follows from the model, and has been proven experimentally, that the saturation coverage depends not only on temperature, but also on the incoming hydrogen flux, i.e. the ambient H_2 pressure at which adsorption is performed.

11:00am SS1-MoM9 Charge Exchange between Metal Ions and Surfaces, X. Chen, J. Doan, University of California, Riverside; Z. Sroubek, Czech Academy of Science, Czech Republic; J.A. Yarmo, University of California, Riverside

Ion-surface charge exchange is important in surface analytical methods that employ ion beams, such as ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS) and electron stimulated desorption (ESD). In earlier work, we showed that the probability for neutralization of an alkali ion scattered from a metal surface is determined by the local electrostatic potential (LEP) a few Å's above the scattering site. We are now extending this work to investigate homogeneous charge exchange between metal ions and identical metal surfaces. In the first set of experiments, Ar^+ and Kr^+ ions are used to induce direct recoil of fast Al from Al(100). The neutral fraction of the recoils is then measured with time-of-flight as a function of emission angle and energy. From this data, and with the aid of Monte-Carlo simulations using scattering and recoiling imaging code (SARIC),¹ we can obtain information on homogeneous charge exchange processes. Adsorbates, such as Cs and O, will be used to modify the surface work function so that measured changes in neutralization can be used to further reveal the charge transfer process. In the next set of experiments, we are producing metal ion beams for scattering. Al ions are being produced in an $Al(CH_3)_3$ plasma, and Ga ions from a liquid metal ion source. Such pure metal ion beams will allow for simple scattering experiments in which a clear correlation between can be made neutralization and trajectory.¹ V. Bykov, C. Kim, M. M. Sung, K. J. Boyd, S. S. Todorov and J. W. Rabalais, Nucl. Instrum. Meth. B 114 (1996) 371.

Surface Science

Room 327 - Session SS2-MoM

Catalysis I: Adsorption and Reactions of Small Molecules at Surfaces

Moderator: J.E. Reutt-Robey, University of Maryland

8:20am SS2-MoM1 Atomic Level Explanation of the Compensation Effect in Heterogeneous Catalysis, T. Bligaard, K. Honkala, A. Logadottir, Center for Atomic-scale Materials Physics, Denmark; J.K. Norskov, Technical University of Denmark, Denmark; S. Dahl, C.J.H. Jacobsen, Haldor Topsoe A/S, Denmark

For a class of heterogeneously catalyzed reactions, we explain the compensation effect in terms of a switching of kinetic regimes leading to a concomitant change in the apparent activation energy and in the prefactor for the overall rate of the reaction. We first use the ammonia synthesis to illustrate the effect. Both experiments and a detailed kinetic model show a compensation effect. Secondly, we use density functional theory calculations to show that the compensation effect is not only due to changes in the activation barrier and prefactor of the rate-determining step, N_2 dissociation. We compare N_2 dissociation on Ru and Pd. The barrier for dissociation differs by more than 2 eV (200 kJ/mol), but calculations of the prefactor based on harmonic transition state theory shows a difference of less than 10%. In order to analyze the origin of the compensation effect we construct a general kinetic model for a surface catalyzed reaction, and show that the effect can be related to a shift in kinetic regime, from one dominated by the rate of activation of the reactants to a regime where the stability of the reaction products on the surface becomes increasingly important. Finally, we present arguments, why this should be a general effect for a broad class of reactions. We will show that the compensation effect in the rate is intimately linked to the underlying linear relationships between activation energy and stability of intermediates, which have been found to hold for a number of surface reactions.

9:00am SS2-MoM3 Formation of Surface Cyanide through Carbon-Nitrogen Coupling Reactions on Pt(111), E. Herceg, M. Trenary, University of Illinois at Chicago

The C-N coupling reaction to form CN on the Pt(111) surface has been studied with temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). This reaction underlies the industrially important synthesis of HCN from NH_3 and CH_4 over platinum catalysts. In the absence of oxygen, the catalytic reaction is endothermic and occurs at 1200 °C. In previous kinetic studies using model reactors, it has been inferred that the C-N coupling reaction occurs through surface C and N atoms.¹ The surface CN formed is then hydrogenated to HCN. However, direct support for this mechanism has been lacking. Alternatively, surface CH_x and NH_y with $x = 1, 2, \text{ or } 3$ and $y = 1 \text{ or } 2$, may react to form a CNH_z species with $z \geq 2$, which is then dehydrogenated to HCN. Therefore characterization of the possible CH_x and NH_y surface species is important. Although NH_3 and CH_4 do not react on Pt(111) under ultrahigh vacuum conditions, the present study shows that the C-N coupling reaction is readily achieved in UHV in various ways, such as from coadsorbed CH_3 , produced from thermal decomposition of CH_3I , and NH , produced from electron beam induced dissociation of adsorbed NH_3 . The conversion of adsorbed NH_3 to NH_2 , NH , and N was monitored with RAIRS and TPD. The surface N atoms readily react with hydrogen to reform surface NH , which is identified by its intense NH stretch peak at 3317 cm^{-1} .¹ The presence of surface CN is detected through its reaction with hydrogen to form a surface CNH_2 (aminocarbyne) species, which has characteristic RAIRS peaks, as well as by HCN desorption. From the fact that C-N bond formation occurs at a temperature above where all CH_x and NH_y species have dehydrogenated indicates that the reacting species are in fact surface C and N atoms.¹ D. Hassenberg and L. D. Schmidt, J. Catal. 97, 156 (1986).

9:20am SS2-MoM4 The Effect of Atomic Steps on the Adsorption and Desorption of CO on Ru(109), G.A. Morgan, Jr., T. Zubkov, J.T. Yates, Jr., University of Pittsburgh; O. Köhlert, M. Lisowski, R. Schilling, D. Fick, H.J. Jänsch, Philipps University, Germany

Ru is well known as an effective catalyst for the hydrogenation of CO to produce hydrocarbons. CO hydrogenation likely occurs after CO dissociation on Ru. We have shown that the dissociation of CO occurs

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preferentially on the atomic step sites of the Ru(109) surface, which exposes 9-atom wide terraces of (001) orientation, separated by double-atom height steps. This was demonstrated by isotopic mixing studies where @super 12@C@super 16@O and @super 13@C@super 18@O were shown to extensively mix above 480 K, a temperature where the C-O bond has just disappeared in the reflection IR spectrum. The isotopically mixed CO desorbs in a distinct recombination process at about 500 K, a kinetic process which is absent on the planar Ru(001) surface. Carbon atoms deposited from the decomposition of ethylene can poison the step sites, which are responsible for CO dissociation. Thus the well known activity of Ru as a Fischer-Tropsch catalyst may be due to the special activity of defect sites with low Ru-Ru coordination numbers compared to Ru(001) sites.@footnote *@ @FootnoteText@ @footnote *@ Work Supported by DOE-BES.

9:40am **SS2-MoM5 Medard W. Welch Award Address: Get Real ! --- The Importance of Complexity for Understanding the Function of Surfaces, M. Scheffler**¹, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

INVITED

Knowledge of the surface composition and atomic geometry is a prerequisite for understanding the physical and chemical properties of (most) modern materials as for example hardness, electronic and magnetic properties, and chemical activity. In this talk I will emphasize that to understand the function of surfaces it is important to "get real !", i.e. to go out of the vacuum and to take into account the influence of environmental gas and liquid phases at finite (possibly high) temperature and pressure.@footnote 1@ We employ ab initio, atomistic thermodynamics to construct a phase diagram of surface structures in the (T, p)-space from ultra-high vacuum to technically-relevant pressures and temperatures.@footnote 2-4@ The value of such phase diagrams as well as the importance of the reaction kinetics that may be crucial e.g. close to phase boundaries will be emphasized. -- We also calculated reaction pathways and energy barriers and use this information for a long time-scale modeling of surface diffusion, island nucleation, crystal growth, and oxidation catalysis. Examples in this talk are: semiconductor quantum-dot formation,@footnote 5@ the function of transition metals and transition-metal oxides, and heterogeneous catalysis.@footnote 6@ @FootnoteText@ @footnote 1@ C. Stampfl, et al., *Catalysis and Corrosion: The Theoretical Surface-Science Context*, Surf. Sci. 500, 368 (2002). @footnote 2@ X.-G. Wang, et al., *Phys. Rev. Lett.* 81, 1038 (1998). @footnote 3@ K. Reuter and M. Scheffler, *Phys. Rev. Lett.* 90, 046193 (2003); and *Phys. Rev. B*, in print. @footnote 4@ W. X. Li, C. Stampfl, and M. Scheffler, *Phys. Rev. Lett.*, in print (June 2003); and *Phys. Rev. B*, in print. @footnote 5@ P. Kratzer and M. Scheffler, *Surface Knowledge: Toward a Predictive Theory of Materials*, Computing in Science & Engineering 3, 16 (2001); and *Phys. Rev. Lett.* 88, 036102 (2002). @footnote 6@ K. Reuter and M. Scheffler, to be published.

10:20am **SS2-MoM7 CO and Ethylene Dissociation on Ni(111): Influence of Steps, R.T. Vang, E.K. Vestergaard, F. Besenbacher**, University of Aarhus, Denmark

Steps on metal surfaces are well known to be more reactive than terraces and often provide the important active sites for catalytic processes. From high-resolution STM experiments we have found direct atomic-scale evidence that CO and C@sub 2@H@sub 4@ (ethylene) dissociate on the step edges of Ni(111) with a much higher rate than on the terraces. When CO is dosed at 400 K onto a clean Ni(111) surface small carbon islands are nucleated at the step edges. The coverage of these carbon islands saturates as soon as a thin brim of carbon is formed along the steps, indicating that adsorbed carbon prevents further CO dissociation, thus blocking the step sites. Concerning ethylene adsorption we observe the same mechanism of carbon growth at steps saturating after the formation of a thin carbon brim, when the dosing is performed at room temperature (RT). At higher temperatures (above 350 K), however, ethylene dosing leads to a continuous growth of carbon islands, which is interpreted as dissociation on terrace sites. When the step sites are blocked by small amounts of Ag, Au or S, we find that the dissociation rate of the two molecules is dramatically changed. No carbon is seen along the modified step edges after exposure to CO at 400 K or ethylene at RT. It is, however, still possible to form carbon islands by dosing ethylene at elevated temperatures owing to dissociation at terrace sites. These findings exemplify the concept of active sites in catalytic reactions and provide new directions for designing selective catalysts from fundamental surface science studies.

10:40am **SS2-MoM8 From Atomic Scale Reactant Ordering to Mesoscale Pattern Formation: CO Oxidation on Pd(100), D.-J. Liu, J.W. Evans**, Iowa State University

We successfully connect-the-length-scales from the realistic modeling of reactant ordering in CO+O/Pd(100) to the prediction of mesoscale reaction front propagation. Description of ordering of CO on bridges sites, and O on four-fold hollow sites requires atomistic lattice-gas modeling. Repulsive CO-CO and O-O interactions beyond nearest-neighbor in range must be carefully selected to match experimentally observed ordering. Precise description of reaction-diffusion fronts also requires sophisticated analysis of chemical diffusion of CO which reflects CO-CO interactions and the presence of the coadsorbate. Numerical techniques are developed to analyse both reaction kinetics and diffusion under inhomogenous conditions using realistic lattice gas modeling. The results are then incorporated into a continuous reaction-diffusion equation. Pattern formation problems on the mesoscale, e.g., chemical wave profiles, can then be studied efficiently.

11:00am **SS2-MoM9 The Correlation between the Electronic Structure and the Energetics of CO Chemisorption on Pd/Re (0001) Surfaces, B.S. Mun, C.M. Lee, V. Stamenkovic, N.M. Markovic, P.N. Ross**, Lawrence Berkeley National Laboratory

We explored the nature of CO chemisorption on a Pd thin film electrode by utilizing ex-situ x-ray photoelectron spectroscopy (XPS) and in-situ Fourier transform infrared (FTIR) spectroscopy. The Pd film was deposited on Re (0001) single crystal by evaporation in UHV. Upon the deposition of the Pd thin film, the valence band (VB) photoemission spectrum shows a significant change from the bulk Re VB spectrum, yet also unlike the VB of bulk Pd(111). The morphology of the Pd thin film on the Re surface is discussed from LEED measurements. Careful analysis and comparison of lineshape and peak positions of the VB spectrum of the monolayer Pd film revealed a valence band spectrum similar to that of Ag(111), implying a filling of the Pd d-band from the intermetallic bonding with the Re substrate. Analysis of FTIR spectrum on this same sample transferred from UHV to the in-situ electrochemical cell indicated direct evidence of a modified (unlike Pd) CO bonding state consistent with reduced back-bonding from the Pd d-band to the CO π^* antibonding orbitals. It is also found that this "weakly bonded" CO is oxidized to CO₂ at a much lower (ca. 0.2 V) electrode potential than on the Pd multilayer film.

11:20am **SS2-MoM10 Chemisorption Bond Weakening on Finite Size Terraces: CO on the Stepped Ru(109) Surface Compared to Ru(001), T. Zubkov, G.A. Morgan, Jr., J.T. Yates, Jr.**, University of Pittsburgh

We have compared the bonding energy, compressional LEED structures, and vibrational frequency of chemisorbed CO on the 10 atom wide (001) oriented terrace sites of Ru(109) with chemisorbed CO on the Ru(001) surface as a function of CO coverage. The measurements indicate that the Ru-CO bond energy is significantly smaller on the 22 Å wide (001) terrace sites than on the Ru(001) surface, except at the zero coverage limit where equal bond energies are observed. This results in lower saturation coverage and in a less dense saturated CO overlayer on the terraced surface with finite-width (001) planes. The results are explained by compressive relaxation of the (001) Ru terrace sites, leading to a decrease of the average d-band energy and to weaker chemical bonding of the CO. The implication of a finite-size substrate effect on chemical bonding to transition metal catalyst crystallites is important since, within the framework of this finding, smaller facets will exhibit weaker chemisorptive bonding than larger facets.@footnote *@ @FootnoteText@ @footnote *@ Work supported by DOE-BES.

11:40am **SS2-MoM11 Orientation of N@sub 2@O on Pd (110) and Rh(110) at Low Temperatures, H. Horino, I. Rzeznicka, K. Imamura, T. Matsushima**, Hokkaido University, Japan; K. Takahashi, E. Nakamura, Institute for Molecular Science, Japan

Catalytic N@sub 2@O decomposition on Pd(110) and Rh(110) has attracted much attention because N@sub 2@O is a major by-product in catalytic NO decomposition and also the intermediate emitting N@sub 2@ in an inclined way along the [001] direction. To understand this peculiar desorption, the orientation of adsorbed N@sub 2@O was examined at 60 K on Pd(110) and Rh(110) by near-edge X-ray absorption fine structure (NEXAFS). On Pd(110), N@sub 2@O adsorbs in a molecular form. Remarkable anisotropy was found in the X-ray incidence angle dependence of two π resonance NEXAFS peaks at 401 and 405 eV of the photon energy, i.e., with increasing shift of the x-ray incidence from the surface normal up to grazing angles, their intensities increased about 70% when the x-ray polarization was in a plane along the [001] direction, and for the

¹ Medard W. Welch Award Winner

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polarization in a plane along the [11-0] direction, the intensities decreased about 25 %. It is derived that major N@sub 2@O is lying along the [001] direction and minor species is standing. This is consistent with DFT calculations. On Rh(110), at small exposures, only one @pi@ resonance at 401 eV was observed and its polarization dependence was very similar to that of N@sub 2@ (a), indicating dissociation of N@sub 2@O. N@sub 2@ (a) stands on the surface. At saturation, N@sub 2@O is partly standing, and lying either along the [001] or the [11-0] direction with similar populations, since with increasing shift of the x-ray incidence from the surface normal, the @pi@ resonance at 405 eV decreased only slightly when the polarization was in a plane in either the [001] or [11-0] direction. No anisotropy was found in NEXAFS peaks. The signal at 401 eV is affected by the contribution from co-adsorbed N@sub 2@ (a).

Surface Science

Room 328 - Session SS3-MoM

Surface Diffusion and Wetting

Moderator: J.B. Hannon, IBM Research Division

8:20am SS3-MoM1 Determining Diffusion Mechanisms Using STM, B.S. Swartzentruber, Sandia National Laboratories **INVITED**

Determining a diffusion path is not a simple task; for it is the nature of kinetic processes that atomic configurations are arranged in low energy states most of the time. The move from one low energy state to another occurs on timescales usually not accessible to experimental observation. Although the transition path is inaccessible to direct measurement, in some cases it is possible to infer how motion occurs through indirect means. Using atom-tracking STM, in which the tip is "locked" onto the diffusing species using lateral feedback, the diffusion statistics are measured explicitly. >From the diffusion statistics of a dilute surface alloy of palladium or lead impurity atoms embedded in the outermost layer of Cu(001), we determine that the mass transport occurs predominantly via exchange with surface vacancies. Furthermore, the nature of the vacancy-impurity interaction has a dramatic effect on the overall diffusivity. For the case of Pb embedded in the Cu(111) surface, measurements of diffusion on two length scales are necessary to determine the active mechanisms. Short-range motion is predominantly vacancy mediated, while long-range diffusion occurs through exchange with surface adatoms and subsequent transport on top of the surface. Comparison of measurements with first-principles calculations yields valuable insight into diffusion processes, because the energetics of arbitrary diffusion paths can be calculated. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE. .

9:00am SS3-MoM3 Surface Characterization and Inter-diffusion Study of Copper on Ruthenium Thin Film Deposited on Silicon Substrate, O. Chyan, T. Arunagiri, R. Chan, R.M. Wallace, M.J. Kim, University of North Texas; T.G. Hurd, Texas Instruments

The dual-damascene patterning processing, coupled with the bottom-up Cu electrofill of damascene features and chemical-mechanical planarization, will continue to be the key for the future success of advanced IC chips. Recent advances in physical vapor deposition development allow highly engineered Ta/TaN diffusion barrier to be extended through 90 nm node. However, the tri-layer Cu-seed/Ta/TaN will likely encounter scaling difficulties in the Cu damascene trench/via features of advanced 65 and 45 nm nodes. We recently reported, J. Electrochem. Soc., 150, C347(2003), that Ruthenium (Ru) metal can function as a directly plate-able, seedless barrier materials. In this presentation, we report new findings centered on the interfacial and inter-diffusion studies of Cu/Ru system. Specifically, comparative study of wetting properties between electroplated-Cu and PVD-Cu on Ru barrier film (~ 10 nm) was carried out by XPS, SEM and AFM. Both electroplated and PVD Cu were found to wet well on Ru, based on SEM, AFM imaging and the scribe/peeled test, before and after thermal annealing over 450C. A strong adhesion between Cu/Ru interconnect microstructures is critical in order to withstand the demanding chemical-mechanical planarization process. Interfacial profiling was performed on Cu/Ru/Si samples using secondary ions mass spectroscopy (SIMS) depth profiling. To avoid knock-in ion-mixing interference, SIMS profiling was directed through the silicon back substrate. The backside SIMS profiling through Cu/Ru/Si samples show distinct interfaces without Cu inter-diffusion after annealed at 450C. TEM was further used to provide detailed cross-sectional imaging of Cu/Ru/Si interfaces. The wetting and inter-

diffusion data of Cu/Ru systems will be discussed in the context of Cu diffusion barrier application.

9:20am SS3-MoM4 Dynamics of Surface Alloys: Decay of 2D Islands on Pb/Cu(111), M.L. Anderson, N.C. Bartelt, G.L. Kellogg, B.S. Swartzentruber, Sandia National Laboratories

To achieve control of nanostructure formation via self-assembly or growth processes, it is critical to gain an understanding of the complex physics governing mass transport. Observing thermal decay of 2D islands has proven useful to quantify atomic mechanisms of surface diffusion in single component systems. In this work we use this method to study more complicated issues of diffusion in multi-component systems. Using both STM and LEEM, we studied thermal decay of Pb-overlayer and Pb-Cu alloy islands on Pb/Cu(111). By combining techniques we extend the length scale from nanometers to microns and measure decay rates over 4 orders of magnitude. When Pb atoms are deposited on Cu(111), they place exchange with surface Cu atoms, forming a 2D surface-alloy phase. At Pb coverages above 0.22 ML, the surface alloy is saturated and further deposition causes Pb to de-alloy and form overlayer (pure Pb) islands. Despite large differences in structure, measured decay rates of both overlayer and alloy islands as a function of temperature follow an Arrhenius form with the same activation barrier (~0.8 eV). Equivalent barriers indicate that the same rate-limiting process is effective for both types of islands. The measured energy is comparable to DFT calculations of Cu adatom formation plus diffusion energies@footnote 1@ suggesting that transport of Cu is the rate-limiting process. Although the barriers are the same, the absolute rate at a given temperature is ~20 times slower for the alloy than for the overlayer islands. The rate difference is partially accounted for by the fact that, for equal size islands, there are 5 times more Cu atoms to transport in the coarsening of alloy islands. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE. @FootnoteText@@footnote 1@ P. J. Feibelman, private communication.

9:40am SS3-MoM5 Edge Diffusion on Spiral Steps on Pb(111) Microfacets*, D.B. Dougherty, W.G. Cullen, J.E. Reutt-Robey, E.D. Williams, University of Maryland at College Park

A classic source of steps on solid surfaces is a screw dislocation intersecting the surface.@footnote 1@ From the intersection a spiral step emerges that can provide active sites for mass transport. To investigate the local kinetics associated with spiral steps, we have employed highly pure micron-size Pb crystallites grown on Ru(0001) with spiral steps on flat Pb(111) facets. Spiral step fluctuations have been observed with STM from 300-390 K and analyzed using the temporal correlation function and the persistence probability.@footnote 2@ The scaling of both functions points to a rate-limiting relaxation mechanism of step edge diffusion, exactly as observed for steps on single-crystal Pb(111).@footnote 3@ The kinetic parameter governing edge diffusion, the hopping mobility, has been extracted from the temporal correlation function and an activation energy has been extracted from the temperature dependence of the mobility. To investigate step fluctuations away from equilibrium, we have made fluctuation measurements on slowly rotating spiral steps on Pb crystallites in the process of thermal equilibration. The continuous unwinding due to the presence of the dislocation is distinct from the previously observed layer peeling process.@footnote 4@ The magnitude of the temporal correlation function for the fluctuations of a rotating spiral was observed to increase with the spiral curvature. The dynamic scaling was unaffected, showing that edge diffusion is still the rate-limiting transport mechanism. * Supported by UMD-NSF-MRSEC DMR-00-80008. @FootnoteText@ @footnote 1@ W.K. Burton, N. Cabrera, F.C. Frank, Proc. R. Soc. London, Ser. A 243 (1951) 299.@footnote 2@ D.B. Dougherty, O. Bondarchuk, M. Degawa, E.D. Williams, Surf. Sci. 527 (2003) L213. @footnote 3@ S. Speller, et al., Surf. Sci. 331-333 (1995) 1056; L. Kuipers et al., Phys. Rev. B 52 (1995) 11387.@footnote 4@ K. Thurmer, et al., Phys. Rev. Lett. 87 (2001) 186102.

10:00am SS3-MoM6 Sb-mediated Ge and Si Growth on Ge(001), J. Wang, M. Li, E.I. Altman, Yale University

Antimony-mediated Ge and Si growth on Ge(001) were studied using scanning tunneling microscopy and other surface characterization techniques. For the homoepitaxial growth on intermixed SbGe(001) with submonolayer Sb incorporated into the surface and below the Sb-Ge exchange temperature (470 K), Sb decreased the Ge island size with isolated ad-dimers seen on intermixed surfaces but not on pure Ge. The islands were found on top of Ge not Sb indicating that diffusion was not

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significantly inhibited on the Sb-passivated surface. The islands were always seen near Sb-Ge substrate domain boundaries. STM movies recorded at elevated temperatures showed that Ge dimers rapidly moved along Ge substrate dimer rows but could not pass or move onto Sb dimers embedded in the surface. These results can be explained by a repulsive barrier at Sb-Ge domain boundaries that inhibits Ge dimer diffusion from Ge to Sb domains but not from Sb to Ge domains. For Si heteroepitaxial growth at 520 K where Sb-Si and Sb-Ge exchange happens, a high density of small clusters were observed when Si was pre-deposited at 520 K and then 0.3 ML Sb was deposited at room temperature. The observed enhanced nucleation was attributed to zero-order nucleation due to both surface defects and adatom-surfactant exchange. The surface becomes smoother than Si deposition on bare Ge(001), with a much lower density of deep trenches on the terraces. Further annealing up to 590 K caused the small clusters to disappear producing a surface with square-shaped islands with typical sizes of $6 \times 6 \text{ nm}^2$. The isotropic island shape suggests that the anisotropic surface diffusion was disrupted due to the existence of domain boundary barriers between Sb and Si or Ge. Growth with different Sb coverages will also be discussed.

10:20am **SS3-MoM7 The Frustrated Alloying of Ge on Ultra-Flat Si(001)**, *J.B. Hannon, M. Copel, M.C. Reuter, R.M. Tromp*, IBM

Using low-energy electron microscopy and atomic-force microscopy, we have investigated the alloying of Ge at the Si(001) surface during growth at elevated temperature (750 to 900 C). We show that alloying occurs primarily via step flow during growth. However, on large terraces, where step flow does not occur, complex and coordinated step structures ("stripes") spontaneously form and migrate over the surface. The stripes consist of a string of alternating adatom and vacancy islands, and move at speeds approaching 1 micron per sec. As these structures traverse the large terraces, they leave alloyed regions in their wake.

10:40am **SS3-MoM8 New Diffusion Mechanisms on Amorphous Surfaces**, *A.S. Dalton, D. Llera-Hurlburt, E.G. Seebauer*, University of Illinois at Urbana Champaign; *K.R. Bray, G.N. Parsons*, North Carolina State University

The structural and energetic heterogeneity of amorphous surfaces should lead to effective values of the diffusivity that differ significantly from those on crystalline surfaces. However, little work has been done to investigate this possibility. The present work employs a combination of molecular dynamics simulations and experiments involving fractal analysis of surface topography to examine diffusion mechanisms on amorphous silicon (a-Si). Simulations indicate that surface diffusion on a-Si involves substantial exchange with the underlying bulk, but is dominated primarily by short-lived atoms generated from strained three-membered ring structures. The total effective activation energy for mass transport is 2.3 eV, and the formation energy for the most mobile species is about 0.8 eV. Experiments probed crystalline grains grown on a-Si surfaces by simple annealing at 635 to 665°C. Atomic force microscopy images were examined using dimensional fractal analysis to extract the static scaling coefficient and lateral correlation length. The transport rate varied with the length scale over which it was measured—a new result that represents the first experimental measurement of this theoretically predicted phenomenon. At short length scales near 50 nm on amorphous fields, surface diffusion was found to obey an Arrhenius law with an activation energy of 0.9 eV. Measurements over larger length scales including multiple crystal grains exhibited a larger activation energy of 2.4 eV. The significance of the correspondence between the computational and experimental values is discussed.

11:00am **SS3-MoM9 Mobility of Nanostructures on the Surface of a Desorbing Solid: Friction at the Nanoscale**, *V.N. Antonov, J.S. Palmer, A.S. Bhatti, J.H. Weaver*, University of Illinois at Urbana-Champaign

Physical vapor deposition of Au (or other atoms) on rare gas solids leads to spontaneous formation of clusters. The thermal desorption of the buffer causes the clusters to move and aggregate into larger structures, a process known as buffer-layer-assisted growth (BLAG) and desorption assisted coalescence. Our results demonstrate that the initial nucleation density is independent of the buffer thickness. We have studied the extent of aggregation and the size distribution of Au nanostructures as a function of the buffer composition (Xe, Kr, or Ar) and thickness. In the limit of large Au nanostructures (>20 nm), the diffusivity scales as the inverse of the contact area, in agreement with molecular dynamics simulations of fast slip-diffusion of nanocrystals on incommensurate surfaces. A model for BLAG is proposed, based on the concept that nanostructure growth kinetics is controlled by competition between the rate of diffusion and the rate of buffer depletion. From this model, the effective activation energy for Au

cluster diffusion is found to be within a few times the single atom binding energy on the surface. For small Au nanostructures (

11:20am **SS3-MoM10 Time-space Height Correlations of Thermally Fluctuating 2-d Systems; Application to Vicinal Surfaces and Analysis of STM Images**, *L. Barbier, B. Salanon, E. Le Goff*, CEA Saclay, France

For thermally fluctuating 2-d systems, like solid surfaces, time and space correlation of the local surface height diverge logarithmically in the rough phase, whereas saturation is obtained below the roughening transition (at $T_{\text{sub R}}$). A 2-d Langevin formalism with matter conservation within the surface plane is presented. An overall expression for correlation functions is obtained that are related to atom hopping rates and surface stiffnesses¹. In contrast with previous 1-d approaches of step dynamics on vicinal surfaces,²⁻⁴ solution of the 2-d Langevin equation for anisotropic systems gives time correlation functions $G(t)$ depending on energetic and hopping rates in the two main directions and the influence of surface stiffnesses on surface dynamics can be emphasized. At finite times, $G(t)$ cross over to power laws $\sim t^{-(1/n)}$ ($n = 1, 2$ or 4), within limited time ranges as it was observed for isolated fluctuating steps. Limits of time ranges are related to stiffnesses and diffusion anisotropies. For long times, logarithmic divergence ($T > T_{\text{sub R}}$) or saturation ($T < T_{\text{sub R}}$) of $G(t)$ are recovered. Applications to the analysis of STM images of vicinal surfaces are given.¹ ²Le Goff, L. Barbier and B. Salanon, Surface Science 531(3) (2003) 337. ³M. Giesen, Progress in Surface Science 68 (2001) p 1, and references therein. ⁴A. Pimpinelli, J. Villain, D.E. Wolf, J.J. Métois, J.C. Heyraud, I. Elkinani, G. Uimin Surf. Sci. 295 (1993) 143. ⁵T. Ihle, C. Misbah, O. Pierre-Louis, Phys Rev. B 58 (1998) 2289.

11:40am **SS3-MoM11 STM Tip-induced Translation through Excitations of the H₂O and D₂O Bending Modes on Pd(111)**, *E. Fomin*, University of California at Berkeley; *T. Mitsui*, Lawrence Berkeley National Laboratory; *M.K. Rose*, University of California at Berkeley; *D.F. Ogletree*, *M. Salmeron*, Lawrence Berkeley National Laboratory

We have studied the adsorption and manipulation of H₂O and D₂O molecules on Pd(111) using low temperature (~40 K) scanning tunneling microscopy (STM). We investigated the temperature dependence of molecular diffusion using two different approaches: tracking of individual molecules with the STM tip sitting on top of the molecules; and a "movie" technique - a series of consecutive scans showing hopping for an ensemble of molecules. In the course of this work it became clear that under certain conditions the STM tip had a strong influence on molecular motion. We found that the tip-induced hopping rate starts to grow exponentially as the bias reaches 200 meV for H₂O or 160 meV for D₂O, which corresponds to the molecular bending-mode excitation energy. This allows us to propose a coupling between vibrational excitation and molecular translation for water on Pd(111).

Surface Science

Room 326 - Session SS1-MoA

Stimulated Processes at Surfaces

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

2:00pm SS1-MoA1 Growth of Ordered and Disordered Arrays of Silicon Pillars During Laser-Assisted Etching, D. Mills, K.W. Kolasinski, Queen Mary, University of London, UK

We report on the formation of conical silicon pillars on a Si(111) substrate by etching with a nanosecond pulsed excimer laser in the presence of SF₆ or HCl or NF₃. The change in the silicon surface morphology was monitored as the number of shots from the XeCl (308 nm) excimer laser was varied from one to several hundred, for all experiments the energy density at the silicon surface was kept at about 1 J/cm². Significant changes in pillar morphology result from changing the process gas. This is a clear indication that gas-phase/plasma chemistry occurring in the laser ablation plume and plume/surface interactions are instrumental in the pillar formation mechanism. Initial surface morphology also affects pillar dimensions. Exposure of an unpolished surface results in much sharper pillars for a given number of laser shots than does exposure of the polished side. Modulation of the laser intensity profile by the effects of diffraction can be used to enhance the order of the pillars. For instance, the diffraction profile resulting from irradiation of a Gaussian shaped interface produces concentric rings of pillars. Large areas of pillars, on the order of 1 cm², have been formed by rastering the beam across the Si sample under continual laser irradiation at 20-50 Hz. Progress has also been made with the production of ordered arrays of the pillars using near field diffraction effects from fine wires and grids. Further investigation will examine the effects of varying the pressure of the process gas, the partial pressure of process gas mixtures, pre-heating of the surface with an argon ion laser, the effects of pulse repetition rate and diffraction on the pillar height, width and packing densities.

2:20pm SS1-MoA2 Defect-driven Photodesorption at UV and VUV Excimer Laser Wavelengths, L. Cramer, S.C. Langford, J.T. Dickinson, Washington State University

The optical properties of single crystal calcium fluoride make it useful lens material for the ultraviolet to vacuum-ultraviolet region, including possible use at 157 nm (7.8 eV) for high resolution microlithography. Of concern is possible degradation of these properties with prolonged exposure to laser light. Both surface and bulk modification of the material are of interest. Our interest is to obtain fundamental understanding of laser induced emissions (e.g., ions, electrons, and neutrals) from insulators with wide bandgaps (CaF₂ has a band gap of ~11.2 eV) and radiation induced surface/bulk modifications. We report and compare the measured rates of laser desorption from cleaved surfaces of CaF₂ of the observable ionic and neutral species at three excimer laser wavelengths: 157, 193, and 248 nm with pulse lengths ~20-30 ns. Mass selected time-of-flight techniques allows both species and kinetic energies to be determined. At laser fluences well below threshold for plume formation, only positive ions are observed. Ca⁺ is seen at all of the wavelengths; CaF⁺ is seen only at 157 nm. The Ca⁺ intensity vs. fluence shows essentially no dependence on wavelength. Ion energies show slight wavelength dependencies but all emissions are consistent with a multiple-photon electrostatic repulsion model. Neutral emission is dominated by Ca⁰ and the neutral energy distributions correspond to thermal distributions at relatively high temperatures (> 2500 K). Finally, we report on the role of simultaneous keV electron irradiation co-focused on the laser spot. We observe substantial increases in the laser desorbed products which we contribute to the resulting halide vacancy formation (F-centers).

2:40pm SS1-MoA3 Hot Electron Generation and Detection from Chemical Reactions on Metal Surfaces, E.W. McFarland, B. Roldan Cuenya, University of California, Santa Barbara

INVITED

Chemical reactions at metal surfaces have associated charge and energy transfer processes that are both ubiquitous and incompletely understood. There is increasing theoretical evidence that the traditional adiabatic description of reaction kinetics is limited, and that many if not most reactions on metal surfaces involve nonadiabatic elementary steps. Non-adiabatic processes in highly exothermic reactions are well known; however, for low energy reactions, experimental observation of charge carriers generated by electronic excitations during the reaction is difficult. A Schottky junction device structure consisting of an ultra-thin metal film

deposited on a semiconductor allows direct observation of electrons or holes generated during bond forming reactions at surfaces as a "chemicurrent" analogous to a diode photocurrent. Investigations of the chemical reaction induced electron current during adsorption of atomic and molecular species including, H, O, O₂, N₂O, NO₂, C₂H₄ and other hydrocarbons on Ag, Au, and Pd surfaces have revealed complex chemically induced electronic phenomena. The adsorption energies span a large range and we find a general tendency of the chemicurrent to increase with increasing energy and a distinct current amplitude and transient behavior for each species and surface. Detailed interpretation of the electronic signature for each species requires understanding of both the electron/hole excitation spectrum as well as the diode electronic characteristics. These data suggest the direct transfer of reaction energy to electronic excitations is a common feature of a wide range of surface reactions and that the unique electronic signal from such reactions might be used for improving our understanding of surface reactions and in creating new devices and sensors directly coupling chemical processes with electronics.

3:20pm SS1-MoA5 Factors Influencing Ion Yields and Angular Distributions in Electron Stimulated Desorption, N.S. Faradzhev, D.O. Kusmierek, T.E. Madey, Rutgers University

The focus of this work is on scattering processes affecting the survival probability and 'depth of origin' of low-energy ions (F⁺, F⁻) that pass through condensed ultrathin layers of polar molecules (H₂O, NH₃). The ions are generated by electron stimulated desorption (ESD) of SF₆ adsorbed on Ru(0001) at 25K. Electron stimulated desorption ion angular distribution (ESDIAD) and temperature programmed desorption (TPD) reveal predominantly molecular adsorption of SF₆ on Ru(0001) via three F atoms, with the other three pointing away from the surface. Several characteristic angular distributions of F⁺ and F⁻ (halo, hexagon) are observed as a function of temperature, coverage, and electron irradiation. Adsorption of overlayers of polar molecules, e.g. H₂O and NH₃ leads to changes in both the F⁺ and F⁻ ion intensities (attenuation and enhancement), as well as dramatic changes in the ion angular distributions. Analysis of these changes gives insight into the role of charge-transfer and elastic scattering processes during the passage of ions through ultrathin polar films. The polar coadsorbate can also influence the ESD process itself by modifying polarization energies, low-energy electron lifetimes, and potential barriers for electron tunneling.

3:40pm SS1-MoA6 Effects of Water Ice Films on Thermal Stability and Electron-activated Decomposition of CF₂Cl₂ on Metal Surfaces, N.S. Faradzhev, Rutgers University; C.C. Perry, Johns Hopkins University; D.O. Kusmierek, Rutgers University; D.H. Fairbrother, Johns Hopkins University; T.E. Madey, Rutgers University

We report the kinetics of processes, activated by low energy electrons, for an environmentally important molecule CF₂Cl₂ co-adsorbed with water ice on metal surfaces (Ru; Au) at low temperature <100K. The results are compared with similar data obtained for CCl₄. TPD, RAIRS and XPS has been utilized. TPD reveals an increase of thermal stability of molecular CF₂Cl₂ on Ru(0001) when deposited under an amorphous solid water (ASW) overlayer at 25K or adsorbed inside ASW ice matrix; dissociation is completely inhibited. Weakly-bound CF₂Cl₂ desorbs from ASW surface at ~110K, but desorption of CF₂Cl₂ trapped in the ASW matrix is impeded until the onset of ice crystallization at ~155K. All techniques indicate that ionizing radiation (electrons or X-rays) incident on CF₂Cl₂/H₂O layer leads to rapid decomposition of halocarbon, which proceeds via dissociative attachment (DA) of low energy secondary electrons. The rates of decomposition for 1ML of CF₂Cl₂ and CCl₄ are similar on the metal surface and increase in the ASW ice environment indicating a possibly important role of a polar medium in halocarbon dissociation. The highest decomposition cross-sections are observed for submonolayer halocarbon coverage on a water ice surface: 1.0x10⁻¹⁵ cm² for CF₂Cl₂ and 2.5x10⁻¹⁵ cm² for CCl₄. The cross-sections are identical for halocarbon adsorbed on an ice surface and caged in a water matrix. The initial dominant radiation-induced process in adsorbed CF₂Cl₂ is C-Cl bond cleavage. For CF₂Cl₂ in ASW, fragments and reaction products include Cl⁻ and F⁻, H₂O, COF₂, and CO₂; for CCl₄ in ASW, COCl₂ and C₂Cl₄ are also seen. Product distributions, the kinetics of halocarbon damage,

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and subsequent reaction pathways are qualitatively independent of the radiation source.

4:00pm SS1-MoA7 Water Enhanced Decomposition and Nanometer Scale Structure Formation Generated by Radiative Exposure of Solid Surfaces, K. Nwe, S.C. Langford, J.T. Dickinson, Washington State University

Novel nanometer scale structures on insulating inorganic materials with wide bandgaps can be generated by simultaneous exposure of surfaces to electron and laser beams plus low pressure water vapor. Dramatic synergisms are observed on ionic single crystal surfaces due to bond weakening which arises from localized chemisorption. We are able to modify single crystal surfaces of alkali halides and calcium phosphates/carbonates either at the single atomic layer level or, with higher intensities, at the level of several microns. These modifications are due to electronic excitations leading to decomposition of the crystal. Arrays of cones and fractal structures with unique optical properties can readily be generated. Alkali halide and nitrate surfaces exhibit strongly angular dependent "black" surfaces which are generated in a self-organized fashion. The high absorption is due to the high tortuosity of the surface (a "stealth" surface). We also quantify that in the presence of water vapor, the rates of both laser and electron beam induced decomposition/desorption increase by as much as an order of magnitude. We present AFM evidence that this is a highly localized, defect mediated mechanism. We suggest that point defect clusters lead to atomic dimension step structures (e.g., kinks) that peel off due to bond weakening from sorbed water derived radicals. Supporting evidence from spectroscopic and microscopic data on exposed surfaces will be presented.

4:20pm SS1-MoA8 Electron-stimulated Reactions in Thin Amorphous Solid Water Films on Pt(111), G.A. Kimmel, N.G. Petrik, Pacific Northwest National Laboratory

The electron-stimulated production of D₂ from amorphous solid D₂O deposited on Pt(111) is investigated as a function of film thickness. The D₂ yield has two components with distinct reaction kinetics. Using isotopically layered films of H₂O and D₂O demonstrates that the D₂ is produced in reactions that occur at both the Pt/amorphous solid water (ASW) interface and the ASW/vacuum interface, but not in the bulk. The energy for the reactions, however, is absorbed in the bulk of the films and electronic excitations migrate to the interfaces where they drive the reactions. At the Pt(111) surface, the electronic excitations cause dissociation of water molecules at the interface, leading to the build-up of adsorbed hydrogen atoms. A model based on the diffusion of electronic excitations to either interface accounts for the principle experimental observations.

4:40pm SS1-MoA9 Temperature-Dependent Thresholds for Ion-Stimulated Surface Diffusion: Experiments with Second Harmonic Microscopy, Z. Wang, E.G. Seebauer, University of Illinois at Urbana Champaign

Ion-surface interactions at low energies (<100 eV) characterize an increasingly diverse array of material processing steps in ion beam assisted deposition (IBAD), plasma enhanced deposition, reactive ion etching (RIE), and other applications. The governing kinetic phenomena are often tacitly considered to lie at one of two poles: physical effects where momentum matching dominates, and chemical effects involving thermal activation of atomic bonds according to Arrhenius expressions. Here we report surface diffusion measurements demonstrating behavior that lies at neither pole. Optical second harmonic microscopy is used to image diffusion of Ge and In adsorbed on Si(111) under low-energy noble-gas ion bombardment. Both adsorbates exhibit a surprising new form of tradeoff between substrate temperature and the energy threshold at which ion influences become manifest. Molecular dynamics simulations suggest that the effect originates from changes in surface point defect concentrations. Instantaneous nonuniformities in net surface potential induced by thermal vibrations provide a mechanism by which ions can affect these concentrations nonlinearly. The effects generally increase the rate of mass transport across the surface except for Ge above the Si(111)-(7x7) to (1x1) phase transition, where ion-induced changes in charge-mediated complexation of mobile species with surface defects slows the diffusion.

5:00pm SS1-MoA10 Femtosecond Photo-generated Carrier and Reaction Dynamics on a Chlorinated Silicon Surface: Reaction Yield Calculation by Rate Equation of Adsorbed Chlorine, S. Haraichi, F. Sasaki, National Institute of Advanced Industrial Science and Technology, Japan

We have studied the mechanism of a photo-induced reaction of Si/Cl system especially in the low fluence region, which is a promising candidate

for an extremely low-damage etching. The following procedures were employed in the femtosecond pump probe experiment to obtain the photo-generated carrier dynamics during the reaction. First, the variation of surface second-harmonic (SH) intensities generated by probe light, which directly reflects surface chlorine coverage, has been measured during a photo-induced reaction. Here both incident lights respectively produces two reaction factors of carrier generation and instantaneous surface vibration. However the pump beam of 3.1 eV photon energy mainly produces carrier generation, and the probe light of 0.95 eV photon energy mainly produces instantaneous surface vibration. In addition, the pump power is set just under the reaction threshold, so the reaction must be induced only when the carrier generation by pump beam and the surface vibration by probe light simultaneously occur on the surface. After obtaining the variation of surface chlorine coverage during a photo-induced reaction, the reaction yield is calculated by using a first and second-order rate equation of the surface chlorine atoms. Second, the reaction yield is calculated for several delays between two beams, and the obtained reaction yield dependence on the delay time reflects the femtosecond photo-generated carrier dynamics. The dynamics can be described by first and second-order kinetics, and both results show no significant difference but the almost equal excitation peak at around 0.4 ps. Here the excitation time constant in the obtained carrier dynamics is 0.1-0.2 ps and tends to decrease with increasing the power of each excitation lights. On the other hand, we have found two relaxation time constants of 0.2-1.0 ps and 1.5-10.0 ps, and both short and long relaxation time constants tend to increase with increasing the excitation power.

Surface Science

Room 327 - Session SS2-MoA

Tribology, Adhesion, and Friction

Moderator: S.P. Jarvis, Trinity College Dublin, Ireland

2:00pm SS2-MoA1 Super Hydrophobic Interactions: From the Inside and Out, J.E. Houston, Sandia National Laboratories; S. Singh, University of New Mexico; C.J. Brinker, Sandia National Laboratories

Considerable interest has recently been directed toward the study of the processing of "super hydrophobic" (SH) surfaces and their unique properties. These materials are generally characterized by hydrophobic molecules in a fractal-like structure and have contact angle in excess of ~150. We present here studies of the behavior of the interaction force vs. relative separation between a scanning force-probe tip and sample surface using the interfacial force microscope (IFM). The measurements include "inside" interactions for both a SH film (contact angle ~165) and hydrophilic tip (~30) coming into contact with the SH surface in water, and the "outside" case for a SH-coated tip in contact with the outer water surface. As expected, the latter case shows the development of a considerable repulsive force before becoming unstable submersing the coated-tip end. However, the inside case shows a marked contrast depending on the nature of the tip. The hydrophilic tip shows only repulsive forces, as it essentially pushes against the inside surface of the water in contact with the SH film. In addition, the SH surface deformation reveals an unusual creep behavior in this case. In contrast, the SH coated tip shows large, long-range attractive forces prior to contacting the SH film, an effect which is often characterized as due to interfacial bubble formation. These results will be discussed in terms of experimental parameters, such as tip speed and the thickness of the SH film, as well as the mechanical properties of the film itself, both wet and dry. The work at Sandia was supported by the DOE Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

2:20pm SS2-MoA2 Friction Anisotropy at Pd(100)/Pd(100) Interfaces, A.J. Gellman, C.M. Mancinelli, Carnegie Mellon University

Friction anisotropy has been studied between two Pd(100) single crystal surfaces in an ultrahigh vacuum environment. Friction measurements were made using Pd(100)/Pd(100) interfaces modified by adsorption of octane at coverages ranging from 4 to 40 molecular layers. The relative crystallographic orientation of the two Pd(100) surfaces was systematically varied and friction measurements were made at each orientation as a function of octane coverage. These measurements have revealed that friction is anisotropic with respect to Pd(100) lattice orientation. When the surfaces were aligned, forming a commensurate interface, and sheared along the direction with 4ML of octane at the interface, the static friction coefficient was $\mu_s > 8.0 \pm 2.0$. A minimum in the static friction

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coefficient was obtained when the two Pd(100) surfaces with 4ML of octane at the interface were misoriented by $\theta \sim 45^\circ$. Under these conditions the static friction coefficient for sliding along the direction of the stationary surface was $\mu_{\text{sub s}} = 4.0 \pm 2.0$. Higher coverages of octane decreased the friction, but friction anisotropy persisted for coverages of octane as high as 20 ML at the sliding interface between the two Pd(100) surfaces. Wear scars were observed on both surfaces indicating that plastic deformation had occurred during sliding. The observation of friction anisotropy in the presence of disordered overlayers of octane and during shearing of surfaces that deform plastically suggests that friction anisotropy originates with the properties of the bulk crystal lattices rather than surface lattice commensurability. These results corroborate the findings of a previous study of friction anisotropy between Ni(100) surfaces. @footnote 1@ @FootnoteText@ @footnote 1@ Langmuir, 2000, 16(22), 8343.

2:40pm **SS2-MoA3 Direct Observation of Superlubricity**, *J.W.M. Frenken*, Leiden University, The Netherlands; *M. Dienwiebel*, IAVF AG, Germany; *N. Pradeep*, *K.B. Jinesh*, *G.S. Verhoeven*, Leiden University, The Netherlands; *J.A. Heimberg*, Corvis Corporation

We have constructed a frictional force microscope (FFM) that is able to quantitatively track the forces between a tip and sample in three dimensions. At the heart of the FFM is a silicon sensor, the 'Tribolover'. The 3D motion of a metal tip, which is held by this sensor, is detected with four interferometers. The two lateral spring constants of the Tribolovers are typically 1 N/m, which is up to two orders of magnitude lower than the torsional force constants of conventional AFM cantilevers. The spring constant perpendicular to the surface is typically an order of magnitude higher than in the lateral directions. The friction force resolution is as low as 15 pN, even under normal loads up to several tens of nN. We present experiments with W-tips on highly oriented, pyrolytic graphite (HOPG) surfaces. We observe the familiar, atomic-scale stick-slip behavior, in which the tip performs a 'least-resistance', zig-zag path over the corrugated graphite surface. To our surprise, the amplitude of the friction forces depends strongly on the relative orientation of the tip and the graphite surface. When we rotate the graphite around an axis normal to the surface, the average friction force shows characteristic variations between a high value and a near-zero value, close to the detection limit of our FFM. These observations, combined with additional, circumstantial evidence, support a simple interpretation, in which a small graphite flake intervenes between the W tip and the HOPG substrate. Thus, the FFM actually records the lateral forces between two parallel graphite lattices. By rotating the substrate with respect to the tip, we periodically go through fully aligned and completely misoriented configurations. When the misalignment is sufficiently severe, the lateral forces on the C-atoms in the flake cancel, thereby dramatically reducing the total friction force. This phenomenon has been predicted more than ten years ago, and is referred to as superlubricity.

3:00pm **SS2-MoA4 The Role of the Third Body Processes in the Friction and Wear of MoS₂ and MoST Coatings**, *G.Y. Lee*, *I.L. Singer*, *K.J. Wahl*, U.S. Naval Research Laboratory

The sliding friction behavior of MoST@footnote 1@ (Ti-Mo-S) and MoS@sub 2@ coatings has been investigated by in situ tribometry, which allowed real time observation of third body dynamics. The coatings were deposited by closed field unbalanced magnetron sputtering and contained between 0 to 20 % titanium. Reciprocating tests were performed in both dry (< 4 % RH) and ambient (40-50 % RH) air at a sliding speed of 1 mm/s and 24 N normal load (1.1 GPa mean Hertzian stress) using sapphire hemispheres as counterbodies. All coatings showed similar steady-state friction coefficients: about 0.025 in dry air and 0.06 in ambient air, however titanium containing coatings in ambient air exhibited lower friction coefficients at the beginning of the tests. Titanium containing coatings also showed reduced wear in both dry and ambient conditions. In situ optical microscopy observations identified the formation of a transfer film (third body) on the sapphire hemisphere for all tests. Most of the sliding took place between the transfer film and the wear track indicating that the velocity accommodation was interfacial sliding. The titanium containing coatings exhibited an additional velocity accommodation mode, shearing and extrusion of transfer film, correlated to the higher friction in ambient conditions. The role of the transfer film mobility and mechanical properties in controlling friction behavior will be discussed. @FootnoteText@ @footnote 1@ N.M. Renevier, V.C. Fox, D.G. Teer, and J. Hampshire, Surf. Coat. Tech., 127 (2000) 24-27.

3:20pm **SS2-MoA5 Molecular and Bulk Material Mechanisms of Smooth and Stick-slip Sliding**, *J. Israelachvili*, University of California, Santa Barbara
INVITED

There are at least three quite different contributions to the friction force between two ideal surfaces, i.e., smooth surfaces sliding in the absence of wear: load-dependent friction (which depends on the surface structure or topography), adhesion-dependent friction (which depends on any adhesion between the two surfaces) and viscosity-dependent friction (which occurs when the shearing surfaces are separated by a thin layer of liquid). These contributions depend on the surface molecular structure, the contact area, applied load (or pressure), film thickness, film viscosity, and sliding speed (or shear rate). In addition to these purely surface or interfacial properties, the bulk properties of the materials such as the elastic modulus can also play an important role even in the case of wearless sliding of elastic surfaces. Thus, depending on their shape, the friction can be smooth or proceed via stick-slip. The situation with rough and/or viscoelastic surfaces can be very rich and complex, as can the adhesion between the surfaces, and both may depend critically on a combination of surface and bulk properties. The talk will review some recent experimental results, including theoretical modeling and computer simulations, on such systems, i.e., both rough and smooth, hard and soft, adhesive and non-adhesive, lubricated and unlubricated. Such studies are clarifying the molecular basis of many well-established tribological laws and empirical observations such as Amontons laws and the Stribeck Curve, and are also revealing new insights and relationships between tribological processes at the molecular and macroscopic levels.

4:00pm **SS2-MoA7 Evaluation of the Surface Characteristics and Mechanical Properties of Interconnect Films and their Correlation with CMP Process**, *P.B. Zantye*, *A.K. Sikder*, *A. Kumar*, University of South Florida

Chemical Mechanical Planarization (CMP) has emerged as one of the most widely used Back End of Line (BEOL) semiconductor manufacturing process for fabrication of present generation Cu interconnect structures. CMP is synergistic combination of tribological and chemical phenomena occurring at the surface of the polishing pad and wafer in presence of chemically active slurry. Thus, the frictional forces that act upon the wafer during CMP assume significant importance for effective characterization of the CMP process. In this research the surface characteristics and mechanical properties of various candidate materials Cu (wiring metal) and interlayer dielectrics (ILD) SILK@super TM@ (soft polymer), and SiO@sub 2@ (ceramic) have been evaluated. The surface roughness of the candidate materials was determined using the Atomic Force Microscopy (AFM) technique. The mechanical properties (Young's Modulus and Hardness) of Cu, SILK@super TM@ and SiO@sub 2@ were evaluated using MTS Nanoindenter@superTM@. The material removal behavior and dry friction characteristics were studied by micro scratch testing and the CMP process of materials under investigation was simulated on the Bench Top CMP tester. The coefficient of friction (COF) was monitored in situ during initial and final part of wafer coupon polishing. The surface characteristics, mechanical properties, dry friction and material removal were then correlated with the CMP process for each material to get an insight in to the polishing behavior of these candidate materials when planarized with different material specific slurries and polishing pads.

4:20pm **SS2-MoA8 A Comparative Study of the Adhesion, Friction, and Mechanical Properties of CF@sub 3@ and CH@sub 3@ Terminated Alkanethiol Monolayers**, *C.M. Doelling*, *H. Ying*, Princeton University; *J.E. Houston*, Sandia National Laboratories; *T.K. Vanderlick*, *G. Scoles*, Princeton University; *T.R. Lee*, University of Houston

Considerable interest has been given to the potential use of self-assembled monolayer films as lubricants for applications such as MEMS. Of particular interest are fluorinated films because they are inert and show high thermal stability. Research performed directly compares the adhesion, friction, mechanical properties and contact potentials of two alkanethiol SAM films, differing only in the composition of their terminal head group (-CH@sub 3@ vs. -CF@sub 3@). Quantitative data of both friction and normal force was collected using the Sandia-developed interfacial force microscope (IFM). In comparison with the CH@sub 3@-terminated monolayer, we find that the CF@sub 3@-terminated film exhibits a longer-ranged attraction to an approaching metal probe tip, and the work required to separate the surfaces is greater despite the maximum attractive forces being similar. The friction is also larger, as is the force-displacement hysteresis upon loading/unloading cycles. Close inspection of the frictional response shows the presence of "non-contact" friction, namely, significant energy dissipation before the probe and monolayer develop a component of repulsive-contact force. From these findings we conclude that the

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mechanical behavior of the film is influenced by the strong dipole inherent to the -CF₃ terminal group. Finally, atomic force microscopy measurements of friction were also undertaken, taking advantage of nanografting to directly compare both types of films using the same probe tip. At small compressive loads, the friction of the fluorinated film is about two times that of the hydrocarbon film, in agreement with the IFM results. @FootnoteText@ The work at Sandia was supported by the DOE Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

4:40pm SS2-MoA9 Reaction of Trimethylphosphate with TiC and VC(100) Surfaces, H.I. Kim, P. Frantz, S.V. Didziulis, The Aerospace Corporation; L.C. Fernandez-Torres, S.S. Perry, University of Houston

Hard coatings, such as titanium carbide (TiC), are emerging technologies for various tribological applications, including spacecraft bearings due to their higher hardness and greater wear resistance compared to metal components. However, their surface chemical properties, especially with respect to high-performance lubricants, are poorly understood. Therefore, the adsorption and chemical reaction of a model lubricant additive, trimethylphosphate [(CH₃O)₃PO] (TMP), were investigated on the surfaces of TiC and VC(100) as a function of temperature using high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). TMP adsorbs molecularly on both surfaces at cryogenic temperature, and chemical bonding to the surface is evident upon warming to approximately 200 K. At higher temperatures, surface chemical reaction on TiC leads to phosphate-like and carbonaceous products that persist on the surface after heating up to 873 K. The stability of these surface species at such high temperature presents potential implications for modification and lubrication of hard coating surfaces at high temperatures where most organic adsorbates fail to provide tribological benefits. The reaction pathway and the reaction products are determined to be dependent on the initial coverage as well as the substrate chemistry, i.e. TiC vs. VC. These results have interesting implications for potential applications in boundary additives on hard coatings, where desired surface chemical protection may be tuned by the concentration of the organophosphate ester additives in the lubricant and the substrate chemistry.

5:00pm SS2-MoA10 Degradation of Self-Assembled Monolayer in Humid Environments, B.-I. Kim, T.M. Mayer, M.G. Hankins, M.P. de Boer, B.C. Bunker, Sandia National Laboratories

Self-assembled monolayers (SAMs) are used extensively to control friction and stiction in micromachines. While as-prepared coatings are effective at minimizing adhesion, coating performance can deteriorate with time in humid environments. We are using the interfacial force microscope (IFM) to monitor the aging behavior of SAMs as a function of temperature, humidity, time, SAM composition, and fabrication procedures. The IFM provides force-distance curves between functionalized scanning probe tips and substrate surfaces while avoiding the "snap-to-contact" problems associated with conventional atomic force microscopy (AFM). We have simultaneously measured both normal and friction forces between a tip and SAM coated surfaces as a function of separation distance. Together with topographic images taken with AFM, we can correlate adhesion and friction with structural information. Our results indicate that adsorbed water can disrupt hydrogen bonds at the SAM-substrate interface, reorganizing the coating to create bare patches that promote adhesion. To date, coatings that have been tested include standard octadecyl trichlorosilane (OTS), tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS), octadecene (reacted with surface Si-H bonds), dichlorodimethylsilane (DDMS), and an octadecyl coupling agent attached to the surface using amine functional groups. At all humidities and temperatures tested, it appears that FOTS coating that have been annealed to promote condensation reactions with surface silanols are most effective at resisting degradation in hot, humid environments. @FootnoteText@ 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.

Surface Science

Room 328 - Session SS3-MoA

Structure and Reactivity of Metal Clusters

Moderator: C.T. Campbell, University of Washington

2:00pm SS3-MoA1 Catalysis by Supported Metal Nanoclusters, D.W. Goodman, Texas A&M University INVITED

Model catalysts consisting of metal clusters of varying sizes have been prepared on single crystal TiO₂ and ultra-thin films of TiO₂, Al₂O₃, and SiO₂. The morphology, electronic structure, and catalytic properties of these metal clusters have been investigated with emphasis on the unique properties of those clusters <5.0 nm in size. An array of surface techniques including scanning tunneling microscopy (STM) and polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) have been used to study the metal cluster morphology, electronic properties, and chemistry. These studies illustrate the novel physical and chemical properties of nanosized metal clusters, and suggest that their catalytic properties may be tailored for specific chemical transformations.

2:40pm SS3-MoA3 Gold Nano-Clusters on Rutile TiO₂(110) - A Combined UHV and High Pressure STM Study, E. Walström, R. Schaub, E.K. Vestergaard, A. Ronnau, F. Besenbacher, Interdisciplinary Nanoscience Center, Denmark

Through an interplay between scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we show that bridging oxygen vacancies are the active nucleation sites for Au clusters grown on the rutile TiO₂(110) surface under UHV conditions. We show both experimentally and theoretically that a single oxygen vacancy can bind 3 Au atoms on average. A new growth model for the Au/TiO₂(110) system involving vacancy-cluster complex diffusion is presented. The fate of the Au nano-particles in various gas environments is studied in detail through a new high-pressure STM capable of atomic resolution at atmospheric pressures. Sintering and morphological changes are followed in-situ when the Au/TiO₂(110) system is exposed to reducing (H₂, CO) and oxidizing (O₂) conditions.

3:00pm SS3-MoA4 Dimethyl Methylphosphonate Decomposition on Supported Ni Nanoparticles Deposited on a TiO₂(110) Surface, J. Zhou, Y.C. Kang, K. Varazo, D.A. Chen, University of South Carolina

Sizes and structures of oxide-supported metal nanoparticles are very important in determining their catalytic reactivity. In our study, the thermal decomposition of dimethyl methylphosphonate (DMMP) on supported nickel nanoparticles has been investigated as a model system to understand the relationship between the particle size and reactivity. All the experiments were performed under UHV conditions by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). Our STM studies show that various sizes of Ni particles with uniform particle size distributions can be prepared on TiO₂(110) surface by varying the diffusion (D) to deposition flux (F). The most uniform size distribution of Ni nanoparticles can be obtained with the lowest D/F ratio. XPS and TPD studies indicate that mainly molecular DMMP adsorbs on the supported Ni nanoparticles at room temperature. Between room temperature and 800 K, the adsorbed DMMP decomposes to produce H₂ and CO as primary gaseous products and CH₄ and HCHO as minor products. After heating to 800 K, all carbon desorbs from the surface while atomic phosphorous still remains. DMMP decomposition on various sizes of Ni nanoparticles as well as on the bulk Ni surface will be compared. Furthermore, studies of DMMP reaction will be also carried out on the supported Pt nanoparticles.

3:20pm SS3-MoA5 Dynamics and Chemical Reactivity of Au on TiO₂(110) Rutile, D. Pillay, Y. Wang, G.S. Hwang, University of Texas at Austin

Au has long been known to be chemically inert in its bulk form, as compared to other transition metals, such that it has received little attention as a catalyst. However, Au nanoclusters dispersed on oxide (particularly TiO₂) shows an extraordinarily high activity for low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of unsaturated hydrocarbons, and reduction of nitrogen oxides. But, due to weak metal-oxide interfacial bonding interactions, Au nanoclusters become unstable toward sintering even at moderate temperatures. This may in turn undermine their catalytic activity and selectivity. Hence, along with their chemical reactivity, a detailed understanding of dynamical behaviors of Au atoms is necessary for an accurate description of underlying reaction mechanisms and performance

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of the oxide supported nanometal catalytic systems under realistic processing conditions. In this talk, we will present our first principles [DFT with plane waves and pseudopotentials] study of Au adsorption and diffusion on regular and defective (with oxygen vacancies) TiO@sub2@(110) rutile. We will also present the diffusion of oxygen vacancies (Fs center) and their interactions with Au atoms. Based on our calculation results, we will discuss underlying reasons for the enhancement of Au cluster sintering upon exposure to a high-pressure oxygen environment.

3:40pm SS3-MoA6 Oxygen-Induced Morphological Changes in Cu and Ni Islands on TiO@sub2@(110), D.A. Chen, J. Zhou, University of South Carolina; **Y.C. Kang,** Pukyong National University, South Korea

Metal particles supported on oxide surfaces serve as excellent model systems for developing a better understanding of commercial heterogeneous catalysts. Scanning tunneling microscopy (STM) studies of Cu islands grown on a rutile TiO@sub2@(110)-(1x1) surface demonstrate that these islands disappear from the STM images after exposure to oxygen gas. Based on X-ray photoelectron spectroscopy (XPS) experiments, the disappearance of the Cu islands cannot be explained by the loss of Cu from the surface or by a dramatic change in the electronic properties of the islands. The adsorption of oxygen appears to weaken the Cu-Cu bond, allowing two-dimensional (2D) Cu islands to form on the surface at the expense of the existing three-dimensional (3D) islands. The formation of 2D islands is thermodynamically favorable for Cu based on the lower surface free energy of oxidized compared to that of both Cu and TiO@sub2@. Oxygen-induced disappearance of Ni islands has also been observed, but the rate of disappearance is much slower even though Ni is more easily oxidized than Cu. This effect can also be explained in terms of thermodynamics; oxidation of Ni islands does not reduce the surface free energy of the islands below that of TiO@sub2@, and therefore there is less driving force for the Ni islands to become 2D. As expected, oxidation of Cu islands at 500 K increases the rate of disappearance of the 3D islands. However, oxidation of the Ni islands at 500 K causes significant changes in the surface morphology due to the oxidation of the TiO@sub2@ surface itself. The new titania layers preferentially regrow around the Ni islands, resulting in a much rougher surface.

4:00pm SS3-MoA7 Chemical Reactions on Free Iridium and Platinum Clusters, M. Andersson, T. Jarvdalen, P. Nystrom, A. Rosen, Chalmers University of Technology and Goteborg University, Sweden

In a cluster beam experiment metal clusters are produced with a pulsed laser vaporization source, kept at room temperature or liquid nitrogen temperature. The beam of neutral clusters passes two low-pressure collision cells and clusters and reaction products are detected with laser ionization and time-of-flight mass spectrometry. Thus, the reaction probability in a cluster-molecule collision can be determined. We have measured the CO and O@sub 2@ adsorption on iridium clusters, 5-32 atoms. The overall size-dependence in reaction probability is similar for both molecules, with minima at Ir@sub 8@, Ir@sub 12@ and Ir@sub 18@, and a significantly higher reactivity for all clusters with more than 18 atoms. When the cluster source was cooled to liquid-nitrogen temperature, the reaction probability increased. For platinum clusters with more than 6 atoms we measured stable reaction products with both oxygen and hydrogen, with moderate variations with size. Using the two reaction cells we can let the clusters react first with O@sub 2@ and then with H@sub 2@ and observe that reaction of Pt@sub n@(O@sub 2@)@sub m@ with H@sub 2@ results in removal of oxygen atoms from the cluster. This is interpreted as formation of a water molecule, which subsequently desorbs. The efficiency of the catalytic water formation is high on all cluster sizes measured (7-30 atoms), with only a weak dependence on cluster size. M. Andersson, J.L. Persson, A. Rosen, J. Phys. Chem. 100, 12222 (1996). M. Andersson, A. Rosen, J. Chem. Phys. 117, 7051 (2002).

4:20pm SS3-MoA8 STM Study of Copper Growth on ZnO(0001)-Zn and ZnO(0001bar)-O Surfaces, O. Dulub, Tulane University; **L. Vogel Koplitz,** Loyola University; **M. Batzill, U. Diebold,** Tulane University

The study of Cu particles on ZnO surfaces is of great interest due to the wide application of this system in the low-temperature synthesis of methanol, the water-gas shift reaction, and the production of hydrogen by steam reforming. The mechanism that enhances the catalytic activity of Cu is still poorly understood. Therefore, a detailed study of this system on the atomic level is desirable. Scanning Tunneling Microscopy (STM) has been used to study the room temperature growth of Cu on the polar (0001)-Zn and (0001bar)-O surfaces of zinc oxide. The (0001)-Zn surface prepared by

sputtering and annealing at 500-750°C, shows flat terraces with a high density of triangular pits and islands. STM shows that Cu grows on the (0001)-Zn surface as three-dimensional clusters at coverages between 0.05 and 0.25 monolayers (ML); two-dimensional (2D) islands are only observed at very low coverages (0.001-0.05 ML). The average size of the 3D clusters increases with coverage and their density increases slowly. The size and morphology of Cu clusters depends on the terrace size of the substrate. The triangular pits and islands on the terraces do not act as preferred nucleation sites for Cu, but, surface roughness and sputter damage change the growth mode to more 2D-like. The Cu clusters are well-separated and exhibit a well-defined hexagonal shape. Equilibrium crystal shape analysis of the largest clusters yields an apparent work of adhesion of 3.4 ± 0.1 J/m@super 2@, which is size dependent and decreases with the size of the cluster. The morphology of the clean (0001bar)-O surface is distinctly different from that of the (0001)-Zn surface. The terraces are smooth and have no small islands. Formation of two-dimensional Cu clusters at coverages of less than 0.1 ML was observed on the (0001bar)-O surface.

4:40pm SS3-MoA9 Charge Exchange between Alkali Ions and Nanocrystal Metal Surfaces, G. Liu, J. Yarmoff, University of California, Riverside

Au nanocrystals grown on TiO@sub 2@(110) possess unique catalytic properties, which depend on the cluster size. Presumably, the catalytic properties are the result of the electronic configuration of the nanocrystals. Earlier, we showed that the probability for neutralization of low energy alkali ions scattered from metal surfaces is determined by the local electrostatic potential (LEP) a few Å's above the scattering site. In the present work, we are using the charge exchange between alkali ions and metallic nanocrystals as a probe of their electronic structure. 2 keV Na@super +@ ions were scattered from Au nanocrystals grown on TiO@sub 2@(110), and the neutral fractions of the Na particles singly scattered from Au were measured with time-of-flight. As the average size of the Au nanoclusters increases, the neutral fraction decreases until a uniform Au film is formed. The neutral fraction of Na scattered from bulk Au is very small (~2%) due to the large work function of Au. For small Au clusters, however, the neutral fractions can be as high as 30% or more. The high neutral fraction of the small Au clusters suggests that the alkali ions are coupling to electronic states that are specific to the nanocrystals. The work function change, measured as a function of cluster size, shows a smooth change from the clean TiO@sub 2@(110) surface to that of bulk gold. In order to understand the influence of the work function on the neutral fraction, Cs was deposited onto Au/TiO@sub 2@(110) surface to controllably decrease the work function. In addition, the dependence of the neutral fraction on the ion exit angle and energy was studied. X. Lai, T. P. St. Clair, M. Valden, and D. W. Goodman, Prog. Surf. Sci. 59 (1998) 25. C. B. Weare and J. A. Yarmoff, Surf. Sci. 348 (1996) 359.

5:00pm SS3-MoA10 Electronic Detection of Oscillatory Reactions on Supported Platinum Particles, M.C. Wheeler, University of Maine; **R.E. Cavicchi, S. Semancik,** National Institute of Standards and Technology

A MEMS device, capable of surface temperature control and electrical resistance measurements, has been used to detect and explore the oscillatory reaction of CO oxidation on oxide-supported platinum particles. The behavior has been monitored for a range of conditions, but as an example, when the supported platinum is heated to 165°C in a 340 ppm CO/air mixture at atmospheric pressure, periodic switching between a low-resistance (excess CO) state and a high-resistance (excess oxygen) state is observed. During these cycles, the resistance ranges from 7.1 k@ohm@ to 17. k@ohm@ and back to 7.1 k@ohm@ over a period of 200 s. The resistance switching that we have studied on small (on the order of 30 nm) platinum particles is likened to the temporal oscillations of the reaction on platinum films and single crystal samples, which were monitored by infrared and photoemission electron microscopy respectively. We have shown that the frequency of the resistance oscillations can be manipulated by varying the CO partial pressure in order to influence the rate of CO uptake. Also, synchronization observed between oscillations for physically separate devices in multi-element arrays is evidence that the oscillations are due to a globally-coupled, mass-transfer and reaction rate effect. Indeed, effects such as doubling of the oscillation frequency on neighboring devices are similar to the rate behavior observed by Yamamoto et al. In addition to the global synchronization, transient oscillations are observed prior to switching that suggests microscale-coupling occurs between the individual platinum particles on the support. Yamamoto, J. Chem. Phys. 103, 8209 (1995). G. Erli, Science 254, 1750 (1991).

Surface Science

Room 327 - Session SS1-TuM

Catalysis II: Hydrocarbons at Metal Surfaces

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

8:20am **SS1-TuM1 Adsorption Energies of Small Alkane Molecules on MgO(100) and on Pd Nanoparticles on MgO by Temperature Programmed Desorption**, *S.L. Tait, Jr.*, University of Washington; *Z. Dohnalek, B.D. Kay*, Pacific Northwest National Laboratory; *C.T. Campbell*, University of Washington

Catalysts consisting of Pd nanoparticles supported on oxides are active in a variety of important reactions involving small alkanes. Molecular beams and temperature programmed desorption (TPD) were used to study the adsorption of small alkane molecules, C_nH_{2n+2} ($n=1-10$), on the MgO(100) surface and on Pd nanoparticles on MgO(100) at low temperatures (24 K), a regime little explored for such well-defined model catalysts. High quality MgO films are grown on the Mo(100) surface, producing an MgO(100) surface with defect densities comparable to those obtained by UHV-cleavage of MgO crystals. Hydrocarbon molecules are deposited on the surface by a highly collimated molecular beam with a well-defined kinetic energy. King and Wells style sticking measurements are made by quadrupole mass spectrometer (QMS) during deposition. The initial sticking probability increases with alkane chain length until it reaches unity for octane ($n=8$). The sample is heated at a controlled rate and desorption products are observed by line-of-sight QMS. The adsorption energies and kinetic prefactors for desorption are extracted from these TPD data. Adsorption energy increases non-linearly with alkane chain length. The alkanes bind more strongly to Pd particles than to MgO(100). We plan to present preliminary results also concerning Pd particle size effects in alkane adsorption and dissociation. 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. SLT supported by a UW/PNNL Joint Institute for Nanotechnology fellowship.

8:40am **SS1-TuM2 Reactions of Aliphatic Alcohols on WO₃(001) Surfaces**, *B.G. Frederick, S. Ma*, University of Maine

Interactions of ethanol and isopropanol with WO₃(001) thin film surfaces, epitaxially grown on a sapphire substrate, were studied with calibrated thermal desorption spectroscopy (CTDS). The reactivity of reduced and oxidized WO₃ surfaces, as characterized by XPS and UPS, were compared in order to understand the surface structure dependence. Coverage dependent desorption spectra show that alcohol molecules diffuse rapidly on the WO₃ thin film surfaces. Ethanol and isopropanol desorb molecularly between 200 and 450 K with evolution of water. The remaining alkoxy intermediates decompose via β -H elimination, followed by C-O bond scission, to produce ethylene and propylene, respectively. We suggest that diffusion and competition between reaction rates of dehydroxylation vs. associative molecular desorption of alcohol control the alkoxy coverage that determines the selectivity toward alkene under these low coverage conditions.

9:00am **SS1-TuM3 Dissociative Adsorption of Cyclohexene on Pt(111) at 300 K studied by Single-Crystal Microcalorimetry and Sticking Probability Measurements**, *H. Ihm, H.M. Ajo, D.E. Moilanen, C.T. Campbell*, University of Washington

The dehydrogenation reaction of cyclohexene to benzene on platinum surfaces is of fundamental interest due to the importance of the surface chemistry occurring in hydrocarbon conversion. There have been many studies to understand its reaction, mechanism, energetics, and kinetics using experimental and theoretical methods. They agree that cyclohexene on Pt(111) converts to cyclohexenyl between 200-250 K and further converts to benzene between 300-350 K.^{1,2} There have been studies to estimate reaction (activation) energies from cyclohexene to cyclohexenyl or benzene, but these were in a limited coverage regime and either by indirect experimental measurements or by theoretical calculation.^{1,3} Here, we report direct calorimetric measurements of the heats of reactive adsorption of cyclohexene on Pt(111) at 300 K as a function of coverage. These calorimetry measurements were performed by using a pyroelectric detector and a pulsed cyclohexene molecular beam impinging onto a 1 μ m thick Pt(111) sample. We also measured the sticking probability as a function of coverage. The sticking probability is initially high (0.86) and stays constant

up to 0.7 ML then decreases linearly to 0 at 1 ML. The flux of the cyclohexene molecular beam was measured with a liquid-nitrogen cooled quartz crystal microbalance. Work supported by NSF.
¹FootnoteText@footnote 1@ F.C. Henn, A.L. Diaz, M.E. Bussell, M.B. Hugenschmidt, M.E. Domagala, and C.T. Campbell, J. Phys. Chem. 1992, 96, 5965-5974.
²Footnote 2@ W.L. Manner, G. S. Girolami, and R.G. Nuzzo, J. Phys. Chem. B 1998, 102, 10295-10306.
³Footnote 3@ B.E. Koel, D.A. Blank, and E.A. Carter, J. Molecular Catal. A: Chemical 131 (1998) 39-53.

9:20am **SS1-TuM4 The Reaction of 1-chloro-2-methyl-2-propanol (Cl@super t@BuOH) on Oxygen-covered Ag(110): C-Cl Bond Cleavage in Epoxide Formation**, *H. Piao, K. Adib*, Brookhaven National Laboratory; *M. Enever*, University of Delaware; *Z. Chang*, Brookhaven National Laboratory; *D.R. Mullins*, Oak Ridge National Laboratory; *J. Hrbek*, Brookhaven National Laboratory; *M.A. Barteau*, University of Delaware

Synchrotron-based Temperature Programmed X-ray Photoelectron Spectroscopy in combination of Temperature Programmed Desorption has been used to explore the C-Cl scission in the reaction of Cl@super t@BuOH on oxygen-covered Ag(110) surface to produce isobutylene oxide (IBO). Although the C-Cl bond cleavage is involved in the rate-determining step for the evolution of IBO, the mechanism was not fully understood. This motivated the surface reaction mechanism study to determine whether the surface chlorohydrin reaction follows an S@sub N@1 reaction or a concerted S@sub N@2 path. Using experimental data we also developed a kinetic model for surface reaction chemistry. The combination of experimental and theoretical results indicates that Cl@super t@BuO decomposition does not occur by an S@sub N@2 process that releases IBO directly into the gas phase. Instead, C-Cl scission deposits organic intermediates or products on the surface, and that the appearance of these products in the gas phase lags the appearance of atomic chlorine on the surface. Therefore, we can conclude that the production of IBO is the result of a process involving two kinetically significant steps: C-Cl scission that deposits Cl atoms and IBO molecules on the Ag(110) surface followed by desorption of molecularly adsorbed IBO. Low barrier and pre-exponential for the second step on the high coverage surface indicate that the rate of C-Cl scission may be influenced by other factors, e.g., the availability of surface adsorption sites for Cl adatoms.

9:40am **SS1-TuM5 Surface Chemistry of Hydrocarbon Fragments on Transition Metals: Towards Understanding Catalytic Processes**, *F. Zaera*, University of California, Riverside
INVITED

An overview of our efforts to elucidate the mechanistic details of the surface chemistry of hydrocarbons on transition metal surfaces will be presented. Particular emphasis will be placed on the similarities and differences between surface and organometallic systems, and on the relevance of this chemistry to catalysis. The methods developed in our laboratory for the clean production of catalytically-relevant but unstable surface moieties on well-characterized metal surfaces will be described, and the main thermal decomposition pathways of those intermediates will be discussed. An argument will be presented for the definition of catalytic selectivities based on subtle changes in the regioselectivity for early dehydrogenation rates. For instance, the unique ability of platinum in promoting isomerization and cyclization reactions appears to correlate with its preference to catalyze gamma-hydride elimination steps; nickel, in contrast, facilitates dehydrogenation at the alpha position, and catalyzes hydrogenolysis instead. The additional mechanistic complications in hydrocarbon reforming under catalytic conditions introduced by the presence of strongly bonded carbonaceous deposits on the surface of the active catalyst will be addressed. The working reforming metal catalyst is likely to display a bifunctional character, with rapid hydrogenation-dehydrogenation steps taking place on the hydrocarbon-covered surface and more demanding skeletal rearrangement steps occurring on patches of bare metal. Finally, some details behind the imparting of enantioselectivity to metal catalysts via the adsorption of chiral modifiers will be introduced.

10:20am **SS1-TuM7 Fluorinated Carboxylic Acids Deprotonation on the Cu(100) Surface**, *B. Immaraporn*, Fritz-Haber Institute, Germany; *P. Ye, A.J. Gellman*, Carnegie Mellon University

The kinetics of acid deprotonation on the Cu(100) surface have been studied using four different fluorinated carboxylic acids (CF@sub 2@HCO@sub 2@H, CF@sub 3@CO@sub 2@H, C@sub 2@F@sub 2@HCF@sub 2@CO@sub 2@H, and CF@sub 3@CF@sub 2@CO@sub 2@H). All four acids adsorb molecularly on Cu(100) at 90 K and then undergo deprotonation to form carboxylates during heating below 300 K. Temperature programmed reaction spectroscopy and x-ray photoemission spectroscopy were used to verify that the acids deprotonate on the

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Cu(100) surface. Work function measurements were used to study the deprotonation kinetics during heating and estimate the activation energy barriers (ΔE_{OH}) to deprotonation. The nature of the transition state to acid deprotonation on Cu(100) was probed by analysis of linear free energy relationships (LFER) or correlations of with σ_F . The field reaction constant, ρ_F , or the slope of the LFER was found to be $\rho_F = 57 \pm 9$ kJ/mol in the limit of zero coverage and $\rho_F = 22 \pm 2$ kJ/mol at 0.5 ML coverage. These values of ρ_F can be compared to the values of $\rho_F = 104$ kJ/mol for acid deprotonation in the gas phase. This comparison suggests that the transition state for acid deprotonation on Cu(100) must be anionic with respect to the reactant (RCO@sub 2@H@sub (ad)@super $\hat{\rho}$ @RCO@sub 2@super δ @super $\hat{\rho}$ @super $\hat{\rho}$ @H@super δ @super $\hat{\rho}$ @).

10:40am **SS1-TuM8 Enantioselective Reactivity of R-2-bromobutane on Cu(531), D.M. Rampulla, A.J. Gellman**, Carnegie Mellon University

Enantioselective reactions are integral to most biological chemistry and large-scale pharmaceutical production. The difficult aspect of enantioselective reactions is that they require chiral media such as solvents, surfaces, or catalysts. Enantioselective heterogeneous catalysis is a promising method for the preparation of chiral compounds but requires catalytic surfaces with inherently chiral structure. The stepped and kinked high Miller index surfaces of metals are naturally chiral and have been shown to interact enantiospecifically with chiral adsorbates. Enantioselective desorption of small chiral molecules from such surfaces has been demonstrated and studied, but enantioselective reactivity on naturally chiral metal surfaces has not been explored. Temperature Programmed Reaction Spectroscopy (TPRS) has been used to study the decomposition of R-2-bromobutane on the chiral Cu(531)@super R@ and Cu(531)@super S@ surfaces. R-2-bromobutane debrominates to produce a chiral R-2-butyl intermediate. The R-2-butyl group decomposes by β -hydride elimination to form cis- and trans-2-butene and 1-butene. The hydrogen released by β -hydride elimination can also hydrogenate the R-2-butyl intermediate to form butane. In addition to reaction temperatures that are indicative of enantioselective kinetics, the reaction yield is influenced by the chirality of the Cu(531) surfaces.

11:00am **SS1-TuM9 Coupled Experimental and Theoretical Study of Weakly Adsorbed Molecules on Metal Surfaces, H. Ogasawara, H. Ostrom, B. Brena**, Stockholm University, Sweden; *D. Nordlund*, Uppsala University, Sweden; *M. Nyberg, L. Pettersson*, Stockholm University, Sweden; *A. Nilsson*, Stanford Linear Accelerator Center

The heat of adsorption is often treated as an indicator of the strength of adsorbate-substrate interaction. We present the combined experimental and theoretical study of weakly adsorbed systems on metal surfaces. We studied the electronic structure of water and hydrocarbons which are often considered as weakly bound species. We observed significant electron sharing between the adsorbate and metal surface and involvement of both bonding and antibonding molecular orbitals in the molecule-metal bond. These findings are a key to understand the O-H or C-H bond activation mechanism. We also present computational details how we computed the adsorption structure of these systems.

11:20am **SS1-TuM10 H@sub 2@ Production from Ethanol Over Au-Rh/CeO@sub 2@ Catalysts, H. Idriss, P.Y. Sheng**, The University of Auckland, New Zealand

The reactions of ethanol over oxides and metal-oxides surfaces are receiving increasing attention because of the potentially efficient production of hydrogen by oxidation and steam reforming. Ethanol (now viewed as a bio-fuel with potential for making hydrogen) has received considerable attention in the past because it is a simple probe molecule in studying surface reactions on metals and oxides. We have previously investigated the decomposition of ethanol on M/CeO@sub 2@surfaces (M = Rh, Pt, Pd and Au). In this work we show that the addition of Au to Rh, for the reaction of ethanol, enhances both the production of H@sub 2@ and the total oxidation to CO@sub 2@. The reaction of ethanol was conducted by TPD, IR and in steady state catalytic conditions, while catalysts were investigated by XRD and XPS. Among the key results of this work are the following. 1. Addition of Au resulted in the total suppression of adsorbed CO when compared to Rh/CeO@sub 2@ catalyst (IR), at low temperatures. 2. The presence of Rh enhanced the production of H@sub 2@ and the total decomposition of ethanol when compared to Au/CeO@sub 2@ catalyst (steady state reactions). The CO@sub 2@ to CO ratios were found equal to 25 for Au/CeO@sub 2@, 5.6 for Rh-

Au/CeO@sub 2@, and 1.8 for Rh/CeO@sub 2@, catalysts (TPD). The reaction pathway for ethanol on the bimetallic system will be discussed and compared to that on the mono-metallic catalysts. Sheng, P.-Y., Yee, A., Bowmaker, G. A., Idriss, H. J. Catal. 2002, 208, 393; and references therein. Cavallaro, S. Freni, S. Int. J. Hydrogen Energy, 1996, 21, 465. Gates, S.M., Russell, J.N., Yates, J.T., Surf. Sci., 1986, 171, 111. Idriss, H., Seebauer, E.G., J. Mol. Catal. A, 2000, 152, 201. Diagne, C., Idriss, H., Kiennemann, A., Catal. Commun. 2002, 3, 565.

Surface Science

Room 328 - Session SS2-TuM

Nucleation and Growth

Moderator: J.F. Wendelken, Oak Ridge National Laboratory

8:20am **SS2-TuM1 The Dynamics of Crystallite Shape Transformations, J.E. Reutt-Robey, D.B. Dougherty**, University of Maryland **INVITED**

At the nanoscale, the shape of a crystallite is remarkably sensitive to the local chemical potential. While much is known about equilibrium crystal shapes (ECS), the mechanism and rate by which a crystallite morphology evolves in response to abrupt changes in temperature and gaseous environments are largely unknown. Using variable temperature STM as our experimental probe, we have investigated the reshaping dynamics of submicron lead crystallites prepared in their near-ECS on Ru(OO01). In the case of chemical (oxygen) adsorption, we observe a dramatic particle reshaping into a heavily faceted structure. We show that this reshaping is triggered by surface impurities, which are needed to nucleate lead oxide grains. Once nucleated, an oxide grain grows laterally on the crystallite surface in an apparent autocatalytic process. Although nucleation is temperature insensitive, subsequent oxide grain growth rates depend on temperature, presumably due to limiting lead mobility at our temperature of investigation. These results are consistent with independent measurements of step fluctuation kinetics. We show how temperature reduction leads to a "flattening" of supported neat crystallites through a monolayer-by-monolayer peeling mechanism. From the step peeling kinetics, and simulations with continuum models, we find that the kinetics of monolayer peeling is limited by multi-layer relaxations. Atomistically, these relaxations represent limited mass transfer across the curved facet boundary. Within the thermal window of our measurements, we show that particle reshaping is not reversible and discuss the limiting nucleation barriers. Thurmer, E. Williams, and J.E. Reutt-Robey, Science 297, 33-35 (2002). Thurmer, J.E. Reutt-Robey, E.D. Williams, M. Uwaha, A. Edmundts, H.P. Bonzel, Phys. Rev. Lett. 87 (2001) 186102. Thurmer, J.E. Reutt-Robey, E.D. Williams, Surf. Sci., in press.

9:00am **SS2-TuM3 Fluctuations of Islands on Anisotropic Surfaces, F. Szalma, T.L. Einstein**, University of Maryland, College Park

We have performed kinetic Monte Carlo simulations to model the decay and edge-fluctuations of islands containing hundreds to thousands of atoms on (111) crystal surfaces. Investigating the dispersion of the Fourier modes of the fluctuations as a function of wavevector, we observe anomalous dispersion due to the geometrical fact that the equilibrium island shapes are anisotropic because of the intrinsic anisotropy of crystal surfaces. Contrary to results for the isotropic approximation, the Fourier modes are not eigenmodes of the system; however, they can be transformed into an eigensystem, which provides a means to determine the anisotropic line tension of the island. In recent experiments observing how small crystallite droplets approach their equilibrium state, these fluctuations are intimately related to their decay, and the line tension is a factor in determining their ultimate shape. Finally, comparison of theoretical and experimental configurations allows gauging of the suitability of the calculated energies used in the simulations. Khare and T.L. Einstein, Phys. Rev. B 54 (1996) 11752. Stasevich, F. Szalma, and T.L. Einstein, submitted to SS17.

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9:20am **SS2-TuM4 The Importance of Substrate Steps on the Ripening of 3D Particles: Ag and Cu on Ru(0001)**, *W.L. Ling, T. Giessel, K. Thürmer, R.Q. Hwang, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories

Many hetero-epitaxial systems grow in the Stranski-Krastanov mode, in which material added to a wetting layer results in 3D islands. Once nucleated, and after growth has stopped, these 3D islands can minimize surface and interfacial free energy if they grow taller. However, there can be large free-energy barriers to this vertical growth because of the apparent necessity of nucleating new layers on top of these islands. In fact, Mullins and Rohrer have shown that it is unlikely that such nucleation would occur during ripening.¹ In this work, we have studied the evolution of 3D islands of Ag and Cu on Ru(0001) using low-energy electron microscopy. We find that vertical growth does not occur at all during ripening when the Ag or Cu film does not overlay substrate steps. On stepped surfaces, on the other hand, we find vertical growth readily occurs. Using real-time observations, we find that the vertical growth occurs by an unexpected route that does not require nucleation. Islands, which adopt flat tops in an early stage of growth, gain a layer when they descend a monatomic Ru step. In this manner, they maintain the flat tops throughout ripening but grow taller as they migrate downhill on the substrate. We have investigated the vertical growth rate as a function of step spacing and island height. We find that thin islands shrink and tall islands grow, and the growth rate increases with the step density.¹ Mullins and G.S. Rohrer, *J. Am. Ceram. Soc.* 83, 214 (2000).

9:40am **SS2-TuM5 Geometry-Based Simulation Algorithm for Island Formation during Submonolayer Film Growth**, *J.W. Evans*, Iowa State University; *M.C. Bartelt*, Lawrence Livermore National Laboratory; *M. Li*, Iowa State University

A current challenge is to develop efficient new coarse-grained simulation strategies which reliably predict the morphology of growing films. We present a geometry-based simulation (GBS) algorithm which avoids explicit treatment of the terrace diffusion of adatoms and their aggregation with islands - a computationally expensive component of either atomistic KMC simulation or continuum formulations. GBS characterizes island growth in terms of capture zones (CZ's), and implements simple but realistic geometric rules to incorporate crucial spatial aspects of the island nucleation process, i.e., nucleation nearby CZ boundaries. This approach reliably predicts island size distributions and spatial correlations, and is especially efficient for highly reversible island formation.

10:00am **SS2-TuM6 Pyramidal Faceted Ni Nanocrystals on W(111)**, *Q. Wu, J. Kolodziej, H. Wang, T.E. Madey*, Rutgers University

Nanoscale features formed by nucleation of ultrathin Ni films on W(111) are studied by means of ultrahigh vacuum-STM, soft X-ray photoemission spectroscopy (SXPS) using synchrotron radiation, LEED, and AES. Whereas a single monolayer (ML) of Ni covers planar W(111) uniformly, we find that multilayers of Ni (~5 ML) follow the Stranski-Krastanov growth mode, and form clusters and islands on the Ni-covered W(111). Upon heating to ~600K, Ni clusters are found to aggregate into nanoscale pyramidal facets, which coexist with planar regions of Ni-covered W(111). This type of faceting is different from the monolayer-induced faceting of W(111) seen for Pt, Pd, Ir, and Rh: a single ML of Ni does not cause faceting of W(111). Thermal stability of Ni films on W(211) and W(111) is studied by SXPS and AES, which indicates that alloy formation between Ni and W occurs at temperatures $\geq 700\text{K}$. Further annealing of faceted Ni nanocrystals also leads to Ostwald ripening. Reactivity of Ni nanoclusters with adsorbates (e.g. oxygen and thiophene) is also investigated. The nucleation and growth of nanocrystals are discussed in terms of overlayer strain due to lattice mismatch.

10:20am **SS2-TuM7 Growth and Stability of Bi Films on Si(111) Studied by LEEM**, *G.E. Thayer*, IBM T.J. Watson Research Center; *J.T. Sadowski*, Tohoku University, Japan; *R.M. Tromp*, IBM T.J. Watson Research Center

The structural and electronic properties of ultra-thin metal films on semiconductor surfaces have attracted much recent interest primarily due to the dominating dependence of novel device performance on metal contacts. Since contacts are interfaces, contact issues are real problems where surface science can provide insightful solutions. Understanding the factors governing heteroepitaxial growth, such as surface free energies and stress relaxation effects are important, and in situ electron microscopy can play a unique role in investigating the processes involved. Using low-energy electron microscopy (LEEM) we observed real-time growth of Bi on Si(111). With the surprisingly large lattice mismatch of 17% between bismuth and silicon, one might expect growth of Bi/Si(111) to be almost certainly

dominated by strain, and therefore three dimensional. Up to about five monolayers, the Bi film grows with small grain (012) oriented islands on top of a uniform wetting layer. Above five monolayers, the crystal orientation dramatically flips from (012) to (111), from a four-fold symmetry to a three-fold symmetry, into a flat single crystal film (grains are approximately $100\mu\text{m} \times 2\mu\text{m}$ in size). The transition occurs very quickly with grains transitioning at a rate of $1\mu\text{m} \times 2\mu\text{m} \times 1\mu\text{s}$. After the transition into a (111) oriented epitaxial film, the growth continues in a two-dimensional layer-by-layer mode of bi-layers. The thermodynamic stability of Bi/Si(111) films was also investigated by annealing the films to temperatures of up to 150°C (melting temperature of Bi is 220°C), where dewetting becomes important, even prior to melting.

10:40am **SS2-TuM8 Nucleation Kinetics during Homoepitaxial Growth of TiN(001) by Reactive Magnetron Sputtering**, *M.A. Wall, D.G. Cahill, I. Petrov*, University of Illinois at Urbana-Champaign; *D. Gall*, Rensselaer Polytechnic Institute; *J.E. Greene*, University of Illinois at Urbana-Champaign

Polycrystalline TiN is extensively used as a diffusion barrier in microelectronics, as a hard wear resistant coating on cutting tools, and as a corrosion and abrasion resistant layer on optical components. The performance of TiN in all these applications is dependant on the texture of the layer, which is in turn a function of the film growth parameters and nucleation kinetics. To gain an atomic-scale understanding of the processes which govern TiN nucleation, we grow epitaxial layers on TiN(001) via reactive magnetron sputtering in an ultra-high vacuum (UHV) system and employ in-situ scanning tunneling microscopy (STM) to investigate the dynamics. In addition, we perform density functional calculations in order to guide the interpretation of our experimental results. The characteristic island size R_c necessary to nucleate a new layer on a growing island is measured as a function of growth temperature T_s and nitrogen fraction f_{N_2} in an Ar/N₂ mixture. By applying nucleation rate theory to temperature dependant R_c data obtained from layers grown with $f_{\text{N}_2} = 1$, we extract a diffusion activation energy $E_s = 1.4 \pm 0.1$ eV for $T_s \leq 865^\circ\text{C}$ where nucleation is diffusion limited. For $T_s \geq 910^\circ\text{C}$, nucleation becomes limited by the formation of unstable clusters, and we extract an adspecies formation energy $E_f = 1.4 \pm 0.2$ eV. When f_{N_2} is reduced from 1 to 0.1, $E_s = 1.1 \pm 0.2$ eV which results in a factor of two increase in R_c at a given T_s . The activation energy we calculate for Ti diffusion on TiN(001) is 0.4 eV, significantly smaller than E_s extracted from our experiment, indicating that Ti is not the dominant diffusing species. Based on calculated binding energies of TiN_x clusters, the dominant diffusing species is likely TiN_x, with $1 \leq x \leq 3$.

11:00am **SS2-TuM9 Pt Adsorption on Chiral SrTiO₃ Surfaces**, *A. Asthagiri, D.S. Sholl*, Carnegie Mellon University

The existence of intrinsically chiral surfaces provides many opportunities related to the catalytic chemistry and separation of chiral molecules. A key difficulty in realizing the potential of this approach has been the production of surfaces with reasonable surface area. We describe results that underpin efforts to epitaxially deposit ultra-thin films of metal on metal oxide substrates. The success of these efforts requires careful control of the film morphology of the underlying substrate and knowledge of the growth modes of metal on these surfaces. To this end, we have performed extensive plane wave Density Functional Theory (DFT) calculations to describe the bonding of Pt on a variety of SrTiO₃ surfaces. These calculations include both terminations of all three low Miller index surfaces, (100), (110), and (111), and two representative stepped surfaces, (620) and (622). Our results show that epitaxial growth of Pt on the substrates can be expected, and that step flow growth should be feasible for the stepped substrates. Our results provide quantitative insight into the experimental observations made by our collaborators for these systems, including the existence of inversion domains for Pt films on SrTiO₃(111). We will discuss the implications of our calculations for the practical growth of chiral metal films on SrTiO₃ substrates.

11:20am **SS2-TuM10 High-Temperature Low Energy Electron Microscopy Studies of Spiral Dislocation Dynamics on TiN(111) Terraces**, *S. Kodambaka, S.V. Khare, W. Swiech, K. Ohmori, I. Petrov, J.E. Greene*, University of Illinois at Urbana-Champaign

We have grown epitaxial TiN(111) layers by reactive evaporation onto Al₂O₃ substrates and used in situ high-temperature

¹ Morton S. Traum Award Finalist

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low-energy electron microscopy to study surface morphological evolution on large ($> 4 \mu\text{m}$) atomically-smooth TiN(111) terraces during annealing at temperatures $T_{\text{sub a}}$ in the range 1500 and 1750 K ($T_{\text{sub a}} = 0.47-0.55T_{\text{sub m}}$, where $T_{\text{sub m}}$ is the melting point in K). At each annealing temperature, we observe rotation of screw dislocation segments lying in the surface slip plane around the immobilized segment of the dislocation lying out of the slip plane resulting in a spiral with steps oriented along. Step heights are proportional to the number of revolutions in the slip plane. We find that the total length of the dislocation line increases with annealing time as the spirals undergo a shape-preserving anti-clockwise motion with a constant angular velocity. From the temperature-dependent angular velocity measurements, we determine an activation barrier of 5.0 ± 0.2 eV, with a prefactor of $10^{14} \pm 0.5 \text{ s}^{-1}$, for spiral rotation. Studies of this process, a single-ended Frank-Read source, provide insight into understanding dislocation multiplication mechanisms occurring in highly refractory, technologically important transition-metal nitride layers.

11:40am **SS2-TuM11 Conversion from Nanowire to Epilayer: Epitaxial Growth of Bi on Si(114)-2x1**, *S. Cho, J.M. Seo*, Chonbuk National University, Korea

The Bismuth (Bi) adsorption on the reconstructed Si(114)-2x1 has been studied using STM under UHV. Among 1-D features of Si(114)-2x1, such as Tetramer, Dimer and Restatom rows parallel to [-110] direction, Bi atoms preferentially adsorbed on the Tetramer rows and formed 1-D wires whose separation is 1.6 nm. The periodic structure in the Bi wire along [-110] has been converted to $3a$ ($a=0.38$ nm) from $2a$ of clean Si(114). The Bi wire of the second layer adsorbs between the Bi wires of the first layer, and shifts by $1.5a$ along the row. The Bi wires of subsequent layers also adsorb between the previously formed Bi wires in the same fashion. Such epitaxial growth continues unless the defects like substrate vacancies interfere. The packing unit is a Bi-dimer and the hexagonal packing has been confirmed by the hexagonal pattern of the facet near the ledge. It has been concluded that the reasons for 2-D epitaxial growth of Bi on Si(114) are the followings; the first, the existence of preferential adsorption site on Si(114), and the second, the adjustable lattice-matching between the Bi-dimer row and the substrate along as well as perpendicular to the wire.

Surface Science

Room 326 - Session SS1-TuA

Water at Interfaces II: Adsorbed Layers

Moderator: C.J. Hirschmugl, University of Wisconsin-Milwaukee

2:00pm **SS1-TuA1 Why Water Wets Precious Metals**@footnote 1@, **P.J. Feibelman**, Sandia National Laboratories **INVITED**

To categorize surfaces as hydrophobic or hydrophilic by measuring contact-angles is a step toward understanding water-solid interactions, but a small one. To predict wetting, control aqueous surface chemistry or design nanofluidic systems, atomic-scale understanding of water-adlayer structure and dynamics is wanted. The research involved is risky -- systematic error is an ever-present concern in dealing with weakly interacting species, like water, which are commonplace in the natural world. To explore the limits of current ab initio methods for water on solids, I have been applying first principles Density Functional Calculations to the simplest examples: periodic water adlayers on close-packed, precious metal surfaces. On Ru(0001), the calculations invite the inference that wetting involves forming a half-dissociated monolayer with water molecules and hydroxyl fragments hydrogen-bonded in a hexagonal structure and hydrogen atoms bound directly to the metal. Refinements of this idea are needed, however, to make contact with measured vibration spectra. New understanding is also necessary to explain the occurrence of periodic adlayers on surfaces like Rh(111) and Pt(111), too unreactive to make dissociation energetically favorable, and to give meaning to beautiful STM images of water clusters obtained at LBNL on Pd(111). @FootnoteText@ @footnote 1@Work supported in part by the DOE Office of Basic Energy Sciences, Division of Material Sciences and Engineering. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

2:40pm **SS1-TuA3 Absence of Surface Water Crystallization**, **E. Backus**, **M. Grecea**, **A.W. Kleyn**, **M. Bonn**, Leiden University, The Netherlands

For the transition from amorphous solid water to crystalline ice, it has been proposed that the required hydrogen bond rearrangement may occur more readily for the less coordinated water molecules at the surface so that the amorphous-crystalline transition would be expected to nucleate at the solid-air interface. By simultaneously monitoring the phase state of the bulk and the surface passing through this transition, we demonstrate conclusively that crystallization commences in the bulk. In our experiments, water is deposited on a low-temperature Pt substrate by means of a molecular beam in Ultra High Vacuum (UHV), on which it forms a layer of amorphous solid water. By slowly heating the substrate, the water crystallizes. Using RAIRS (reflectance absorption infrared spectroscopy), we can follow the crystallization kinetics real-time, since the RAIRS spectra for crystalline and amorphous ice are very different. Hence by measuring RAIRS spectra while we are heating the crystal, we can deduce the spatially averaged, i.e. bulk fraction of crystalline ice in the water layer throughout the crystallization process. We can also determine surface fraction of crystalline ice in the water layer by monitoring chloroform desorption from the (partially crystallized) ice layer: the desorption of chloroform occurs at temperatures well below the water phase transition, and the desorption temperature from amorphous solid water and crystalline ice differ by 15 K. Therefore chloroform is a good probe for study the crystallinity of the surface of the water layer. In this manner we can correlate surface to bulk crystallinity. We find that the surface crystallinity is always lagging compared to the bulk. We can therefore unequivocally conclude that the crystallization of water nucleates in the bulk and not on the substrate-water interface or on the water-vacuum interface. We further find that initiation of the crystallization process (the nucleation grain) involves ~100 water molecules.

3:00pm **SS1-TuA4 Surface Science - A New Tool for Laboratory Astrophysics**, **M.P. Collings**, **J.W. Dever**, University of Nottingham, UK; **H.J. Fraser**, University of Leiden, The Netherlands; **M.R.S. McCoustra**, University of Nottingham, UK

The evolution of our galaxy, and that of others in the Universe, is subtly controlled by a combination of physics and chemistry. Molecules predate the galaxy and are found to play a key role in controlling the very processes that give birth to new stars, their planetary systems, and potentially the precursors of life itself. Astronomical observations can give us much detail as to the nature of these molecules but laboratory measurements are necessary to understand the physics and chemistry that lead to their

formation. Gas phase chemistry is important in this respect, but in recent years the molecular astrophysics community has come to realize that the interaction of the interstellar gas with solid grains plays a crucial role. Our laboratory effort has sought to apply surface science techniques and methodologies to understanding aspects of the gas-grain interaction. In particular, we will report on combined temperature-programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) measurements of the interaction of carbon monoxide (CO), carbon dioxide (CO@sub 2@) and molecular hydrogen (H@sub 2@) with vapour deposited ultrathin films of water (H@sub 2@O) ice under conditions that closely mimic those in the denser regions of the interstellar medium where stars are known to form. Results will be presented that demonstrate a complex interplay of surface diffusion, substrate morphological change, pore trapping of gases and desorption that modifies the simple model of the behaviour of these systems currently utilised by the molecular astrophysics community.

3:20pm **SS1-TuA5 Formation and Dynamics of Water Clusters on Ru(001)**, **M. Asscher**, Hebrew University, Israel

The adsorption kinetics of water on Ru(001) was simulated using molecular dynamics (MD) and equilibrium-model approach. The results nicely reproduce observations from STM imaging, work function change and IR measurements. The agreement with experimental results is based on the formation of stable clusters already at very low surface coverage and temperature. Tetramers are predicted to be relatively stable compared to smaller and larger clusters. The dipole moment per water molecule continuously decreases from 2.2D for the monomer down to 1.1D for pentamer and larger clusters. Dimers diffuse faster than monomers or larger clusters, in agreement with STM measurements. A unique mechanism for dimers diffusion is proposed. Photo-dissociation of H₂O/Ru(001) with 193nm photons support recent DFT calculations that claim thermal decomposition.

3:40pm **SS1-TuA6 Comprehensive Structural Analysis of H@sub 2@O/MgO(111) using DLD-LEED and IR Spectroscopy**, **D.A. Human**, **C.J. Hirschmugl**, University of Wisconsin-Milwaukee

The polar MgO(111) surface is predicted to be charged, and may dissociate water molecules or reconstruct to minimize its energy. Structural analysis using a powerful combination of Low Energy Electron Diffraction (LEED) and UHV infrared spectroscopy provides new insights into this water/oxide interface. A pico-ampere LEED study reveals a @sr@3x@sr@3 R30° structure, and IR transmission spectroscopy suggests the presence of OH and H@sub 2@O species. To perform the LEED study, a new instrument incorporating a delay line detector has been constructed to rapidly collect high-quality digital LEED images with low total electron exposures, thus reducing incident beam effects. The characteristics of the new LEED instrument and the structure and species identification of monolayer and bilayer water coverages will be discussed.

4:00pm **SS1-TuA7 The Growth of Water Monolayers on Pd(111)**, **T. Mitsui**, **E. Fomin**, **M.K. Rose**, **D.F. Ogletree**, **M. Salmeron**, Lawrence Berkeley National Lab, University of California at Berkeley **INVITED**

Using STM at low temperature we have followed the structures formed by water growing on a clean Pd(111) substrate. Starting with the monomers the process of cluster formation proceeds via formation of dimers, trimers and so forth. We found a surprising increase in diffusivity for the small clusters (2 to 4 molecules), which we attribute to mismatch between the cluster's structure and the substrate. Cluster mobility decreases substantially when the sizes is 5 and above. Continued adsorption of water results in the formation of honeycomb-like structures reminiscent of ice-like hexagonal bilayers. These structures are limited in size below 90K approximately, indicating kinetic limitations to the growth. Above 100K more extensive honeycomb structures are formed. Above 130K new structures with larger periodicity are formed. The observations will be discussed in light of recent wetting models involving the possible partial dissociation of the first water layer.

4:40pm **SS1-TuA9 The Surface Chelate Effect**, **R. Major**, **X.-Y. Zhu**, University of Minnesota

The adsorption of metal ions from a liquid phase to a molecularly functionalized solid surface is important in many disciplines, such as chemical sensing, environmental cleanup, protein purification, and "molecular beaker epitaxy". Few studies have investigated the kinetics and thermodynamics in adsorption at a such a liquid-solid interface. One distinguishing factor related to the coordination of metal ions to surfaces is that the surface functional groups can be arranged in a two-dimensional

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array. We set out to explore how this two-dimensional arrangement may lead to an inherent chelate effect, using the model system of Cu²⁺ ions adsorption on self-assembled monolayers of 16-mercaptohexadecanoic acid (MHA) on Au. The formation constant of Cu²⁺ with the MHA surface was found to be two orders of magnitude greater than Cu²⁺ with succinic acid or glutaric acid in aqueous solutions. Both of these molecules are known to chelate to metal ions forming 7 and 8-membered rings. The greater surface chelate effect is attributed to the presence of the two-dimensional array of ligands on the surface. We believe the surface chelate effect demonstrated here is of general significance to adsorption on functional surfaces and should depend strongly on chemical functionality and monolayer structure.

Surface Science

Room 327 - Session SS2-TuA

Surfaces and Interfaces of Semiconductors and Compound Materials

Moderator: A.A. Baski, Virginia Commonwealth University

2:00pm **SS2-TuA1 The Plasmons of ErAs (100)**, *H.K. Jeong¹, T. Komesu, P.A. Dowben*, University of Nebraska, Lincoln; *B.D. Schultz, C.J. Palmstrom*, University of Minnesota

Momentum resolved inelastic electron energy loss has been exploited to measure the surface and bulk plasmons of ErAs(100). The effects of the electronic band structure is seen in the weak plasmon dispersion. This is consistent with heavy mass of the states near the Fermi energy in the experimentally determined band structure. The ratio of bulk and surface plasmon energy is roughly 1. In both Hg@footnote 1@ and ErAs@footnote 2,3@ there are indications that the surface is significantly less metallic in character than the bulk. The behavior of the surface plasmon is related to the metallicity of the surface, @footnote 1@ so as with mercury thin films, @footnote 4@ the band structure of ErAs@footnote 2@ should strongly influence the surface and bulk plasmons. While there are a number of studies of the plasmons of simple metals, there are only a few studies of plasmons in 4f-5d systems, such as those undertaken from Hg thin films. @footnote 4@ @FootnoteText@ @footnote 1@P.A. Dowben, Surface Science Reports 40, 151 (2000) @footnote 2@H.K. Jeong, Takashi Komesu, P.A. Dowben, B.D. Schultz and C.J. Palmstrom, Physics Letters A 302, 217 (2002) @footnote 3@Takashi Komesu, Hae-Kyung Jeong, Jaewu Choi, C.N. Borca, P.A. Dowben, A.G. Petukhov, B.D. Schultz, and C.J. Palmstrom, Physical Review B 67, art. no. 035104 (2003) @footnote 4@B.-O. Kim, G. Lee, E.W. Plummer, P.A. Dowben and A. Liebsch, Phys. Rev. B 52, 6057 (1995).

2:20pm **SS2-TuA2 Growth Characteristics of ErAs Interlayers in Metal/Ga@sub 1-x@Al@sub x@As Heterostructures**, *B.D. Schultz, J.L. Hilton*, University of Minnesota; *K. Lüdge*, Technische Universität Berlin, Germany; *C.J. Palmstrom*, University of Minnesota

Properties of thin-film metal contacts grown on GaAs substrates have long been explored for electronic device applications. For modern spintronic applications, control of the interfacial properties and the reactions between ferromagnetic metals and semiconductors is important for optimizing spin dependent transport across these interfaces. ErAs interlayers, as thin as 5ML, have been used as diffusion barriers to drastically reduce interfacial reactions between Fe@sub 1-x@Co@sub x@ and GaAs for growth temperatures up to 225°C. However, surface segregation of both Ga and As are observed during the Fe@sub 1-x@Co@sub x@ growth and are related to the growth characteristics of the ErAs interlayer. In-situ scanning tunneling microscopy (STM) studies of ErAs films grown by molecular beam epitaxy (MBE) at 535°C show that ErAs initially nucleates as 3-4 monolayer high islands embedded within, rather than on top of, the GaAs(100) surface. These islands grow laterally in size until a complete uniform film is formed, whereby additional growth occurs in a layer-by-layer mode. X-ray photoemission spectroscopy (XPS) reveals both the presence of Ga and As atoms on the ErAs surface following the formation of a continuous layer and the continued segregation of these atoms to the surface during growth. The excess As atoms dissociate from the ErAs surface upon post-growth anneals above 450°C, and STM images show additional ordering of the ErAs surface following these anneals. Growth of ErAs on AlAs(200Å)/GaAs(100) heterostructures eliminates the segregation of Ga to the ErAs surface and results in no surface segregation

of Al atoms. This paper reports on the control of the growth modes and the surface composition of ErAs interlayers grown by MBE on Ga@sub 1-x@Al@sub x@As(100) surfaces as characterized in-situ by reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), STM, and XPS. Supported by ONR, DARPA, and NSF.

2:40pm **SS2-TuA3 Some Tricks in Photoelectron Diffraction Experiments for Structural Investigations at Surfaces**, *J. Osterwalder*, University of Zuerich, Switzerland

INVITED

A certain class of structural problems at surfaces is readily accessible to investigation by x-ray photoelectron diffraction (XPD). This is usually the case for surface and interface geometries where core levels of specific atoms can be singled out from the XPD spectrum that are located below the topmost atomic layer. Other atoms are thus placed in a forward scattering geometry, and their relative positions are exposed by the associated forward focussing peaks. Prominent examples for such geometries are multilayer epitaxial film growth or intermixing phenomena at interfaces. Yet, there are important structural problems where such forward scattering geometries are often absent, like the internal structure of a single monolayer film, the registry of the film with respect to the substrate, or the adsorption geometries of atomic adsorbates. Over the last several years, various tricks have been devised that expand the scope of XPD to this kind of problems: -(i) For O/Rh(111) it has been demonstrated that the weak backscattering off the substrate atoms can reveal the exact bonding site of the atomic adsorbate. Prerequisites are a high atomic number of the substrate material and low temperature. -(ii) For well ordered monolayer films, the internal film structure can be determined by measuring first and higher order diffraction fringes. This is exemplified by the system of hexagonal boron nitride (h-BN) on Ni(111) as well as several alkali monolayer systems on Al surfaces. -(iii) When a monolayer film is strictly commensurate with the substrate and well ordered, the film structure and registry can be extracted from XPD data of a substrate signal, measured with and without the monolayer present on the surface. The resulting difference data sets need to be compared to simulated data resulting from multiple scattering model calculations. Again, the case in point is h-BN on Ni(111).

3:20pm **SS2-TuA5 Synthesis and Characterization of an Ordered Ge Overlayer and Pt@sub 2@Ge Compound on Pt(100)**, *T. Matsumoto, M. Batzill, C. Ho, B.E. Koel*, University of Southern California

A c(2 x 2)-Ge overlayer and Pt@sub 2@Ge compound were formed by Ge deposition and annealing to 600 K on Pt(100) and characterized by Na@super +@-ALISS, XPD, LEED and STM. STM topographs and LEED patterns indicate a c(2 x 2) structure after 0.5-ML Ge deposition or 1.5-ML Ge deposition with annealing to 600 K. ALISS was used to unambiguously distinguish between the c(2 x 2) overlayer and surface alloy phases. This technique showed Ge-scattering angular peaks assigned to a large separation of Ge atoms along the [011] azimuth corresponding to a c(2 x 2)-Ge overlayer after 0.5-ML Ge deposition. Following 1.5-ML Ge deposition and annealing to 600 K, a new Ge-scattering angular peak appeared that was assigned to scattering from third-layer Ge atoms, however, no second-layer Ge scattering peak was observed. This structure is consistent with a body-centered tetragonal Pt@sub 2@Ge layer surface alloy which has alternating c(2 x 2) Ge-Pt and (1 x 1)-Pt(100) layers. XPD results also support this structural model. Annealing these surfaces to 900 and 1200 K resulted in partial dissolution of Ge atoms deeply into the bulk. XPS was also used to characterize the chemical nature of Ge and Pt at these surfaces.

3:40pm **SS2-TuA6 New Structural Model for Au/Si(111)5x2 from First Principles**, *S.C. Erwin*, Naval Research Laboratory

Gold induces quasi-1D reconstructions on several faces of silicon, including (111), (557), and (995). These systems have been widely studied for their unusual electronic properties, but the lack of any accepted structural model has hampered theoretical understanding and modeling of those properties. Here, a new structural model for Au/Si(111)5x2 is presented, based on first-principles density-functional calculations, which explains a number of experimentally observed features. The model is a variant of the "honeycomb-chain channel" now accepted as the structure of alkali-induced Si(111)3x1, but with Au atoms occupying top-layer Si positions to form a double chain structure. Energetically, the model is far more favorable than all previously published models. Moreover, the model explains the bright "protrusions" commonly observed in STM as single Si adatoms, which serve to stabilize the 5x2 reconstruction with respect to its 5x1 parent structure. The model also reproduces the "Y"-shaped features observed in STM far from the bright protrusions. Electronically, the

¹ Morton S. Traum Award Finalist

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predicted band structure is a combination of p-like cosine bands, consistent with angle-resolved photoemission measurements on the closely related Au/Si(557) surface.

4:00pm SS2-TuA7 First Principles Study of the Stability of Ag Ultra-thin Films on III-V Substrates: An Interfacial Study, D.L. Irving, S.B. Sinnott, University of Florida; R.F. Wood, Oak Ridge National Laboratory

Under normal deposition conditions, most metals grow on semiconducting and insulating substrates in either a Volmer-Weber or a Stranski-Krastinow fashion. However, recent experiments on Ag/GaAs(110) show that atomically flat Ag overlayers can be grown by use of a two-step deposition process. The final morphology of these films is not only dependent on the deposition temperature, but also on the amount of metal initially deposited. Quantum size effects have been proposed as the reason for the preferential stability of the metallic overlayer and a simple theory has been used to predict whether a material system will exhibit it. This study compares the adhesion energy trends predicted by this theory with those calculated by first principles density functional theory calculations. The first principles calculations are performed on both the Ag(111)/GaAs(110) and the Ag(111)/GaSb(110) interfacial systems. The results show how the stability and electronic structure of the Ag films changes as a function of film thickness.

4:20pm SS2-TuA8 A Self-Assembled Two Dimensional Electron Gas: @sr@7x@sr@3 In on Si(111), E. Rotenberg, H. Koh, Lawrence Berkeley National Laboratory; H.W. Yeom, Yonsei University, Korea; J. Schaefer, University of Augsburg, Germany; B. Krenzer, M. Rocha, S.D. Kevan, University of Oregon

We present low-temperature, high-resolution photoemission measurements of the Fermi surface and bandstructure of single-domain @sr@7x@sr@3 Indium on Si(111). Electrons from both indium valence electrons and the silicon dangling bonds form a nearly free, two-dimensional electron gas (2DEG) on a pseudosquare lattice, which is almost completely decoupled from the underlying hexagonal silicon lattice at the Fermi level. Structural analysis with LEED and photoelectron diffraction is consistent with the pseudo-four-fold structure, and rule out both pseudo-six-fold as well as triple (120°-rotated) domains which were reported in previous studies. About half of the Si dangling bond electrons are donated directly to the 2DEG, while the remainder form three bands -- confined to relatively small regions of k-space -- which we associate with In/Si covalent bond formation. The mean free path of carriers in the 2DEG is found to be at least 500 Å along the interface.

4:40pm SS2-TuA9 Buckling of Si and Ge(111)2x1 Surfaces, S. Nie, R.M. Feenstra, Carnegie Mellon University; J.Y. Lee, M.H. Kang, Pohang University of Science and Technology, Korea

The structure of cleaved Si or Ge (111)2x1 surfaces is well established as consisting of @pi@-bonded chains.@footnote 1@ However, the buckling (i.e. tilt) of these chains has been the subject of recent interest, primarily because a determination of buckling will enable a better comparison between optical absorption data and recent quasi-particle calculations of the surface bandgap and optical response.@footnote 2@ Based on such a comparison it has been suggested that the sign of the buckling may be opposite on Si and Ge surfaces.@footnote 2@ Recent voltage-dependent scanning tunneling microscopy results support that interpretation.@footnote 3@ although that data were restricted to a narrow range of voltages and were performed only on Ge (not Si). In the present work we have performed detailed voltage-dependent STM imaging of both Si and Ge (111)2x1 surfaces, over a wide range of sample-tip voltages. The results are compared with first-principles theoretical predictions, for both positive and negative values of the buckling angle. We find that the wide range of voltages used in the study enables a definitive determination of buckling. Our results demonstrate that the sign of the buckling is indeed opposite on Si and Ge surface, in agreement with the prior work.@footnote 2@ We furthermore deduce from a comparison of the experimental and theoretical STM images a comprehensive view of the image contrast mechanism, incorporating energy-dependent contributions from each atom in the unit cell. In particular, for empty states, the contrast shifts as the sample-tip voltage is increased from the lower atoms to the upper ones. @FootnoteText@@@footnote 1@ K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981); 49, 223 (1982).@footnote 2@ M. Rohlfing, M. Palumbo, G. Onida, and R. Del Sole, Phys. Rev. Lett. 85, 5440 (2000).@footnote 3@ R. M. Feenstra, G. Meyer, F. Moresco, and K. H. Rieder, Phys. Rev. B 64, 081306 (2001).

5:00pm SS2-TuA10 Dimer Structure of the Si(001)2x1 Surface Observed below 10K by Scanning Tunneling Microscope, M. Ono, A. Kamoshida, E. Ishikawa, T. Eguchi, Y. Hasegawa, The University of Tokyo, Japan

The dimer structure of the Si(001) surface has been discussed after recent low-temperature STM observations, which reported symmetric dimers at 5K. Various models to explain the observation contradictory to the previous reports, such as anomalous flip-flop dimer motion and new ground state induced by spin configuration, were proposed. To solve this issue, we studied it using an STM which can be operated under multiple extreme conditions of ultrahigh vacuum (>6x10@super -9@ Pa), low temperature (>2.8K), and high magnetic field (

Surface Science

Room 328 - Session SS3-TuA

Organic Functionalization of Semiconductor Surfaces

Moderator: J.J. Boland, Trinity College Dublin, Ireland

2:00pm SS3-TuA1 Adsorption of Substituted Butadienes on Si(100), L.C. Teague, University of North Carolina at Chapel Hill, Ireland; J.J. Boland, Trinity College Dublin, Ireland

Current interest in the addition of small organics to the Si(100) surface is driven by their potential applications in "bottom-up" fabrication methods. The ability to strategically place and/or manipulate individual molecules into functional structures on surfaces has potentially important implications for molecular electronics.@footnote 1,2@ Although several studies have focused on these types of reactions, it is evident from our previous work with 1,3-cyclohexadiene (1,3-CHD)@footnote 3@ that these reactions are more complicated than originally assumed. STM studies of other organics such as 2,3-dimethyl-1,3-butadiene (DMBD) and 2,3-dimethoxy-1,3-butadiene (DMeOBD) on Si(100) can provide additional information about cycloaddition reactions. Both systems are similar to 1,3-CHD in that they are systems of 4@pi@ electrons, therefore possessing the same reaction possibilities as 1,3-CHD, however they are chain-like rather than ringed structures. Reaction products for DMBD and DMeOBD can be characterized in the same manner as those of 1,3-CHD, i.e., via the location of the remaining C=C bond in the adsorbed molecule. We present a study of the reactions of DMBD and DMeOBD on Si(100), and contrast both the appearance and attachment geometry for reaction products of DMBD and DMeOBD with those of cyclic molecules like 1,3-CHD. Several initial differences between 1,3-CHD products and those of DMBD and DMeOBD are reported, including the presence of dimer buckling induced on the surface after exposure to DMBD and DMeOBD. Different attachment geometries available to chain-like molecules such as DMBD and DMeOBD are shown to account for the dimer buckling observed on the surface. @FootnoteText@@@footnote 1@ Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. Nature, 2000, 406, 48; Bent, S. F. Surf. Sci. 2002, 500, 879, and references therein.@footnote 2@ Whitesides, G. M.; Love, C. J. Sci. Am. 2001, 285, 39.@footnote 3@ Teague, L. C.; Boland, J. J. J. Phys. Chem. B 2003, 107, 3820.

2:20pm SS3-TuA2 Surface Chemistry of Conjugated Heteroatomic Compounds on Diamond and Silicon (100), J.N. Russell, Naval Research Laboratory; M.P. Schwartz, University of Wisconsin; D.E. Barlow, J.E. Butler, Naval Research Laboratory; M.P. @ag D@Evelyn, GE Global Systems; R.J. Hamers, University of Wisconsin

Diamond and silicon (100)-2x1 surfaces are comprised of dimers linked by a @sigma@ bond and a highly-strained @pi@ bond, but there are notable differences in their structure and chemical reactivity. Using multiple internal reflection infrared spectroscopy, the surface chemistry of conjugated heteroatomic compounds was examined on diamond and silicon (100). Acrylonitrile chemisorbed on diamond via a [2+2] cycloaddition reaction, resulting in a product spectrum similar to that of chemisorbed CD@sub 3@CH=CH@sub 2@. In contrast, acrylonitrile reacts through the nitrile group on Si(100). Cyclohexanedione, which easily tautomerizes into a keto-enol in the gas phase, maintains the enol structure when adsorbed on diamond, but chemisorbs on silicon as the diether, i.e. the [4+2] reaction product. We will examine the role of ring strain, electron donating and withdrawing groups, and dimer tilt on the adsorption probability and structure of the chemisorbed species.

2:40pm SS3-TuA3 Reaction of Acetyl Chloride on Ge(100)-2x1: Formation of a Surface-bound Carbonyl, M.A. Filler, S.F. Bent, Stanford University

Since the introduction of vacuum-based organic functionalization of group-IV semiconductor surfaces, there has been considerable interest in

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attaching molecules beyond the initial monolayer. However, functional groups that are expected to be reactive in second layer reactions, such as amines and ketones, also react directly with the bare semiconductor surface. It is therefore necessary to protect these groups during the deposition of the initial layer or use a molecule where other pathways can kinetically compete and leave the reactive moiety intact. To this end, we have studied the reaction of acetyl chloride on Ge(100)-2x1 at 300K with infrared spectroscopy, temperature programmed desorption, and density functional theory. Infrared spectra show a strong $\nu(\text{C}=\text{O})$ stretching peak near 1680 cm^{-1} and no vibration modes in the $\nu(\text{Ge}-\text{H})$ region indicating that Cl dissociation to produce a surface-bound carbonyl is the dominant reaction pathway. TPD results provide additional evidence of this surface product; ketene evolves near 525K while at higher temperatures H_2 , HCl, and GeCl_2 desorb. DFT calculations predict that the barrier to Cl dissociation is only 1 kcal/mol above a chlorine dative-bonded state and is considerably smaller than that of any other reaction pathway. All of this data is strong evidence for a Cl dissociation reaction leaving a surface-bound carbonyl, which is expected to be more reactive toward second layer attachment chemistries and possibly enable layer-by-layer deposition of ultrathin organic films.

3:00pm **SS3-TuA4 Diethyl Ether Reactions with the Si(100) Surface**, *S.M. Casey*, University of Nevada, Reno

The interactions of diethyl ether with the Si(100) surface have been examined computationally, using ab initio and density functional theoretical techniques, as well as experimentally, using Auger electron spectroscopy and thermal desorption spectroscopy. This surface appears to be relatively inert with respect to reaction with the ether functional group. The reaction paths available to diethyl ether on Si(100) can be contrasted to the interactions of this surface with alcohols and amines, both of which can undergo facile addition reactions upon interacting with this surface. The interactions of ether molecules containing additional, more reactive functional groups, such as a C=C bond, with the silicon surface will also be discussed.

3:20pm **SS3-TuA5 Modification of Silicon Surfaces: Toward Functional Organic and Bioorganic Interfaces**, *B. Fabre*, National Research Council of Canada; *G.P. Lopinski*, National Research Council of Canada, Canada; *D.D.M. Wayner*, National Research Council of Canada

INVITED

Over the last decade there has been increasing awareness of the opportunities presented by the convergence of surface science and organic chemistry. This work is underpinning the development of revolutionary concepts for the design of molecular scale devices and for the integration of solid state, inorganic structures with biologically active interfaces. Although the reactions of organic molecules with silicon surfaces are not new, this area which traditionally has been dominated by physical scientists has increasingly been influenced by organic and bioorganic chemists. This organic perspective has brought new levels of complexity of structure and function and greater understanding of the molecular basis of reactivity. Much of the work so far has focused on exploring the scope of the chemistry and on understanding the structure and quality of the organic-silicon interfaces. An example is the reaction of hydrogen-terminated silicon with styrene that proceeds as a chain reaction on the silicon surface. We have developed simple chemical approaches to introduce essentially any chemical function at the ends of Si-alkyl monolayers. Most recently, we are developing strategies to pattern silicon surfaces with biologically active molecules such as proteins and DNA as well as with conducting polymers (polythiophene). A few simple devices have been prepared using electrochemically grafted polythiophene as a top contact. I will describe the preparation as well as the electrochemical and electrical characterization of these simple metal-insulator-semiconductor structures

4:00pm **SS3-TuA7 Investigation of the Adsorption of Acetic Acid on Ge(100)-2x1**, *J.A. Van Deventer*, *M.A. Filler*, *S.F. Bent*, Stanford University

The modification of group-IV semiconductor surfaces has been an active area of research over the past several years because a greater understanding of semiconductor surface reactivity may lead to applications in nanopatterning, biological recognition, and molecular electronics. In the present work, we investigate the reaction of acetic acid and related isotopes on Ge(100)-2x1 at 300K using infrared spectroscopy and density functional theory. This reactive system is noteworthy because it combines the carbonyl and alcohol functional groups studied in previous investigations into one bifunctional molecule, allowing competition and selectivity to be studied in detail. IR spectroscopy following chemisorption of acetic acid shows a strong absorption at 1664 cm^{-1} in the $\nu(\text{C}=\text{O})$ region and two large peaks at 1962 and 1925 cm^{-1}

in the $\nu(\text{Ge}-\text{H})$ region. We attribute these features to intradimer and interdimer O-H dissociation products. DFT calculations suggest that these O-H dissociation products are likely to occur through one of two oxygen dative-bonded states. Interestingly, the more stable dative-bonded precursor state is the result of a stabilized ring formed by electron donation from the nucleophilic dimer atom to the nearby hydroxyl hydrogen atom of the adsorbed molecule. The kinetic barrier to reaction of this pathway is calculated to be 3.09 kcal/mol above the dative-bonded state, leading to a final product that lies 39.52 kcal/mol below the vacuum level. The O-H dissociation product is both kinetically and thermodynamically favorable compared to the other pathways, such as $\alpha\text{-CH}$ dissociation and [2+2] C=O, available to the molecule.

4:20pm **SS3-TuA8 Electron Beam Effect of Diethylsilane on Si (100) Surfaces Investigated by TPD and LISD**, *P. Wang*, *J. Lozano*, *K. Kimberlin*, *J. Craig*, Bradley University

Various coverages, from 0.03 to 5.0 L, of diethylsilane (DES) on Si (100) surfaces at 100 K were bombarded by 600 eV electrons and the effect of electron on DES/Si(110) system was investigated by using Temperature Programmed Desorption (TPD) and Laser Induced Stimulated Desorption techniques. Laser photons from Nd:YAG were used in LISD technique. TPD and LISD spectra were immediately taken after each dosing and compared to the spectra after the system was irradiated by 600 eV electrons. Desorption of physisorbed species of mass 2, 28 and 59 species was seen at 130 K after coverages of DES larger than 0.07 L. However, mass 2 and 28 species were also thermally desorbed at 810 and 770 K, respectively. Desorption peak areas of mass 2, 28, and 59 with and without electron/photon bombardment were investigated as functions of coverage and electron/photon fluences. It was found that the carbon hydrides were removed from surface after both electron and laser photon radiation. The concentration changes in desorption species in TPD and LISD beam dissociation effects as well as beam induced state will be discussed.

4:40pm **SS3-TuA9 Adsorption of Naphthalene on a Si(100)-2x1 Surface Investigated by Infrared Absorption Spectroscopy**, *K. Okamura*, *H. Ishii*, *Y. Kimura*, *M. Niwano*, Tohoku University, Japan

Recently, adsorption of organic molecules on a Si surface has attracted a lot of interest in relation to possible application to organic-inorganic hybrid devices. Understanding of the adsorption process is required for the control of the structural and electrical properties of the interface between organic and inorganic materials. In this study, the adsorption of the naphthalene molecule, with two benzene-like rings fused together, onto the Si(100)-2x1 surface was investigated using infrared adsorption spectroscopy in the multiple internal reflection geometry. To determine the most preferred adsorption structure of naphthalene on Si(100)(2x1) at room temperature, we have carried out cluster calculations based on the hybrid density-functional theory (DFT), and compared the calculated C-H vibration frequencies with the experimental ones. The central result is that naphthalene adsorbs in different manners depending on the surface coverage of naphthalene, which is the same trend as observed for the adsorption of benzene on Si(100)(2x1). At low coverage the molecule adsorb in the bridging manner between two adjacent dimers. On the other hand, at high coverage the molecule adsorb on the Si surface so as to reduce the repulsive interaction between two adjacent naphthalene molecules adsorbed on the same dimer row. We discuss the reason why the adsorption structure depends on surface coverage, in comparison with the results of cluster calculations.

5:00pm **SS3-TuA10 Vapor-phase Adsorption Kinetics of 1-Decene on H-terminated Si(100)**, *M.R. Kosuri*, *H. Gerung*, *Q. Li*, *S.M. Han*, University of New Mexico; *B.C. Bunker*, *T.M. Mayer*, Sandia National Laboratories

We have investigated in situ and in real time the vapor-phase self-assembly of 1-decene on Si, using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS). The adsorption of 1-decene on hydrogenated Si(100) results in an alkane terminated hydrophobic surface. The sessile drop water contact angle after the self-assembly of 1-decene is $107 \pm 2^\circ$. The absolute saturation coverage of decane is approximately $3.2 \times 10^{14} \text{ cm}^{-2}$ based on the IR absorbance of C-H stretching vibrational modes near 2900 cm^{-1} . We also report the adsorption rate constant of 1-decene on hydrogenated Si(100) at 160 °C under 30 mTorr of vapor-phase 1-decene. The adsorption rate constant based on a Langmuir isotherm is $1 \pm 0.1 \text{ Torr}^{-1} \text{ min}^{-1}$. The estimated thickness of the decane monolayer, determined by X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry, is approximately 16 Å. Monitoring the decane monolayer over a period of 2 months using XPS has shown that the silicon surface underneath the

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decane monolayer gets oxidized with time, leading to the degradation of the decane layer.

Tuesday Evening Poster Sessions, November 4, 2003

Surface Science

Room Hall A-C - Session SS-TuP

Poster Session

SS-TuP1 Ultrastable Besocke Type Scanners, N. Pertaya, K.-F. Braun, K.H. Rieder, Freie Universit@um a@t Berlin, Germany

A widespread used construction for the coarse approach mechanism in scanning probe microscopy is the Besocke beetle type. Using stick-slip motion the scanner can thereby be positioned on the nm scale covering usually a range of several mm horizontally and vertically. This apparent advantage of a high flexibility is bought on the expense of a reduced mechanical stability. Mechanical resonances around one kHz are attributed to so-called rattling modes (dependent on the contact forces between moving and fixed parts), other modes result from the scanner itself, and limit the performance of the microscope. @footnote 1@ Here we present a detailed analysis of the vibrational response of a beetle type scanner and based on this a very stable optimized scanner setup. Three scanners were assembled using different type of and differently dimensioned piezoceramics. Type (a) and (b) are using tube piezos of different length and thickness. Covering the same scanning area the overall size was reduced and the lowest measured mechanical resonance shifted from 300 to 900 Hz. In a recent setup (c) shear stack piezoelectric elements (PI - ceramics) were used, which resulted in a shift of the lowest resonance frequency to 6 kHz. Freshly cleaved graphite surface was imaged using a mechanically cut golden tip. Typically atomic-resolved images obtained under ambient conditions show a triangular lattice or a honeycomb array respectively. @FootnoteText@ @footnote 1@ S. Behler, M.K. Rose, D.F. Ogletree, M. Salmeron, Rev. Sci. Instr. 68, 124 (1997).

SS-TuP2 Studying Surface Phenomena by Pulsed Heating of Microdevices, O.C. Thomas, R.E. Cavicchi, S. Semancik, National Institute of Standards and Technology

MEMS microheater devices have been operated with periodic (2-40 Hz), short duration (5ms) temperature pulses to investigate the relationship between surface adsorbate concentrations and surface electronic behavior of high surface area, oxide films. Tin oxide films were grown by CVD on microscale (40 μm X 100 μm), thermally isolated bridge structures that possess embedded polysilicon heaters and surface electrodes. These structures permit the rapid thermal cycling and real time conductometric measurement of the deposited oxide films. In air devoid of reducing analyte, the application of short, high temperature (500°C, 5 ms) heating pulses results in the generation of surface bound O@super -@ from surface adsorbed O@sub 2@, and as a consequence a tin oxide film that is both highly resistive and highly sensitive to reducing gases. Exposure of such a film to trace concentrations of reducing gas results in large conductometric changes (from 1x10@super -7@ @OMEGA@@@super -1@ in dry air to 2.5x10@super -4@ @OMEGA@@@super -1@ in 10 ppm MeOH; measured at 25 °C). In the presence of reducing gases, the heating pulses activate the titration of the surface bound O@super -@ by the reducing species. Modulating the period between heating pulses from 25 ms to 500 ms reveals an increase in room temperature conductance, which is interpreted in terms of the adsorption dynamics of the reducing species. Results on a number of reducing gases show conductance vs. period profiles, which may be explained in terms of both molecular adsorption dynamics and stoichiometric capacity for reduction. These results provide a basis for analyte recognition and a level of mechanistic insight about interfacial transduction processes.

SS-TuP3 A Novel Study using XANES Spectroscopy, XPEEM, and Nanomechanical Techniques to Correlate the Microchemistry and Nanomechanical Properties of Zinc-dialkyldithiophosphate Tribofilms on Steel Surfaces, M.A. Nicholls, P.R. Norton, M. Kasrai, G.M. Bancroft, The University of Western Ontario, Canada; T. Do, Atomic Energy of Canada; G. De Stasio, The University of Wisconsin, Madison

Additives with special functions have long been components of engine oils, designed to improve the performance and prolong the life of an engine. One particular additive, zinc-dialkyl-dithiophosphate (ZDDP) has been added to improve the lifespan of an engine by reducing wear at high pressure contacts. ZDDPs have been found to break down under the extreme conditions in an engine and produce products that, under high pressure and temperature, form a sacrificial polyphosphate film that reduces wear. This film has been studied thoroughly for decades, but the origins of its effectiveness still remain a mystery. Advanced synchrotron

radiation techniques such as X-ray absorption near edge structure (XANES) spectroscopy and X-ray photoelectron emission microscopy (XPEEM), are now providing the detailed chemical and spatially resolved chemical analysis required to help understand how these films form. In combination with nanoindentation techniques, it is now possible to measure the chemical and nanomechanical properties of these films on the same length scales. We describe how XANES can determine the polyphosphate chain-length in a film, and also illustrate the interaction of ZDDP decomposition products with steel surfaces. Further, XPEEM and nanoindentation have been used to correlate, for the first time, the spatially-resolved chemistry and mechanical properties of the same, selected regions of an antiwear film at a resolution of approximately 200 nm.

SS-TuP4 Monosaccharide Adsorption on Hydrophobic and Hydrophilic Surfaces, J.W. Clemens, M.A. Cobleigh, K.T. Queeney, Smith College

The adsorption of encapsulated bacteria to both natural and synthetic surfaces is governed by extracellular polysaccharides. In order to gain insight into the interactions of these large starch molecules with such surfaces, and specifically to separate out effects of their primary and secondary structure, we have undertaken a comprehensive study of the adsorption properties of the constituent monosaccharides of xanthan gum, a model bacterial polysaccharide. A combination of surface infrared spectroscopy and atomic force microscopy is used to investigate the adsorption properties of glucose, mannose and glucuronic acid on silicon and functionalized silicon surfaces. Access to the full mid-IR frequency range allows us to analyze both the OH-stretching region, in order to probe the role of hydrogen-bonding in adsorption, and the fingerprint region of the molecules, which is more sensitive to configurational changes in the molecules upon adsorption. Combining this information with AFM images allows us to correlate spectroscopic signatures associated with sugar-surface and sugar-sugar interactions.

SS-TuP5 Effect of Multidirection Ion Beam Treatment and Alignment Property of Nematic Liquid Crystal, S.J. Rho, H.J. Ahn, K.C. Kim, H.K. Baik, J.Y. Hwang, Y.M. Jo, C.J. Park, D.S. Seo, Yonsei University, South Korea; K.M. Song, Konkuk University, South Korea; S.J. Lee, Kyungsoong University, South Korea

We have investigated the alignment properties of liquid crystals induced by multi-directional ion beam irradiation on the a-C:H films. Ion beam treatment of alignment layer is the new method which does not contact with alignment layer and prevent from debris or electrostatic discharge. Amorphous carbon (a-C:H) films for alignment layer were deposited by remote plasma enhanced chemical vapor deposition and were modified by an Ar ion beam at an films. For the multi-domain of LCD, the direction of ion beam exposure was changed about 0deg, 90deg, 180deg, 270deg and at each step, ion beam is overlapped. It is experimentally found that the aligning direction of the liquid crystal depend on the final irradiating direction of ion beam and by these results, we analyzed the structural transition of a-C:H layer after ion beam irradiation. Raman, IR, and AFM data were used for analysis of these phenomena. Also we prove the merit of ion beam method, which decrease the masking step for multi-domain of LCD manufacturing.

SS-TuP6 Dynamic Mechanical Analyses of Polymers, T.J. Mullen, U.S. Naval Research Laboratory; S.A. Syed Asif, Hysitron, Inc.; K.J. Wahl, U.S. Naval Research Laboratory

Thin polymer films are of considerable interest for applications in electronics packaging, biomedical devices, MEMS devices, lubrication, antifouling and adhesives. However, evaluating the mechanical properties of polymer thin films is difficult due to the low elastic moduli and substrate influence. In this paper, we present an approach for measuring the dynamic mechanical properties of thin, compliant polymer films using AC force-modulation coupled with a hybrid scanning indenter. This combination allows surface sensitive, quantitative mechanical properties measurements at a single point as well as while scanning. Dynamic response of the indenter is monitored during tip-sample approach, enabling sensitive detection of the surface, and during contact for evaluation of storage and loss moduli of polymer samples. Examples of dynamic mechanical properties analyses using force-displacement curves, frequency sweeps, and imaging will be presented for polyethylene, poly(dimethylsiloxane) (PDMS) and other polymer surfaces.

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SS-TuP7 Patterning and Selective Metallization of Polymer Films Bearing Chloromethylphenyl Groups, *W.J. Dressick, M.-S. Chen, T.L. Schull, S.L. Brandon*, Naval Research Laboratory

The ability to spatially control polymer surface reactivity without affecting bulk properties for the selective deposition of materials, such as metals, ceramics, or other chemical and biological species, is critically important for microelectronics, optics, and sensor technologies. We have been investigating the top-surface imaging of thin polymer films containing surface chloromethylphenyl groups to address this challenge. Recently we demonstrated that solvent-templated nanocavities could be formed in chloromethylphenyl-based films that are capable of non-covalently binding reactive adsorbates. Exclusion of the adsorbate from aqueous solution and binding within the film nanocavity are driven by favorable hydrophobic interactions between the adsorbate and the aromatic residues of the polymer film. Spatial control of adsorbate entrapment is demonstrated using a variety of patterning tools (e.g., microcontact printing, deep UV, proximity x-ray, high-energy e-beam, and low voltage scanning tunneling microscope) to selectively inhibit entrapment through chemical modification of the films or displacement of entrapped adsorbate from film nanocavities. Spatial control of adsorbate binding allows the subsequent selective deposition of Pd-based catalytic nanoparticles of controlled size for electroless metal deposition. Fabrication of nanoscale structures in metal with good control of feature critical dimensions is demonstrated. Details of the largely aqueous based process will be presented and factors contributing to feature critical dimensions and optimization of ligand physisorption will be discussed.

SS-TuP8 Surface Lattice Dynamics of KCl(001) by Helium Atom Scattering, *R. Fatema*, Florida State University; *F.A. Flaherty*, Valdosta State University; *S.A. Safron, J.G. Skofronick, D.H. Van Winkle*, Florida State University

High-resolution helium atom scattering (HAS) has been employed to investigate the surface lattice dynamics of the KCl(001) surface, produced by cleaving a single crystal sample in ultra high vacuum (UHV). Several branches of the surface phonon dispersion have been mapped out in the and high symmetry directions, across the surface Brillouin zone (SBZ). These include the low-energy Rayleigh wave, a "crossing mode" which increases in energy from the SBZ boundary to the zone center, and optical modes which appear dispersionless across the SBZ. These results are compared with "shell model" calculations and with experimental results, which were reported previously. The implications of these results for the use of KCl(001) as a substrate for films of soft materials is also discussed.

SS-TuP9 The Effect of Water Vapor on the Surface Composition of Alkali Halides, *S. Ghosal*, University of California, Irvine; *F.G. Requejo*, University of La Plata and CONICET., Argentina; *D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory; *J.C. Hemminger*, University of California, Irvine

We present here results from our studies on the aqueous ionic solvation of alkali halide surfaces. Using a novel high pressure X-ray Photoelectron Spectroscopy (XPS) system based on the ALS synchrotron radiation source we have for the first time made direct experimental measurements of the surface composition of alkali halide crystals while in contact with water vapor pressures approaching and at the point of dissolution. The salt crystals were cleaved in vacuum and then analyzed by XPS as the water vapor pressure was increased. Our results show that the anion/cation ratio at the interfacial region initially decreases with increasing water vapor pressure. At higher water vapor pressures, approaching the dissolution point of the salt, the surface composition behavior varies depending on the particular salt. These results are further supported by Scanning Polarization Force Microscopy experiments. The primary focus of the study was to determine the structure and composition of the interfacial region between the salt and air as a function of water vapor exposure. This is of particular interest since the solid/vapor interfacial composition of salt solutions and salt particles has implications for heterogeneous atmospheric chemistry involving sea salt aerosols. @footnote 1@ @FootnoteText@ @footnote 1@Finlayson-Pitts, B. J.; Hemminger, J. C. J. Phys. Chem. 2000, 104(49), 11463.

SS-TuP10 Secondary Phases on Oxide Surfaces, *C.B. Carter, S.R. Gilliss*, University of Minnesota

The wetting of a ceramic surface by a secondary phase is a technologically relevant problem that is encountered under many situations. Processing of ceramics using liquid-phase sintering relies on the wetting of the ceramic powder compact by a lower melting additive. The additive may be a non-metallic glassy phase, as in oxide ceramics, or can be a liquid metal as in the case of Co additives for WC ceramics. The wetting of ceramics by liquid

metals is also encountered in joining applications like active metal brazing. Wetting and dewetting of liquid metals and glasses on ceramic substrates has been investigated using a combination of microscopy techniques. The influence of surface structure on dewetting behavior and the influence of the dewet droplets on the morphology of surface steps has been shown with the aid of experimental observations from many systems. The role of chemistry and kinetics on the wetting behavior will also be discussed. The manner in which the secondary phase wets the crystalline ceramic at processing temperatures dictates the microstructure and therefore the properties of the material. Model systems of anorthite and sapphire and silica and rutile will be emphasized. Thin films (100 nm) of the secondary-phase (anorthite or silica) are deposited onto a single-crystal substrate of sapphire or rutile by pulsed-laser deposition. The specimens are then heat-treated in air at high temperature (1400°C-1650°C). At high-temperature and during cooling steps and facets form on the oxide surface and the secondary-phase may dewet or continue to wet the surface. The effect of the secondary-phase on the kinetics of step/facet formation and an analysis of the wetting behavior will be presented. The degree of dissolution and reprecipitation of the substrate material within the secondary phase has been monitored by X-ray energy dispersive spectroscopy and electron energy-loss spectroscopy and will be discussed.

SS-TuP11 Evidence of Surface Pre-melting of Bi Ultrathin Film on Si(111), *S. Yaginuma*, Tohoku University, Japan; *T. Nagao*, Tohoku University and PRESTO, JST, Japan; *J.T. Sadowski, Y. Fujikawa, T. Sakurai*, Tohoku University, Japan

Semimetal bismuth has attracted much attention because of its various unique transport properties. Recently, we have successfully fabricated high-quality Bi (001) films on the Si (111)-7x7 substrate. The Bi (001)/Si (111) system self-organized into an atomically flat single crystal Bi (001) film, experiencing the unique orientation flipping from interconnected close-packed Bi {012} films to the two-dimensional (2D) Bi (001) films, which then grew into a nearly perfect uniform film by layer by layer growth. Temperature-dependent spot-profile-analysis low-energy electron diffraction (SPA-LEED) study revealed that suitable annealing of the as-deposited Bi (001) films resulted in an increase of the peak intensity and a change in the spot profile, marked improvement in the crystallinity and surface roughness. The resulting surface was ideally flat over the ~100 nm range. With this ideal 2D system, we further performed the systematic SPA-LEED experiment as a function of annealing temperature and estimated the surface Debye temperature to be approximately 90 K. In addition to the expected Debye-Waller decrease, a steeper decrease in the spot intensity was observed above 350 K in a reversible manner without hysteresis. Since the separate in-situ STM observations have clarified the decrease in step density, this anomalous thermal behavior of the diffraction peak intensity is attributed to the surface pre-melting instead of the surface roughening. By fitting the data with the logarithmic growth law, the correlation length of this phase transition was determined within the length of one bilayer. Negligible thickness dependence reflects the layered structure of Bi with mobile bilayer stacking. A possible mechanism of the surface pre-melting of the Bi (001) films will be discussed.

SS-TuP12 Crater Wall Shape Evolution During Annealing Induced Flattening of Si(001), *B.J. Gibbons, J.P. Pelz*, The Ohio State University

We have studied high temperature annealing induced flattening of large (up to 50 μm @super 2@) "craters", formed using a new double wet thermal oxidation process on silicon (001). This process was used to eliminate the initial "trenching" around the perimeter of the crater floor that can occur during normal dry etching procedures. It has been suggested that such trenching can interfere/delay the process of flattening.@footnote 1@ Surprisingly, we have found that trenches are formed during extended annealing even if not initially present, as well as a "peak" around the upper crater wall perimeter. Above the roughening temperature (~ 1200 °C for Si(001)) the profile of the crater wall can be described using a continuum model.@footnote 2@ For temperatures below roughening the trench and peak features can be qualitatively described using microscopic step models,@footnote 3@ although a good quantitative description has not yet been achieved. To date we are able to remove the initial sample miscut over an area of up to 30 x 40 μm @super 2@, leaving behind a region with concentric closed steps formed by pit nucleation.@footnote 4@ We will discuss the optimum conditions for creating large flat regions "blindly", as well as ongoing electromigration experiments in the presence of a Si flux. @FootnoteText@@footnote 1@Tanaka, et al., Appl. Phys. Lett., 69(9), 26 Aug. 1996 @footnote 2@W.W. Mullins, J. Appl. Phys. 28(3), Mar 1957 @footnote 3@Liu, et al., J.

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Vac. Sci. Technol. B 14(4), Jul/Aug 1996) @footnote 4@J.-F. Nielsen, et al., Phys. Rev. Lett. 87(13), 24 Sep. 2001

SS-TuP13 Structure-optimized CoSi@sub 2@-buried-metal-layer Substrates for IRRAS Fabricated by Wafer-bonding, S. Yamamura, The Graduate University for Advanced Studies, Japan; S. Yamauchi, DENSO Research Laboratories, Japan; S. Watanabe, Fujitsu Laboratories Ltd., Japan; T. Urisu, Institute for Molecular Science, Japan

The conventional IRRAS (infrared reflection absorption spectroscopy) is applicable only for the metal substrates. So, the IRRAS using buried metal layer (BML) substrates has been developed to apply this technique to the semiconductor surfaces. To obtain high sensitivity in BML-IRRAS, it is essentially important to control the top Si layer thickness less than 200 nm. In this work, we have successfully fabricated a BML substrate with 200 nm thick top Si layer by wafer-bonding for the first time using a SOI wafer having controlled thickness (260 nm) of Si layer. Comparing with the ion implantation method, the wafer bonding method has advantages of (1) atomically flat top Si surface, and (2) unnessariness of epitaxial growth process, which is essentially required in the ion implantation method to remove the ion implantation damage. The fabrication process is as follows; (1) overlapping of a Co (~ 200 nm thickness) deposited Si wafer on the SOI wafer with face to face, (2) annealing at 800°C for 30 min under N@sub 2@ atmosphere, (3) polishing of the back side Si layer of SOI to ~ 100 nm, followed by complete removal by 10 % KOH solution etching at 70°C for 3 ~ 4 h, and (4) the residual top SiO@sub 2@ layer was removed by etching using 2.5 % HF solution, and the Si(100)/CoSi@sub 2@/base Si(100) BML substrate was obtained. The preliminary formation of thin (100 nm) SiO@sub 2@ layer on the SOI surface was effective to reduce the interface roughness between the top Si and the CoSi@sub 2@ layers. The self-assembled alkyl monolayer was deposited on the BML substrate, and its IRRAS was observed in the wide frequency range from stretching to bending regions.

SS-TuP14 Relating Polarization to Optical Absorption and Ablation of Silicon/Silicon Oxide Surfaces, Y.N. Picard, H. Liu, J.C. Pentland, J.P. MacDonald, J. Nees, G. Mourou, S.M. Yalisove, University of Michigan, Ann Arbor

A significant benefit of machining materials using lasers with pulse lengths on the order of femtoseconds, rather than nanoseconds or picoseconds, is the reduced size of the damage region associated with the machined areas. However, depth of absorption, absorption mechanisms, and nano-scaled modifications of the near surface are still not fully understood and characterized when machining at or just below the ablation threshold of the material using femtosecond lasers. The direction of the laser electric-field vector relative to the sample surface is estimated to be directly proportional to the magnitude of optical absorption, and as a consequence, the ablation threshold of the material. Our recent studies have demonstrated a factor of 3 difference in the estimated ablation threshold for S versus P polarization (referenced to the sample surface plane) when machining silicon at grazing incidence (86°) in air. We extend these studies to grazing incidence machining of silicon with no native oxide on the surface as well as silicon with different oxide thickness, all under vacuum. We use a Ti:sapphire laser with 800 nm wavelength, 120 femtosecond pulses to irradiate the surface at both S and P polarizations. The intensity of the laser irradiation ranges from below to above the ablation threshold for silicon (~200mJ/cm@super 2@). We present results from clean Si (native oxide removed by HF etching or Shiraki method) as well as those from Si with a native oxide and thermally grown oxide layers. Samples are machined inside a vacuum chamber capable of reaching a pressure of 10@super -11@ Torr. For silicon samples with no oxide present on the surface, surface structure during irradiation is monitored using reflected high energy electron diffraction (RHEED). SEM and AFM results show differences in the size and morphology of the damage region, which are then correlated to the ablation threshold.

SS-TuP15 Controlling Silicon Surface Morphology with Aqueous Etching: The Surprising Effect of Barriers, H. Bao, S.P. Garcia, M.A. Hines, Cornell University

For reasons that are not completely understood, nanoscale surface morphology can influence the electronic, chemical and mechanical properties of a variety of devices. Thus, the ability to fabricate atomically smooth micron-scale regions of silicon would be beneficial to many technologies. In this research, we use chemical etching to force the atomic height steps on a vicinal surface bunch into "macrosteps" -- micron-high macroscopic steps that separate terraces of near-atomic flatness. Interestingly, we find that the orientation of the macrosteps does not

always correspond to the vicinal step direction. Instead, the orientation of the macrosteps can be controlled by lithographically patterned etch barriers. A variety of surface morphologies created by the barriers are presented and characterized by a combination of optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). In some cases, the patterned barriers lead to large, nearly atomically flat regions. In other cases, macrosteps are curved and oriented by the barrier structure.

SS-TuP16 Low-Dimensional Plasmons in a Metallic Strip Monolayer on a Semiconductor Surface, T. Inaoka, Iwate University, Japan

The Si(111)-@sr@3x@sr@3-Ag surface can be formed by depositing one monolayer of Ag atoms on a Si(111)-7x7 surface. One of the surface-state bands at this surface provides an ideal two-dimensional system of conduction electrons (2DES). The 2DES is confined in a @sr@3x@sr@3-Ag domain surrounded by atomic steps or out-of-phase boundaries. In this work, we consider a strip domain with finite width and infinite length. By means of the time-dependent local-density approximation, we investigate low-dimensional plasmons (LDPLs) in a metallic strip monolayer on the semiconductor surface, namely, LDPLs in a 2DES confined in a strip region. We analyze the energy-loss intensity, the energy dispersion, and the induced charge distribution of the two plasmon modes at each wave number q along the strip. When wavelength @lambda@ (= 2@pi@/q) of the mode is considerably smaller than the strip width D, the higher-energy mode (HEM) has its induced charges extending widely in an interior region, showing a definite character of the area plasmon (APL). Its energy is quite close to that of the two-dimensional plasmon in an infinite area (pure 2DPL). However, as the mode energy deviates upward from that of the pure 2DPL with increase in @lambda@, the induced charge distribution of the APL evolves into a standing-wave pattern with its free end at the edge. In contrast, the lower-energy mode (LEM) has its induced charges localized near the strip edge, exhibiting a definite character of the edge plasmon. When @lambda@ is small compared with D, the induced charge density of the LEM decays slowly on the inside of the strip owing to the influence of the HEM (APL) close to the LEM in energy. At larger @lambda@ values, the quick attenuation of the induced charge density inside the strip involves conspicuous oscillations due to the interference of electronic waves impinging on and reflected from the edge.

SS-TuP17 Conductance Switching of Single Molecules in Alkanethiolate Self Assembled Monolayers, A.M. Moore, Z.J. Donhauser, The Pennsylvania State University; J.M. Tour, Rice University; P.S. Weiss, The Pennsylvania State University

Phenylene ethynylene oligomers (OPE) have been studied as candidates for molecular electronic devices using scanning tunneling microscopy (STM). These molecules were inserted into host alkanethiolate self-assembled monolayers (SAMs) for isolation and individual addressability. OPE molecules were probed using STM and exhibited reversible conductance switching, which is observed as a change in the topographic height of the molecule in the STM images. The rate of active switching has been shown to be mediated by the structure of the host matrix. Using shorter chain alkanethiolate SAMs we have shown multistate switching of these molecules and have suggested molecular motion changing the molecule to substrate contact conductance. Analysis of this switching mechanism has involved changing functionality, bonding, size and rotational freedom of the molecules under study.

SS-TuP18 The Interaction of Water with Oligo(Ethylene Glycol)-Terminated Self-Assembled Monolayers on Gold and Silver Investigated by IR and Vibrational Sum-Frequency Spectroscopy, R.-Y. Wang, M. Himmelhaus, J. Fick, S. Herwerth, W. Eck, M. Grunze, University of Heidelberg, Germany

Oligo(ethylene glycol)-terminated self-assembled monolayers (SAMs) have been the topic of intense research over the last years, due their unique protein repulsion properties.@footnote 1,2@ Recently, in particular, the structure of the films in contact to aqueous solutions has been in the focus of interest.@footnote 3,4@ In the present study, we used infrared reflection absorption spectroscopy (IRRAS) and vibrational sum-frequency spectroscopy (VSF) to investigate water-induced structural changes in methyl (1-mercaptopundec-11-yl) hexa (ethylene glycol)- terminated alkanethiol (EG6OMe) monolayers self-assembled on gold and silver. The spectra were recorded right after preparation of the films and after their exposure to water. In the case of gold as a substrate, the layers were also investigated during water contact. The spectra show that water causes pronounced disorder in the EG6OMe monolayers, which is only partially reversible after drying of the films under vacuum conditions.

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@FootnoteText@footnote 1@ K. L. Prime and G. M. Whitesides, *J. Am. Chem. Soc.*, 115, 10714,1993@footnote 2@P. Harder, M. Grunze, R. Dahint, G. M. Whitesides, and P.E. Laibinis, *J. Phys. Chem. B*102, 426-436, 1998 @footnote 3@M. Zolk, F. Eisert, J. Pipper, S. Herrwerth, W. Eck, M. Buck, and M. Grunze, *Langmuir*, 16,5849-5852,2000@footnote 4@D. Schwendel, T. Hayashi, R. Dahint, A. Pertsin, M. Grunze, R. Steitz, F. Schreiber, *Langmuir* 19, 2284, 2003.

SS-TuP19 Switching Dynamics of Ladder Molecules in Low Defect Self Assembled Monolayers, A.A. Dameron, The Pennsylvania State University; *J.W. Ciszek, J.M. Tour*, Rice University; *P.S. Weiss*, The Pennsylvania State University

We have fabricated 1-adamantanethiolate self assembled monolayers (SAMs) on Au(111) and characterized them with scanning tunneling microscopy.@footnote 1@ Adamantanethiol molecules have a bulky cage structure and orient in both fcc and hcp packing structures. The adamantanethiolate SAMs display fewer defect sites and less prominent domain boundaries than alkanethiolate SAMs. The switching dynamics of 2-thioacetylphenanthrene ("ladder molecules") and 4-thioacetyl-biphenyl molecules were studied by insertion of the molecules into both adamantanethiolate and short chain alkanethiolate SAMs. The switching dynamics in the two SAMs are similar; in both cases the molecules insert primarily into the defect sites in the monolayer and display switching between two states. @FootnoteText@@footnote 1@ L. F. Charles, M. S. Thesis, The Pennsylvania State University (1999).

SS-TuP20 Photodegradation Phenomena of Si-C Linked Monolayer Induced by 126, 172 and 254 nm Ultraviolet Light, K. Oda, Waseda University, Japan; *N. Shirahata*, National Institute of Advanced Industrial Science and Technology, Japan; *S. Asakura, A. Fuwa*, Waseda University, Japan; *Y. Yokogawa, T. Kameyama, A. Hozumi*, National Institute of Advanced Industrial Science and Technology, Japan

Micropatterned Si-C linked monolayers have recently attracted attention for their use as templates to fabricate electronic- and bio-devices in micro~nanometer-scale. Among numerous approaches, photolithography is one of the most promising techniques in order to design and fabricate the microtemplates arbitrarily. However, there have no papers describing photodegradation mechanism of Si-C linked monolayers. In order to optimize the micropatterning of the monolayers, further understanding of the photochemistries which proceed when the monolayers are exposed to various kinds of ultraviolet (UV) light sources is vital. In this study, we report the photodecomposition of a Si-C linked monolayer of 1-octadecene (ODM) induced by three types of UV light sources, i.e., 126 and 172 nm vacuum UV (VUV), and conventional 254 nm UV light. This ODM was attached to Si substrate terminated with hydrogen (Si-H) through Si-C bond. As control experiments, we have similarly examined the photodegradation of a self-assembled monolayer (SAM) of n-octadecyltrimethoxysilane (ODS) formed onto Si substrate covered with native oxide (SiO@sub 2@/Si) through Si-O-Si bond. Due to the formation of ODM and ODS-SAM, the Si-H and SiO@sub 2@/Si substrates became highly hydrophobic with their water-contact angles changing from about 80 and <5 ° to 110°, respectively. After 254 nm UV-irradiation for the appropriate period in air, the hydrophobic surfaces became completely hydrophilic one. However, photodecomposition rates of these monolayers were quite different, although our monolayers thicknesses were nearly identical. The rate of ODM was found to be about one-sixth as fast as that of ODS-SAM. This marked difference in photodecomposition rate may be responsible for the nature of the Si-C bonds, that is, the difference in electron distribution in the bonds, in ODM and ODS-SAM.

SS-TuP22 Atomic Structure of InGaAs Surfaces, A. Riposan, J. Mirecki Millunchick, B.J. Dall, C.A. Pearson, B.G. Orr, University of Michigan

The atomic structure of compound semiconductor alloy surfaces is important for heteroepitaxial growth, as it has an impact on the subsequent microstructure of the film. We examined the morphology and surface reconstruction of In@sub x@Ga@sub 1-x@As alloy layers during growth and after annealing. Films of different compositions were grown by molecular beam epitaxy on GaAs and InP (001) substrates to thicknesses less than the critical thickness for 3D islanding, and examined using in-situ Scanning Tunneling Microscopy (STM). The surface reconstruction of lattice matched In@sub 0.53@Ga@sub 0.47@As/InP alloys is highly disordered; nearly 25% of the surface is covered with a 4x3 reconstruction and 15% with a c(3x4). Models developed based on the STM data suggest that these reconstructions are terminated by both cation and anion dimers. The surface reconstruction during the growth of alloys under compressive misfit strain was 2x3 according to reflection high energy electron

diffraction. However, STM shows that the surfaces are covered with a number of differently reconstructed domains. The majority of the surface of In@sub 0.27@Ga@sub 0.73@As/GaAs layers is covered by a disordered c(3x4), while 34% of the surface consists of short segments of @alpha@2(2x4) with in the terrace. The reconstruction of In@sub 0.81@Ga@sub 0.19@As/InP surfaces, which have the same amount of lattice mismatch, consists of @beta@2(2x4) regions resting upon an underlying 4x3. The coverage of the @beta@2(2x4) decreases from 50% to 34% after a 25 minute anneal at the growth conditions. This behavior is consistent with the decrease of the surface In concentration during annealing, suggesting that the @beta@2(2x4) regions on this surface are related to In surface segregation.

SS-TuP23 Low Energy Li Ion Scattering from Iodine Adatoms on Si and SiO@sub 2@ Surfaces, Y. Yang, J.A. Yarmoff, University of California, Riverside

We recently showed that the neutralization of alkali ions backscattered from halogens adsorbed on metal surfaces depends sensitively on the internal polarization of the adatom. Charge-resolved time-of-flight spectra collected from backscattered @super 7@Li@super +@ ions display consistently larger neutral fractions for scattering from the halogen adatoms than that from the substrate. An increased neutral fraction indicates that the potential at the halogen site is reduced from that of the substrate, which is surprising considering that the halogen adatom is overall negatively charged. We thus propose that there is a region of positive charge at the very top of the adatom, which is consistent with the results of density functional theory. The positive region is presumably formed as the electron charge is attracted to its image in the metal substrate. This internal electronic structure of the halogen adatom was verified by measurements of the angular dependence of the neutralization. The neutral fraction of Li scattered from the halogens decreases as the exit beam moves off-normal, demonstrating that the charge associated with the adsorbate is non-uniform and that ion scattering is sensitive to this internal structure. Surprisingly, we found the same behavior for iodine adsorbed on Si surfaces, although the image charge in the substrate and the consequent charge rearrangement might be expected to be weaker. This implies that the iodine adatoms above a Si substrate are internally polarized. We are currently exploring the role of the substrate by investigating the neutralization of alkali ions scattered from Si wafers that are oxidized in situ prior to iodine exposure. This will allow us to determine how the conductivity of the substrate is involved in facilitating the internal charge rearrangement.

SS-TuP24 Chemistry of Bifunctional Nitro Group-containing Molecules on Silicon: a Cryogenic Approach to Selective Self-assembly in Vacuum, S. Bocharov, A.V. Teplyakov, University of Delaware

Surface chemistry of alkyl and aryl compounds containing nitro-group on Si(100)-2x1 has been investigated using multiple internal reflection Fourier-transform infrared spectroscopy, Auger electron spectroscopy, and temperature-programmed desorption/reaction mass spectrometry. Despite theoretical prediction for essentially barrierless interaction of nitromethane with this silicon surface, all the nitroderivatives studied physisorb molecularly within a monolayer coverage on Si(100)-2x1 at 95 K. Surface chemical reaction involving nitro-group occurs around 140 K regardless of the nature of the alkyl/aryl substituent studied. Thus, a significant energy barrier, approximately 8 kcal/mol, is established for the interaction of these molecules with the Si(100)-2x1 surface. An opportunity of selective self-assembly using the advantage of cryogenic conditions to control the kinetics of surface reactions will be discussed. Further surface annealing studies suggest that all nitrogen and oxygen atoms remain on a surface even at the temperatures as high as 900 K, while some carbon is removed as a corresponding hydrocarbon molecule.

SS-TuP25 Adsorption and Reaction of Amines on Germanium and Silicon Surfaces, P. Prayongpan, C.M. Greenlief, University of Missouri, Columbia

The bonding and structure of organic molecules with semiconductor surfaces is important for a variety of potential applications. This work focuses on the interaction between small organic molecules; ethylamine and allylamine, with Si(100)-2x1 and Ge(100)-2x1 surfaces. Ab initio calculations are used to investigate the transition states and predicted adsorption products for the reactions between the organic molecules and a dimer cluster model of the semiconductor surfaces. The cluster models include Si@sub 9@H@sub 12@, Ge@sub 9@H@sub 12@, and a mixed cluster; Ge@sub 2@Si@sub 7@H@sub 12@. Ultraviolet and x-ray photoelectron spectroscopy are used to examine the chemical bonding of the adsorbed products. This work will examine the effect of electron

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donating organic molecules with semiconductor surfaces. The selectivity and reactivity of functional groups in the surfaces will be described. According to our recent experimental and theoretical studies, the adsorption products for the interaction between amine molecules with Si(100)-2x1 and Ge(100)-2x1 surfaces are temperature dependent.

SS-TuP26 Adsorption of 1,3-butadiene on Si(001) 2x1 Surface, J.Y. Baik, Korea Research Institute of Chemical Technology and Sungkyunkwan University, Korea; *H.-N. Hwang*, Korea Research Institute of Chemical Technology; *K.-S. An*, Korea Research Institute of Chemical Technology, Korea; *E.S. Cho*, Sungkyunkwan University, Korea; *K.J. Kong, Y. Kim*, Korea Research Institute of Chemical Technology; *J.-Y. Park*, Sungkyunkwan University, Korea

Recently unsaturated organic molecules playing a role of multifunctional layer adsorbed on Si(001)2x1 surface has come into the focus of research in semiconductor fabrication and semiconductor devices. The well-known unstable π bond of up and down dimer atoms of Si(001)2x1 surface, ethylene-like(C@sub 2@H@sub 4@), is reactive with the unsaturated organic molecule through charge transfer in order to minimize the total energy on the surface. 1,3-butadiene(C@sub 4@H@sub 6@) among these molecules leads to the [4+2] reaction forming the organic molecule/Si hybrid of six-membered cycle with the Si dimer even at room temperature. And also, it was reported that the [2+2] reaction could occur at less possibility than the [4+2] reaction. In this study, the adsorption and thermal behaviors of 1,3-butadiene on the Si(001)2x1 surface were investigated by high-resolution photoelectron spectroscopy(HRPES), scanning tunneling microscopy(STM) and thermal desorption spectroscopy(TDS) with theoretical calculations. In STM images, three different-typed adsorptions were observed and well identified as the [4+2], the [2+2], and the end-edge bridge reaction by the STM simulation. For C 1s core level spectrum reported as only one asymmetric component, despite of two kinds of quite different chemical surroundings, it was found that the broad spectrum consisted of two components with abnormally small core level shift based on the calculation. In addition, TDS shows successive desorption of 1,3-butadiene and acetylene molecules with increasing the substrate temperature, different to previous reported hydrogen desorption by C-H bond breaking, without acetylene desorption.

SS-TuP27 Adsorption and Thermal Decomposition Reaction of Vinylacetic Acid on Si(100)2x1 Surface, K.-S. An, J.Y. Baik, Korea Research Institute of Chemical Technology, Korea; *H.-N. Hwang, Y. Kim*, Korea Research Institute of Chemical Technology; *C.-Y. Park*, SungKyunKwan University, Korea; *C.C. Hwang, B. Kim*, POSTECH, Korea

Covalent attachment chemistry of organic molecules on silicon surfaces has been of recent interest in surface science. Several molecule attachment chemistry on the Si(001)2x1 surface has been reported for organic molecules including various single and multi-functional groups such as alkene, hydroxyl, thiol, amine, and carboxyl groups, etc, which can be applied important building blocks for organic molecule/Si surface. In this study, the adsorption and thermal decomposition of vinylacetic acid (VAA) on the Si(001)2x1 surface is investigated using photoelectron spectroscopy and thermal desorption spectroscopy. Vinylacetic acid is a typical monomer having both vinyl (C=C) and carboxyl groups (COOH) with alkyl chain, which can well adsorb on the Si dimer as the [2+2] cycloaddition and dissociative reaction, respectively. Curve fitting of the Si 2p core level spectra taken after VAA exposures shows the development of two new surface components, S@sub O@ and S@sub H@, shifted by +0.93 and +0.40 eV, respectively, with respect to the bulk component. From the result, it is found that VAA adsorbs on the Si(001)2x1 surface, not through the cycloaddition reaction with vinyl group (C=C) but through the dissociative adsorption of RCOOH (R = CH@sub 2@CHCH@sub 2@) into RCO(ad) and H(ad) without breaking the Si dimer. The dissociative adsorption is confirmed by the analysis of the C 1s and O 1s core level spectra. Based on the line-shape changes of the Si 2p, C 1s, O1s core level spectra and TDS measurement with increasing the substrate temperature after the VAA saturation, the thermal decomposition and desorption behaviors of the VAA molecules are also investigated.

SS-TuP28 Plasmons in Ag Ultrathin Films on Si(111) Studied by Energy Loss Spectroscopy with High Momentum Resolution, T. Nagao, Tohoku University and PRESTO, JST, Japan; *S. Yaginuma, T. Sakurai*, Tohoku University, Japan

Self-organized metallic overlayers deposited on semiconducting substrates constitute an interesting class of materials since one can explore a variety of physics related to low dimensionality and size effects. The collective behavior in electron systems (plasma oscillation, or plasmon) confined in

atomically thin region is expected to be very different from plasmons in three-dimension. In the present talk, we report on the thickness dependence of the plasmon dispersion curve of several- monolayers-thick Ag films supported on Si(111), by use of high-momentum-resolution HREELS. The films were prepared by "electronic growth" scheme with lateral grain size larger than 70 nm characterized by the spot profile analysis using the spectrometer in high-resolution LEED mode. In addition to the surface plasmon peak, a steeply dispersing peak was observed around the (00) Bragg spot, which rapidly decays in intensity and broadens in a very narrow momentum window of 0.04 [1/A] as a function of momentum transfer. The energy dispersion curve of this mode was explained in terms of a quasi-2D mode of thin film plasmon and its loss energy approaches the value of 1900eV which is close to the interfacial plasmon mode at the semiinfinite Ag/Si system. The details of the analysis together with the development of the spectrometer will be presented. We also plan to present some data of sheet-type plasmons in surface-state bands at silicon surfaces.

SS-TuP29 Semiconductor Surface Reconstructions of the Si(100) Surface at 5K, B. Grandidier, L. Perdigao, D. Deresmes, M. Dubois, C. Delerue, G. Allan, D. Stievenard, IEMN-CNRS, France

The reconstruction of the Si(100) is related to the formation of dimers to lower the surface energy. Their bonding consists of a weak double bond so that the symmetric configuration is not held and give rise to buckled dimers. As several types of reconstructions have been predicted, with well defined electronic properties, we have studied the reconstructions of the Si(100) surface by scanning tunneling microscopy (STM) and spectroscopy at 5K. At low positive sample voltages, when well-ordered surfaces are prepared, two phases, the c(2x4) and the p(2x2) reconstructions, are visible. By increasing the number of surface defects, a third arrangement, the p(2x1) asymmetric reconstruction, appears. Scanning tunneling spectroscopic measurements indicate that all the surfaces are semiconductor. However at higher positive voltages or at negative voltages, the appearance of the dimers change into a symmetric features. While spectroscopic data show that the tip does not induce a modification of the surface reconstruction whatever the sample voltage and the reconstruction types of the surface, the voltage-dependent STM images are investigated by theoretical calculations for the p2x2 arrangement.

SS-TuP30 Surface Oxidation of Silicon Blisters formed by Hydrogen Ion Irradiation, S. Igarashi, A.N. Itakura, National Institute for Materials Science, Japan Science and Technology Corporation, Japan; *M. Kitajima*, National Institute for Materials Science, Japan; *K. Hojyou*, Japan Atomic Energy Research Institute

Blister is a local protrusion of solid surface induced by gas ion irradiation. Si (100) substrate was irradiated with H@super +@ (ion energy of 10 keV and fluence of 1x10@super 22@ ions/m@super 2@) at an angle of 30 deg. to the surface normal. The blisters of several μ m in diameter at the bottom were formed. After the ion irradiation, the substrate was exposed to an O@sub 2@ gas. By means of scanning Auger microscopy, we observed that the rims of the blisters have higher oxygen intensities than the flat surfaces and the tops have lower than the flats. The blistering is considered to create local stress on surface layers; the surface layers should be stretched laterally at the top of blisters and are compressed at the rim, relative to the flat surfaces. The O distribution clearly consists with the stress distribution of the surface. Our results demonstrate a patterned oxidation of Si surface applying its reactivity depending on the surface stress.

SS-TuP32 Synthesis of a Sinter Resistant Mixed-oxide Support for Au Nanoclusters, B.K. Min¹, A.K. Santra, D.W. Goodman, Texas A&M University

The synthesis of a sinter-resistant oxide support for Au clusters has been explored using scanning tunneling microscopy (STM). Nano-sized Au clusters supported on a reducible oxide such as TiO₂ are active catalysts for CO oxidation; however, rapid deactivation occurs at reaction conditions due to an increase in the cluster size. To prevent this deactivation, a sinter-resistant oxide support has been synthesized by patterning oxide domains consisting of small islands of a strongly-interacting support (TiO₂) on second weakly-interacting oxide (SiO₂). The size of the TiO₂ domains can be controlled by the amount of Ti deposited. The Au nanoclusters preferentially decorate the TiO₂ domains and are resistance to sintering when exposed to elevated pressures of O₂, CO, and mixtures of the two gases under reaction conditions.

¹ Morton S. Traum Award Finalist

Tuesday Evening Poster Sessions, November 4, 2003

SS-TuP33 Dissociation of Methyl Iodide on the Al(111) Surface - An STM and DFT Study, *S. Mezhenny*¹, University of Pittsburgh; *D.C. Sorescu*, U.S. Department of Energy; *P. Maksymovych*, *J.T. Yates, Jr.*, University of Pittsburgh

The reaction of methyl iodide (CH₃I) with the Al(111) surface was studied by room temperature scanning tunneling microscopy (STM) and by first principles calculations. It was found that at 300K CH₃I decomposes on the Al(111) surface forming methyl, CH₃, methyldyne, CH, and adsorbed iodine. CH₃ groups were observed to occupy atop sites by STM, while CH species occupy hollow sites. Total energy density functional theory calculations have shown that CH₃ species occupy atop Al sites (E=45.3 kcal/mol), CH species adsorb on fcc hollow sites (E=155.0 kcal/mol), while individual iodine atoms can bind on both top or hollow sites with adsorption energies 54-56 kcal/mol.

¹ Morton S. Traum Award Finalist

Biomaterial Interfaces

Room 307 - Session BI+SS-WeM

Cell Interactions with Patterned Surfaces

Moderator: M. Textor, ETH Zurich, Switzerland

8:20am **BI+SS-WeM1 Patterned Surfaces using Masking during Plasma Deposition or Pulsed Laser Ablation**, *H. Thissen*, CSIRO Molecular Science, Australia; *J.P. Hayes*, Industrial Research Institute Swinburne, Australia; *P.G. Hartley*, *G. Johnson*, CSIRO Molecular Science, Australia; *E.C. Harvey*, Industrial Research Institute Swinburne, Australia; *H.J. Griesser*, University of South Australia, Australia

The patterning of biomaterial surfaces has attracted much recent interest for various fundamental and applied purposes, such as the control of the location and shape of attached anchorage-dependent cells. Patterned surfaces are also of interest for bio-diagnostic arrays, cell culturing and separation, some tissue engineering products, and some biomedical implants. We have used two different approaches for the fabrication of patterned surface chemistries. One approach involves the use of masks during the deposition of thin plasma polymer coatings. The other approach is based on the deposition of multilayer coating structures followed by laser ablation through a mask; the top layer is a non-adhesive coating such as PEG and the laser beam exposes adhesive regions "underneath" by ablating the PEG layer in spatially controlled areas. Cell-adhesive proteins can then adsorb only onto the exposed areas capable of adsorbing proteins. The second approach is very attractive because of its speed and ease of fabrication; ablation of the thin PEG layer using a pulsed 248 nm excimer laser is fast with nanometre thickness control by controlling the number of laser pulses. The patterned surface chemistries and their protein adsorption characteristics were analyzed by several surface analytical techniques and by antibody assay. Cell culture using bovine corneal epithelial cells confirmed that cell attachment is controlled by these surface chemistry patterns. Our work has so far focused on fluoropolymer and Si wafer substrates and the use of plasma polymer interlayers for the covalent anchoring of a cloud point grafted PEG top layer; the use of a plasma polymer interlayer has the advantage of being readily transferable to a variety of substrates both ceramic and polymeric. However, the use of laser patterning is not restricted to those coating structures and can be applied to burn adhesive "holes" into other non-adhesive coatings equally well.

8:40am **BI+SS-WeM2 Patterning Surfaces with "Nonfouling" Oligoethylene Glycol "Bottle Brushes" by Soft Lithography and Surface-Initiated Atom Transfer Radical Polymerization**, *H. Ma*, *A. Chilkoti*, Duke University

A "grafting from" strategy is described for creating patterned biologically-nonfouling polymer coatings. Initiators presenting a bromoisobutyrate moiety and a thiol group at two ends of the molecule were synthesized and patterned on gold by soft lithography. The patterned SAM was used as a substrate for surface-initiated atom transfer radical polymerization (SI-ATRP) of oligoethylene glycol methyl methacrylate (OEGMA). The SI-ATRP was carried out in an oxygen-free environment with CuBr/Bipy as catalysts in a water/methanol mixture. Ellipsometry showed that the thickness of the poly(OEGMA) "bottle brush" could be easily manipulated from 0 to 50 nm by control of the polymerization conditions. The patterns were characterized by imaging ToF-SIMS, imaging XPS, and AFM. This "bottle brushes" are exceptionally protein-resistant. Surface plasmon resonance (SPR) spectroscopy showed no adsorption of fibronectin (1 mg/ml), 10% or 100 % fetal bovine serum (FBS) onto those surfaces. NIH 3T3 fibroblasts were confined to regions demarcated by the patterned poly(OEGMA) brushes. The cellular patterns were maintained for over 30 days, which is significantly longer than is possible with EG-terminated alkanethiol SAMs. This "grafting from" strategy is not limited to gold-coated surfaces as demonstrated by SI-ATRP on glass and silicon, and overcomes the intrinsic limitation of low surface density of PEG chains by physisorption or the "grafting to" approach. The poly(OEGMA) grafts synthesized in situ by SI-ATRP recapitulate in a polymer brush some of the key features of oligoethylene glycol-terminated SAMs, namely the high surface density of oligoethylene glycol in a thicker and more robust coating. These patterned "nonfouling" surfaces have utility in the design of experimentally useful model system to investigate the response of cells to chemical and topographical cues, in addition to a wide range of applications in bioanalytical devices.

9:00am **BI+SS-WeM3 Molecular Assembly Patterning by Lift-off (MAPL): A Novel Approach to Produce Biologically Designed Micropatterns for Biosensor Applications and Cell-Surface Interaction Studies**, *D. Falconnet*, Swiss Federal Institute of Technology (ETH) Zurich; *F. Assi*, Swiss Federal Institute of Technology (ETH) Zurich, Switzerland; *A. Koenig*, Swiss Federal Institute of Technology (ETH) Zurich; *M. Textor*, Swiss Federal Institute of Technology (ETH) Zurich, Switzerland

A new chemical micropatterning technique is presented for cell-surface interaction studies. The MAPL technique allows creating patterns of bioactive molecules (such as biotin, peptides, oligonucleotides) at a controlled surface density and embedded in a background resistant to the adsorption of proteins. A simple photoresist lift-off process is exploited in conjunction with the spontaneous assembly of polycationic poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) onto negatively charged metal oxide surfaces. A positive photoresist on a metal-oxide-coated substrate (e.g. niobium oxide coated on glass) is developed resulting in a micropattern of resist and bare metal oxide areas. Bio-functionalized (e.g., biotin or cell-adhesive peptide) PLL-g-PEG is immobilized at the bare metal oxide regions by spontaneous assembly from aqueous solutions of the polymer. The photoresist is lifted off in an organic solvent without affecting the integrity of the adsorbed functionalized PLL-g-PEG monolayer. Subsequently, the background is backfilled with protein- and cell-resistant PLL-g-PEG. The resulting pattern of bio-interactive and non-adhesive areas shows an excellent contrast on the protein level, demonstrated by fluorescence microscopy using labeled streptavidin to specifically decorate the PLL-g-PEG/PEG-biotin patches. Cell attachment to such micropatterns consisting of PLL-g-PEG/PEG-RGD-peptide was tested using human foreskin fibroblasts. This lift-off-based biochemical patterning is a 'soft', robust, simple and reproducible technique that does not require specialized clean room and heavy etching facilities. It is an interesting alternative to microcontact printing because it circumvents many disadvantages of the printing technique. The high signal-to-noise ratio and the feasibility of tailoring the bioligand (capture molecule) density in the interactive patches make MAPL a promising technique also for biosensor microarray applications.

9:20am **BI+SS-WeM4 Micrometer-scale Fibronectin Patterning for Control of Focal Adhesion Dynamics in Fibroblasts**, *D.S. Rhoads*, *R.N. Orth*, *M. Wu*, *B.A. Baird*, *J.L. Guan*, Cornell University

We have developed a new method for analyzing the processes of fibroblast adhesion and spreading using micro- and nanometer-scale fibronectin patterns. Fibronectin is an extracellular matrix protein that provides mechanical stability for cells and tissues, by being a ligand for integrin cell surface receptors which anchor the actin cytoskeleton to the plasma membrane. These anchor points are referred to as focal adhesions, and are composed of numerous scaffolding and signaling proteins in addition to forming focus points of the actin cytoskeleton. Here, we patterned fibronectin using a technique previously shown to produce feature sizes as small as 700nm. The fibronectin features are used to observe small focal adhesions and the morphological effects of minimal activation by fibronectin per cell area. For fabrication of patterned surfaces, polymer-coated silicon wafers were patterned using photolithography and reactive ion etching. Fibronectin was then deposited onto the wafer samples prior to polymer removal and cell application. The resulting patterns contained features ranging from 76 μm to $> 1 \mu\text{m}$, and were used in cell adhesion and spreading experiments. Cells adhering to the pattern were fixed, permeabilized and analyzed by immunofluorescence, using antibodies to fibronectin, f-actin, paxillin, and focal adhesion kinase. Fluorescence microscopy was complemented with scanning electron microscopy to image focal adhesions, stress fibers, lamellipodia and filopodia. From this analysis, we propose that this method for analyzing cellular responses to subcellular cues from their surroundings is a model system for spatially isolating and studying focal adhesions.

9:40am **BI+SS-WeM5 Microengineering Surfaces to Interface with Mammalian Cells**, *C.S. Chen*, Johns Hopkins University **INVITED**

The interactions between cells and their surroundings provide the basis for the coordinated functions of tissues. To understand and control these interactions, we have developed several microfabrication-based approaches to provide model environments for cells. We will describe these approaches, and how they are beginning to elucidate how cells probe and make sense of their environment through biochemical and mechanical means. Integrating microfabricated devices and cells will pave the way for a new era in biomedical research and medicine.

Wednesday Morning, November 5, 2003

10:20am **BI+SS-WeM7 Analyzing Lymphocyte Adhesion, Membrane Receptors and Cytoskeletal Rearrangement on Micron Scale Mitogen Patterns**, *R.N. Orth, M.J.B. Flaminio, J. Kameoka, T.G. Clark, H.G. Craighead*, Cornell University

In this study, we investigated an in vitro immune reaction on a planar surface between T cells, B cells, and micron scale patterned mitogens as a model system for analyzing cell surface ligand responses. To form functionalized biomaterial microdomains, a polymer-coated substrate was patterned using photolithography and reactive ion etching. The samples were incubated in antibody and mitogen solutions prior to polymer removal and cell application. Uniform mitogen patterns ranging from 76 μm to $<1 \mu\text{m}$ were created to target cell surface receptors, upregulate intracellular signaling cascades and cell activity, and stimulate proliferation. Several methods were used to analyze the patterned mitogens' effects on the lymphocytes. Carboxy-fluorescein diacetate, succinimidyl ester (CFSE)-stained lymphocytes harvested from the substrate demonstrated a proliferative response when assayed by flow cytometry. Mouse monoclonal antibodies against equine membrane cell receptors (anti-major histocompatibility (MHC) class II, anti-CD4, anti-CD3, and anti-leukocyte function associated-antigen (LFA)-1) provided a view of stimulated cells' surface receptor distribution. Secondary anti-mouse antibodies with a conjugated 1.5 nm gold sphere were bound to the primary antibodies. The samples were incubated in a silver solution to form 10-100 nm spheres as the silver nucleated off the gold particles. Scanning electron microscopy (SEM) imaging provided high resolution images of the cell surface ligands' spatial distribution as marked by the silver spheres. This patterning technique provided a precise and reproducible means to structure biomaterial surfaces at subcellular resolutions.

10:40am **BI+SS-WeM8 Directed Motoneuron Growth on Self-Assembled Monolayer (SAM) Patterned Surfaces**, *M.G. Poeta, M. Das, C.A. Gregory, P. Molnar, D.C. Henry, L.M. Riedel, J.J. Hickman*, Clemson University

We are investigating the directed growth of embryonic rat motoneurons on glass substrates and are determining if they exhibit proper morphological and electrophysiological characteristics in this defined environment. This is the first step in recreating the reflex arc, one of the fundamental controls circuits in the body, with biological components on a MEMS chip. Recreating this system in vitro could have significant implications for improving treatment for people with spinal cord injuries, which affect 10,000 people every year in the United States. Throughout the last century, many methods have been developed to direct the growth of different cell types. These include fibroblasts, glial cells and hippocampal neurons grown on spider webs adhered to coverslips, grooves scratched in polystyrene and palladium deposited on petri dishes. In order to direct the growth of the motoneurons, we are using two recently developed patterning techniques, microcontact printing and laser ablation. Microcontact printing is a patterning method where a polydimethyl siloxane (PDMS) stamp is cast from a mold. It is inked in our case with a hydrophilic silane, diethyltriamine trimethoxysilane (DETA), and brought into contact with a substrate. The substrate is then backfilled with a hydrophobic silane, tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane (13F). Laser ablation is a patterning method where, again in our system, a substrate is coated with DETA and exposed with an excimer laser fitted with a beam homogenizer through a photomask. The exposed regions are then backfilled with 13F. Embryonic rat motoneurons are plated on these patterned substrates. XPS and contact angle are used to verify the surface modification procedures. We have found that the motoneurons orient themselves along the hydrophilic patterns. We will report on the characterization of these patterns using patch-clamp electrophysiology to measure the electrophysiological characteristics of the cells.

Surface Science

Room 328 - Session SS1-WeM

Adsorption on Semiconductor Surfaces

Moderator: E.D. Williams, University of Maryland at College Park

8:20am **SS1-WeM1 H Transfer and Ge/Si Site Exchange during Germane Adsorption at Si(001)**, *T. Murata, M. Suemitsu*, Tohoku University, Japan
Germane adsorption at Si(001) is important as an initial elementary step for Ge/Si heteroepitaxy. It also provides an ideal platform to investigate Ge adsorption at Si sites, one of the elementary processes in SiGe epitaxy. Little is known, however, on its details. Among the remaining issues are whether H atoms from germane are transferred to Si atoms or they stay intact at Ge sites and whether a site exchange occurs between Si and Ge during adsorption. To tackle these problems, we have combined TPD and multiple-internal-reflection FTIR, and have investigated the Si(001) surface adsorbed with germane at room temperature. These two methods form a complementary pair since TPD backs up the quantitative aspect of the characterization while FTIR is most powerful in state-resolved analysis. The findings we present here are (1) that almost all the H atoms are transferred from germane to Si atoms and (2) that the site exchange does occur between Si and Ge even at room temperature. The finding (1) is supported by exhaustive dominance of both the SiH-related β peak in TPD and the SiH-related stretching band in FTIR. Persistence of these SiH-related signatures up to $\sim 1\text{ML}$ of hydrogen coverage is hardly understood without considering a site exchange between substrate Si and adsorbed Ge atoms, leading us to the conclusion (2). Recent ab-initio calculations suggest that the two findings originate from a single event: adatom diffusion. According to Jeong and Oshiyama, *Phys. Rev. B* 58(1998)12958. *Footnote 1* @ Jeong and Oshiyama: *Phys. Rev. B* 58(1998)12958. *Footnote 2* @ Jeong and Oshiyama: *Surface Science* 436(1999)L666.

8:40am **SS1-WeM2 Surface Interaction of SiH₃ Radicals with Amorphous Silicon: Temperature Dependence of the SiH₃ Surface Reactivity and the Surface Hydride Composition**, *W.M.M. Kessels, J.P.M. Hoefnagels, P.J. Van den Oever, Y. Barrell, A.H.M. Smets, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands
The growth of hydrogenated amorphous silicon (a-Si:H) thin films from SiH₄ plasmas is expected to be dominated by SiH₃ radicals created in the plasma. To obtain insight into the surface reactions of SiH₃ on the a-Si:H surface, the surface reaction probability of SiH₃ has been determined by time-resolved cavity ringdown spectroscopy. The experiments have been carried out under nearly pure SiH₃ conditions for substrate temperatures between 50-450 °C. It has been found that the surface reaction probability of SiH₃ is 0.30±0.03 independent of the substrate temperature. Information about the chemical state of the a-Si:H surface in terms of surface silicon hydrides has been determined by in situ attenuated total reflection infrared spectroscopy combined with Ar-ion induced desorption experiments. These experiments - carried out in the same temperature range - have revealed that the a-Si:H surface composition changes drastically with increasing substrate temperature from a -SiH₃ covered surface at low temperatures to a -SiH₂ and a -SiH covered surface at higher temperatures. From the combination of the experimental results and ab initio calculations and molecular dynamics simulations in the literature, it is concluded that a-Si:H film growth takes place by a two-step reaction mechanism of SiH₃ in which H abstraction from the surface by SiH₃ in an Eley-Rideal reaction is the rate-limiting step. This abstraction reaction, which requires nearly zero activation energy, is unaffected by the changing surface silicon-hydride composition and leads to temperature independent growth site creation. SiH₃ radicals can subsequently stick on the dangling bonds created. Furthermore, some preliminary ideas on an (associated) surface diffusion mechanism will be discussed on the basis of the surface roughness evolution of a-Si:H at different temperatures.

9:00am **SS1-WeM3 Interface Structure of an Ultrathin SiO₂ Film Fabricated by Ozone on Si(100)**, *K. Nakamura, S. Ichimura*, National Institute of Advanced Industrial Science and Technology (AIST), Japan
Highly concentrated ozone gas is one of the alternative oxidants to fabricate an ultrathin silicon oxide film at low temperature for the microelectronics technology. Our previous study using an HF etching rate of oxide films has implied that, in contrast to a thermally grown oxide film, the thickness of structural transition layers of an ozone-oxide film is so limited within a much thinner region. *Footnote 1* @ However, direct information on the structure of this interface has not been so far obtained. Thus, we investigated the structure of an ozone-oxide film at the interface on Si(100) by analyzing transverse optical (TO) and longitudinal optical (LO) phonon modes of Si-O-Si asymmetric stretching vibration with Fourier-transformed infrared spectroscopy (FT-IR). The Si-O-Si bond angle in the ozone-oxide film was found to be undistorted even in the region close to the interface. In the case of a thermally grown oxide film, both peaks are known to make a clear red-shift. *Footnote 2,3* @ However, the position of a TO phonon peak of an ozone-oxide film fabricated at 350 °C kept

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constant at 1065 cm⁻¹ within <2 nm thickness. Only the LO phonon peak made a red-shift from 1240 to 1200 cm⁻¹. Since the TO phonon frequency is a function of a Si-O-Si bond angle, the result shows that the Si-O-Si angle in the thermally grown oxide is distorted close at the interface, but that this bond angle in the ozone-oxide remains unchanged, thus reducing the thickness of structural transition layers compared to that of the thermal oxide.

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2@ S. Miyazaki, H. Nishimura, M. Fukuda, L. Ley, J. Ristein, Appl. Surf. Sci. 113/114 (1997) 585.
3@ K. T. Queeney, M. K. Weldon, J. P. Chang, Y. J. Chabal, A. B. Gurevich, J. Sapjeta, and R. L. Opila, J. Appl. Phys. 87 (2000) 1322.
4@ F. L. Galeener, Phys. Rev. B 19 (1979) 4292.

9:20am **SS1-WeM4 Application of MIR-FTIR to Multilayered Structures Built on Silicon Substrate: TiCN and Al Deposition and Effects of Hydrogen Diffusion**, S. Bocharov, A.V. Teplyakov, University of Delaware

A combination of infrared spectroscopy, thermal desorption mass spectrometry, ToF-SIMS and AFM was used to analyze deposition of TiCN and Al from CVD precursors onto a Si(100)-2x1 surface. The TiCN films were easily deposited from tetrakis-(dimethylamino)-titanium (TDMAT) on a clean Si(100)-2x1 surface at slightly elevated temperatures and pressures of 2 microrr and even lower. Monolayer chemistry does not lead to TiCN deposition. On the other hand, at 593K deposition of TiCN can be easily achieved. The onset of the deposition process coincides with the thermal decomposition of surface species resulting from the monolayer reactions. The unusual application of MIR-FTIR to study multilayered structures was successfully performed for TiCN and Al deposition onto a TiCN-precovered Si(100). Interestingly, not only surface chemistry of the CVD precursors on TiCN, but also the transformation of the TiCN/Si interface can be followed by such an approach. Hydrogen diffusion from surface decomposition was shown to play a significant role in the formation of the multilayered structure. It was also observed that the diffusion of hydrogen atoms produced by hydrogen dissociation on a hot tungsten filament drives hydrogen towards TiCN/Si interface.

9:40am **SS1-WeM5 Indium Phosphide (001)-(2x1): Evidence for a Hydrogen-Stabilized Surface Reconstruction**, G. Chen, D. Cheng, D. Tobin, Y. Sun, University of California, Los Angeles; K. Raghavachari, Indiana University; R.F. Hicks, University of California, Los Angeles

Metalorganic vapor-phase epitaxy (MOVPE) is widely used to produce InP-based optoelectronic devices. Deposition of InP (001) films occurs in a large excess of the group V precursors, resulting in the formation of a P-rich (2x1) reconstruction. Scanning tunneling microscopy indicates that the (2x1) is terminated with a complete layer of buckled phosphorus dimers. This structure has been the subject of debate, because it should violate the electron counting model and exhibit partially filled P dangling bonds. In this work, we report on a vibrational study of the (2x1) surface prepared in the MOVPE environment. Infrared spectra collected during deuterium titration reveals the presence of a single sharp P-H stretching mode at 2308 cm⁻¹. Based on theoretical cluster calculations using density functional theory, this mode results from a single hydrogen atom bonded to one end of the buckled phosphorus dimer. This structure does not violate the electron counting model. In addition, slab calculations by another research group indicate that hydrogen-termination of the P dimers should yield the most stable configuration for the (2x1). Therefore, it may be concluded that adsorbed hydrogen atoms stabilize the phosphorus-rich surface structure during indium phosphide film growth by MOVPE.

10:00am **SS1-WeM6 Chemically Resolved STM Imaging of Al on Al_{0.1}Ga_{0.9}As(001)-c(2x8)/(2x4)**, M.J. Hale, D.L. Winn, A.C. Kummel, University of California, San Diego

It has been proposed that growing an oxide/AlGaAs/GaAs stack will prevent interface roughness from interfering with carrier mobility within the channel when attempting to create a GaAs-based MOSFET. Before attempting to grow an oxide/AlGaAs interface, one must first characterize the AlGaAs(001) surface. We will present STM images of the AlGaAs(001) surface in which Al and Ga can be distinguished. Al atoms in the second layer of Al_{0.1}Ga_{0.9}As(001)-c(2x8)/(2x4) cause the adjacent As atoms in layer one to be brighter than As atoms bonded to Ga atoms in STM images. Al is a stronger charge donor than Ga, which makes the As atoms in layer one bonded to Al atoms in layer two to have a greater charge density than As atoms bonded to Ga. This affect was only seen for p-type AlGaAs grown on a p-type GaAs substrate. Scanning tunneling spectroscopy (STS) measurements show that the excess charge transferred to the first layer As atoms from the second layer Al atoms causes electrical

inversion to occur on the surface. For n-type Al_{0.1}Ga_{0.9}As(001)-c(2x8)/(2x4) grown on an n-type GaAs substrate, the ability to differentiate Al from Ga atoms in STM images is not possible. STS spectra show that the Fermi level resides near the conduction band, typical of a non-inverted n-type sample. This result is consistent with our model of a strong charge donation by Al since excess charge would not affect the position of the surface Fermi level in n-type material. The ability to differentiate between second layer Al and Ga atoms on p-type AlGaAs(001) with STM will enable further studies to understand the oxide/AlGaAs(001) interface.

10:20am **SS1-WeM7 Atomistic Mechanisms of Fermi-level Pinning at the Oxide-Semiconductor Interface**, J.Z. Sexton, M.J. Hale, D.L. Winn, University of California, San Diego; M. Passlack, A.A. Demkov, Motorola Inc.; A.C. Kummel, University of California, San Diego

Understanding the mechanism of Fermi-level pinning is critical in the development of an electronically passive oxide - III/V semiconductor interface. This insulator-semiconductor interface is important in the development of a practical of III / V MOSFET technology. We have observed Fermi-level pinning and un-pinning in STM and STS at the GaAs(001)-2x4 surface in three cases, upon sub-monolayer a) deposition of oxygen atoms, b) vapor deposition of Ga₂O and c) vapor deposition of In₂O. We have seen that the oxide layer formed upon atomic oxygen exposure forms a pinned interface. However, when a vapor deposited gallium oxide layer is formed, the surface remains unpinned. When In₂O is vapor deposited on the GaAs-2x4 surface, several bonding structures are formed, ultimately leading to a pinned interface. We have identified the bonding structures using first-principles calculations and have identified the mechanism for Fermi-level pinning for all the cases listed above. The Fermi-level pinning in case a) is due to a deep-level state, caused by significant charge withdrawal from the gallium atoms by oxygen. The Fermi-level unpinning in case b) is due to the bonding configuration resulting in a geometrically favorable and charge balanced structure. The Fermi-level pinning in case c) is dependent on the specific structure observed in STM. We have done calculations to elucidate the bonding and electronic structure of the observed bonding configurations and have observed that some structures are pinned and some are unpinned. We have seen two types of Fermi-level pinning: 1) deep level pinning caused by a fixed interface atomic state in the band-gap region and 2) a dipole-like pinning that is distributed over the covalent bonding network which induces states on the valence and conduction band edges. In summary, the bonding structure at the interface determines the existence and type of Fermi-level pinning.

10:40am **SS1-WeM8 Coupling Reactions of Trifluoroethyl Iodide on GaAs(100)**, N.T. Kemp, N. Paris, N.K. Singh, The University of New South Wales, Australia

Alkyl coupling reactions studied to date have been restricted to gold, silver and copper surfaces, where the only coupling product formed has always been the corresponding higher alkane. In this paper we report, the coupling reactions of trifluoroethyl iodide on GaAs(100) which forms, not only the higher alkane, but a higher alkene as well. In this respect the alkyl coupling reactions on the GaAs surface differ from those on transition metal surfaces. Additionally, the ability of a semiconductor surface to catalyze carbon-carbon bond formation has not been reported previously by other researchers. The techniques of X-ray photoelectron spectroscopy and thermal desorption spectroscopy have been used to study the surface reactions of 2-iodo-1,1,1-trifluoroethane (CF₃CH₂I) on GaAs(100). Our results show that coupling of surface CF₃CH₂ species, generated via the dissociative adsorption of CF₃CH₂I, yields both CF₃CH₂CH₂CH₂CF₃ and CF₃CH₂CH=CF₂. The coupling pathway competes with the disproportionation reactions of CF₃CH₂, to form CF₃CH₂CH₂ as the major product of this pathway. In addition, we observe the formation of volatile etch products IF_x, GaI, AsI, GaF, AsF and As₂. This paper will discuss the mechanisms by which these products form from the adsorbed CF₃CH₂ and I species, and the role that the GaAs surface plays in the reaction pathways proposed.

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Surface Science

Room 327 - Session SS2-WeM

Surface and Interface Structure: Metals

Moderator: R.J. Hamers, University of Wisconsin-Madison

8:20am SS2-WeM1 Dislocation Mediated Interactions in Self-assembly: The S-induced Triangular Hole-array in Ag/Ru(0001), K. Thurner, N.C. Bartelt, R.Q. Hwang, Sandia National Laboratories

By depositing S onto a monolayer of Ag/Ru(0001) we are able to create very regular arrays of 2D-vacancy islands. Real-time STM measurements reveal the mechanisms of such adsorbate induced restructuring: Starting from a herringbone pattern of the clean Ag-film, the S transforms the film by a sequence of dislocation reactions that individually decrease the Ag density. Eventually all threading dislocations are eliminated and the film assumes a Moire-like structure, in which on-top Ag-atoms are replaced by holes filled with S. These holes form a strikingly regular triangular lattice with a nearest neighbor spacing of 5nm. The conventional assumption is that such pattern formation is caused by substrate-mediated long-range elastic interaction. To test this assumption, we have used STM to measure the thermal vibrations of the hole array as a function of temperature. Surprisingly, we find we can account for these observations without invoking substrate relaxations: By comparing the measured vibration amplitudes to 2D Frenkel-Kontorova simulations we find that the hole-array is stabilized by a pattern of partial dislocations connecting the holes. First principles electronic structure calculations of the 2D FK model parameters for Ag/Ru quantitatively reproduce the hole-hole interaction strength extracted from our measurements. @FootnoteText@ @footnote 1@K. Pohl et al. Nature 397 (1999) 238.

8:40am SS2-WeM2 Molecule-Metal Surface Interactions Evidenced Quantum Mechanically via Tip-induced CS2 Interaction with Friedel Oscillations on Au{111}, E.C.H. Sykes, P. Han, P.S. Weiss, The Pennsylvania State University

Sub-monolayer coverages of CS₂ adsorbed on Au{111} at 4 K were studied using scanning tunneling microscopy. The molecule forms well ordered islands on the terraces and molecular chains at the bottoms of the steps. The adsorption of the CS₂ molecule at specific surface sites is explained in terms of the substrate electron density. Strong tip/molecule interactions are shown to be prevalent in this system at negative tip biases and yield images showing reversed corrugation. At low positive tip bias, the tip again perturbs the molecules, but in this regime the tip/molecule interaction is comparable to the molecule/surface interaction and higher residence times at certain surface sites are observed. This effect is explained fully in terms of the CS₂ molecule having increased interactions with the areas of high electron density on the peaks of standing waves arising from electrons close to the Fermi energy. The importance of this result is discussed in terms of the fundamental surface physics of adsorbate/metal bonding.

9:00am SS2-WeM3 Interactions Mediated by Surface States: Lines and Ordered Overlayers@footnote 1@, P. Hyltdgaard, Chalmers University of Technology and Göteborg University, Sweden; T.L. Einstein, University of Maryland, College Park

Since surface states on (111) noble metals are free-electron like, their propagators can be evaluated analytically. @footnote 2@ Since they are well-screened, one can use simple tight-binding formalism@footnote 3@ to study their effects. @footnote 4@ Applications to metallic surface states on semiconductors may also be fruitful. The needed phase shifts can be extracted from experiment. @footnote 2,4@ Hence, we can now make quantitative predictions of indirect interactions--at least the asymptotically dominant contribution from surface states. @footnote 2,4@ Here, we discuss the interactions of linear defects, relating them to the interactions of (n x 1) ordered overlayers and to the constituent pair and trio interactions. We discuss implications for step-step interactions (on vicinal surfaces), for extracting pair interactions from first-principles calculations of ordered overlayers or from experiments, and for atoms approaching large clusters. @FootnoteText@ @footnote 1@PH supported by ATOMICs, financed by the Swedish Foundation for Strategic research; TLE supported by NSF Grants EEC-0085604 and MRSEC DMR 00-80008. @footnote 2@ J. Repp et al., Phys. Rev. Lett. 85 (2000) 2981; P. Hyltdgaard and M. Persson, J. Phys.: Condens. Matt. 12 (2000) L13. @footnote 3@ T.L. Einstein, in Handbook of Surface Science, vol. 1, ed. W.N. Unertl (Elsevier, Amsterdam, 1996), chap. 11. @footnote 4@ P. Hyltdgaard and T.L. Einstein, Europhys. Lett. 59 (2002) 265; Surf. Sci., in press [doi:10.1016/S0039-6028(03)00173-0].

9:20am SS2-WeM4 Structural Evolution of an Atomically Rough Surface: Faceting and Alloying of Re(12-31), A.S.Y. Chan, H. Wang, W. Chen, Rutgers University; J.E. Rowe, United States Army Research Office; T.E. Madey, Rutgers University

The thermal stability of ultrathin metal and oxide films on an atomically rough Re(12-31) surface has been studied using Low Energy Electron Diffraction (LEED) and High Resolution Soft X-ray Photoelectron Spectroscopy (HRSXPS) using synchrotron radiation. Re(12-31) is a morphologically unstable surface with 6 surface layers of atoms exposed. This highly corrugated surface exhibits a surface shift in the Re4f core levels of 0.17 eV towards higher binding energy, relative to the bulk peak. Adsorption of oxygen at room temperature leads to a disordered chemisorbed oxygen overlayer with a rich distribution of chemical binding states, while the surface retains a planar morphology. However, when the O-precovered surface is annealed to temperatures above 700 K, drastic restructuring of the surface occurs to form nanosized facets with a ridged "hill-and-valley" morphology. The facet planes are identified as (01-10) and (11-21) based on kinematic simulations of LEED patterns, and are consistent with Field Emission Microscopy results of our collaborators. By controlling the coverage of oxygen, different oxygen coordination sites on the Re facet planes can be selectively populated and identified by distinct chemical shifts (up to 0.73 eV) to higher binding energies in the Re4f core levels. In contrast, the Re substrate does not facet when precovered with a Pt or Pd overlayer and annealed. Ultrathin Pt films form a dilute alloy with the Re substrate at temperatures as low as 300 K; this surface alloy becomes increasingly Re-rich as the film is annealed.

9:40am SS2-WeM5 Multilayer Thermal Expansion at Surfaces from Surface Core Level Shifts, A. Baraldi, Sincrotrone Trieste S.C.p.A. and Università di Trieste, Italy; S. Lizzit, Sincrotrone Trieste S.C.p.A., Italy; K. Pohl, University of New Hampshire; Ph. Hofmann, University of Aarhus, Denmark; S. de Gironcoli, Scuola Internazionale Superiore di Studi Avanzati (SISSA), Italy

Understanding the thermal properties of nanostructures is of great importance when it comes to making reliable predictions on their stability. By decreasing the size of nanoparticles the thermal behavior of the surface is going to dominate their properties. A basic manifestation of these anharmonic effects is thermal structural expansion. However, some open surfaces are violating our common sense by exhibiting significant negative thermal contraction while some close-packed surfaces show anomalously large thermal expansion. A theoretical understanding of the anharmonic effects at surfaces does not exist and state-of-the-art LDA calculations show large disagreements with experimental results. An especially puzzling case is the thermal expansion of Be(0001). A recent LEED investigation measured an anomalously large thermal surface expansion between 110 K and 700 K, 6 times larger than the bulk. This observation seems inconsistent with measurements reporting no anharmonicity in the out-of-plane surface phonon modes and with a subsequent LDA study within the quasiharmonic approach resulting in no significant thermal expansion. We will present a novel, independent, approach to determine the thermal expansion of Be(0001). We measured the binding energy of the surface state and the values of the surface core level shifts as a function of temperature and compared them to calculated DFT values for different geometries. Our results reveal that, in the temperature range from 300 to 700 K the 1st-to-2nd, 2nd-to-3rd and 3rd-to-4th interlayer coefficient of thermal expansion are 88 ± 15 , -10 ± 15 and $-6 \pm 20 \times 10^{-6} \text{ K}^{-1}$, respectively, to be compared with a bulk value of $12 \times 10^{-6} \text{ K}^{-1}$. Our results confirm the anomalously large thermal expansion of the surface and establish Be(0001) as a firm experimental standard for advances in our theoretical understanding of the thermal behavior of surfaces.

10:00am SS2-WeM6 The Electronic and Geometrical Structures of Ultrathin Bimetallic Films of Pd and Cu on Ru(0001), J. Onsgaard, L. Beach, Aalborg University, Denmark; Z. Li, University of Aarhus, Denmark; T.H. Andersen, University of Southern Denmark; S.V. Hoffmann, University of Aarhus, Denmark

Alloying conditions, low-dimensional effects and catalytical properties of ultrathin bimetallic films of Pd and Cu have been studied. Codeposition of the two metals on a relative inert substrate, Ru(0001), with overlayer thicknesses in the range 1 ML to 4 ML, were carried out. Deposition temperatures were either room temperature or 550 K and the thin films were characterized as a function of temperature. The information is based upon photoelectron spectroscopy based upon use of synchrotron radiation with high resolution core level studies of Pd 3d, Ru 3d, Cu 2p and valence band measurements. LEED was used to follow the order of the overlayers.

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Cu and Pd are distributed in one layer with temperature dependent mixing when the total coverage is one monolayer. The valence bands of the surface alloys are characterized by the Cu 3d band separated from the Pd 4d band at a temperature of 550 K. Heating causes hybridization of the Cu 3d and Pd 4d bands with formation of a new band between the individual metal bands. Surface alloying takes place at 660 K and above this temperature the structures of the overlayers are independent of the order of deposition. Cu 2p core-level binding energy shifts show two linear relationships with the composition of the film in 2- and 3 dimensions. An effect which is attributed to the different coordination numbers between Pd and Cu in 2- and 3 dimensions.

10:20am **SS2-WeM7 A Novel Local Free Energy Minimum on the Cu(001)-Surface**, *H. Wormeester, M. Ovsyanko, G. Stoian, B. Poelsema*, University of Twente, The Netherlands

Glancing incidence Ar⁺ ion bombardment of the Cu(001) surface leads to the formation of two atom layer deep nanogrooves parallel to the incident ion beam. High resolution LEED patterns show that sputtering along [110] and [100] leads to an intergroove distance that depends on temperature, ionfluence and -energy. Suprisingly, prolonged sputtering along [100] leads at various temperatures (175 to 235 K) to a persistent feature located at 1.0% BZ of the Brillouin Zone (BZ). Annealing at temperatures between 250 and 290 K of nanogrooves prepared after a much shorter sputtertime leads to an increase of their separation distance. Here too, the appearance of this persistent feature at 1.0% BZ is observed. These various preparation routes are indicative of a thermodynamic origin of this 1.0% feature, i.e. a local free energy minimum. Mild annealing above 400K transfers the surface to the global free energy minimum: It suffices to remove both the nanogroove structure and the feature at 1.0% BZ. The occurrence of the 1.0% BZ feature is attributed to the relieve of tensile strain, generally present at (001) fcc metal surfaces, leading to a contraction of the in-plane lattice constant of the (001) surface along the [010] azimuth. The energy balance between gain by stress relieve and cost due to lattice mismatch will be discussed. The presence of the nanogrooves along a azimuth turns out to be essential for the relieve of this strain.

10:40am **SS2-WeM8 Low Energy Electron Microscopy of the Quantum Electronic Structure and Stability of Ag Films on Fe(100)**, *K.L. Man*, Hong Kong University of Science and Technology; *Z.Q. Qiu*, University of California at Berkeley; *M.S. Altman*, Hong Kong University of Science and Technology, Hong Kong

Laterally resolved measurements of the reflected electron intensity from Ag films on the Fe(100) surface have been made with low energy electron microscopy (LEEM). Intensity peaks are observed at very low energy that are associated with quantum well resonances in the Ag film above the vacuum level. The dispersion of the quantum well peaks with increasing film thickness is well accounted for by the phase accumulation model, which has been used widely to explain the occupied quantum well states that are observed with photoemission in this and other systems. The signature quantum well peaks that are observed in electron reflectivity are then used in combination with real-space LEEM measurements to monitor film stability during annealing. We find that uniform three monolayer (ML) thick films decompose directly into spatially separated two and five ML thick film regions, whereas uniform four ML thick films decompose initially into three and five ML thick regions and eventually into two and five ML thick regions. The greater stability of two and five ML thick films has been attributed to band structure features near the zone center, which are the source of long period magnetic oscillatory coupling through Ag films. The relative stability of three and four ML thick films may be evidence that band structure features related to the neck of the Fermi surface, which give rise to the short period oscillatory coupling, also play a role in film quantum electronic stability.

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Surface Science

Room Hall A-C - Session SS-WeP

Poster Session

SS-WeP1 High Temperature Catalytic Water Formation Studied with Laser-induced Fluorescence and Cavity Ringdown Spectroscopy, S. Hemdal, A. Johansson, M. Forsth, M. Andersson, A. Rosen, Goteborg University and Chalmers University of Technology, Sweden

Catalytic reactions are successfully studied with Laser-Induced Fluorescence (LIF) and valuable information about mechanisms and reaction paths can be obtained. However, due to the infamous quenching problem absolute concentrations are difficult to measure. Knowledge of exact concentrations of reactants and intermediates are valuable for successfully doing simulations. Cavity Ringdown Spectroscopy (CRDS) is a laser absorption method suitable to measure exact concentration of reaction intermediates in trace amounts. In this study we have combined LIF and CRDS to study OH radicals in the water formation reaction desorbing from polycrystalline palladium and platinum catalysts. In CRDS a laser pulse is injected between two highly reflective mirrors that constitute the optical cavity. In each roundtrip some light will leak out and be detected as a function of time. Assuming single exponential decay, the ring down time τ is defined as the time it takes for the intensity of the detected light to decrease to $1/e$ of its original intensity. By comparing the ring down times for on and off a resonant transition in the OH molecule, the number density can be obtained. The temperature of the catalyst was set to 1500 K, the pressure varied between 7 and 26 Pa and the flow was 100 SCCM. In this study we have successfully detected OH in the H₂/O₂ reaction with CRDS and calibrated the LIF profiles. From the CRDS data we have also calculated the rotational temperature of the OH molecule. The quenching rate for OH is also analysed.

SS-WeP2 Relevance of the Use of XPS and AES to Characterize the Electrochemical Interface, F. Reniers, Universite Libre de Bruxelles, Belgium

XPS and AES are often used in corrosion studies to identify the chemical composition of the interface. Moreover, the last developments of the technology makes available lateral resolutions of 10 nm in AES and 10 Å μ m in XPS, which is interesting for grain boundary corrosion or pitting corrosion. These techniques are also used to characterize the surface of electrodes in fuel cell systems, or mixed (alloys) electrodes used for environmental purposes. AES and XPS are good complement to classical electrochemical techniques (cyclic voltammetry, coulometry) which give access to the current flowing through the interface, as they can identify the nature and the number of surface atoms, as well as their chemical environment. However, as XPS and AES are UHV-based techniques, the physical nature of the interface probed is different from the original solid-liquid one, and transfer in air can modify the sample surface. This paper shows selected examples of coupled UHV-electrochemical studies (adsorption, corrosion, electrocatalysis), using transfer systems, and describes the information which can and which cannot be extracted from such studies. The persistence of the constituents of the electrical double layer and the nature of the electrode metal on the reliability of the results is discussed. A description of some transfer systems, designed to minimize the experimental artefacts, is proposed. @FootnoteText@ @FootnoteText@ @FootnoteText@ F. Reniers, J. Physics D: Appl.Phys.35 (2002)R169-R188.

SS-WeP3 A Laser Plasma Vacuum Ultraviolet Light Source for Photo Desorption Studies, I. Arakawa, J. Sato, T. Miura, Gakushuin University, Japan; T. Hirayama, Rikkyo University, Japan

We have developed a laser-plasma vacuum ultraviolet light source (LPLS) as an excitation light source for the experimental studies of desorption induced by electronic transitions (DIET). Radiation from metal plasma, which is produced by laser beam focused on a metal surface, has a wide spectrum from infrared to X-ray and can provide a substitute for a conventional synchrotron radiation. In comparison with the synchrotron light source, LPLS has the advantage of being intense in short duration: the pulse width is the order of 10 ns, which is determined by a laser pulse. This distinctive feature makes it possible to obtain higher time resolution in a time-of-flight measurement of desorbed particles. The specifications of the Q-switched Nd-YAG laser we used in our LPLS are the followings; wave length: 532 nm with a second harmonic generator, maximum power: 210 mJ/pulse, pulse width: 10 ns, and repetition rate: 50 Hz. The radiation from the metal plasma is monochromatized by the three toroidal type gratings

which cover the wavelength ranges of 4 - 12, 12 - 36, and 36 - 108 nm. We have chosen Ta as the target metal for plasma source. This is because (1) a continuum like spectrum of primary radiation from plasma is expected in VUV range and (2) evaporated Ta will act as a getter pump in a vacuum chamber. The photon intensity of our LPLS apparatus is 10^{10} photons/pulse - 10^{11} photons/pulse in the pulse width less than 15 ns and with the resolution $\Delta\lambda/\lambda = 50 - 100$ in the range of 12 - 108 nm. On application of our apparatus to the PSD experiment of a solid Ne, it was proved that the performance was satisfactory both in photon intensity and in time resolution for the DIET study.

SS-WeP4 Ellipsometric and XLEED Observation of Growth and Structure of Xenon and Krypton Films on the Surface of Silver Single Crystals, A. Tosaka, T. Mitake, K. Ishii, M. Sato, T. Miura, I. Arakawa, Gakushuin University, Japan

The layering growth and the structure of Xe and Kr films on Ag(111), Ag(100) and Ag(110) has been observed by means of ellipsometry and extremely-low-current Low Energy Electron Diffraction (XLEED) under the quasi-equilibrium condition from a submonolayer to a thick film. We chose the surfaces of Ag(111), Ag(100) and Ag(110) as the substrates in order to investigate the effect of the substrate geometry on the overlayer growth and structure. In the case of Xe/Ag(111) and Kr/Ag(111), it was confirmed that the overlayer is incommensurate with the substrate while the unit vectors of the Xe or Kr overlayer align with those of the substrate. This alignment is likely due to the pinning of overlayer at the steps of the substrate surface. @FootnoteText@ We found that there were two types of alignment of a Xe or Kr overlayer on Ag(100): the unit vector of the overlayer was along of Ag in one alignment and along in the other. It was observed that Xe and Kr films on Ag(110) had centered-rectangular structure, which is uniaxially commensurate with [001] of Ag, just after the first layer condensation. In the case of Xe/Ag(110), lowering the sample temperature or raising the surrounding pressure brings out the uniaxial compression of Xe film along [110] of Ag. After this uniaxial compression along [110], the compression along [001] of Ag commenced. Finally, the Xe-Xe spacing reached to the bulk value before the second layer condensation. On the other hand, in the case of Kr/Ag(110), such compression did not observed in monolayer. @FootnoteText@ @FootnoteText@ G. S. Leatherman, R. D. Diehl, M. Karimi and G. Vidali: Phys. Rev. B 56 (1997) 6970.

SS-WeP6 Chemical Structure of the Pt/CdZnTe Interface*, D.J. Gaspar, M.H. Engelhard, D.E. McCready, Pacific Northwest National Laboratory; A.A. Rouse, Cs. Szeles, eV PRODUCTS

We have determined the interfacial electronic and chemical structure for the Pt/CdZnTe system using scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX), X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). XRD was performed on aggressively aged controls (such as Pt/Te, where PtTe₂ was formed) to elucidate the phases expected to form under normal annealing conditions. The presence of the phases was confirmed by looking at the specimens in cross-section with SEM/EDX. This was followed by XPS depth profiling experiments to determine binding energy shifts associated with the various phases, which were then used to determine the phases present in the more narrow interfacial regions of typical Pt/CZT structures for a variety of annealing conditions and for varying compositions. @FootnoteText@ *This work supported by the DOE NNSA NA-22 program

SS-WeP7 Modeling Nano-Structure Evolution in the Continuum Step Model: Decay of Pb Crystallites@Footnote1@, M. Degawa, D.B. Dougherty, K. Thum u@rmer, J.E. Reutt-Robey, E.D. Williams, T.J. Stasevich, T.L. Einstein, University of Maryland

The evolution of crystalline nanostructures can be described accurately down to surprisingly small size scales using the continuum step model. @FootnoteText@ Quantitative predictions for rates in general cases requires understanding the balance of competing kinetic mechanisms (step-edge attachment vs. terrace diffusion), competing driving forces (Gibbs-Thomson vs. step-step repulsions) and the influence of the initial shape and boundary conditions on the nanocrystal. Using numerical modeling, we demonstrate the evaluation of best fits in this multi-parameter space for the case of the relaxation of Pb crystallites after thermal quench@FootnoteText@ and after triggered decay. @FootnoteText@ The experimental system involves a volume-conserving change in the shape of the Pb crystal, which proceeds via cylindrically symmetrical layer-by-layer removal from the top facet of the crystal and transfer of mass to the sides of the crystal. The rate of peeling of all the layers yields non-unique combinations of the diffusion coefficient and attachment detachment rate, which can be limited by the range of physically

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reasonable the step-step repulsions. The time difference between sequential layer peelings, and the slow-down to the final state is governed by the choice of the boundary conditions and the step-step repulsions. The relationship of the best fit parameters to atomistic models for Pb, and the physical significance of the boundary conditions will be discussed. @FootnoteText@ This work has been supported by the DOE-NNI and NSF-MRSEC. @footnote 1@ A. Ichimiya, K. Hayashi, E.D. Williams, T.L. Einstein, M. Uwaha and K. Watanabe, Phys. Rev. Lett. 84, 3662 (2000). @footnote 2@ K. Thurmer, J.E. Reutt-Robey, E.D. Williams, M. Uwaha, A. Emundts and H.P. Bonzel, Phys. Rev. Lett. 87, 186102-1 (2001). @footnote 3@ D. B. Dougherty, K. Thurmer, M. Degawa, W.G. Cullen, J.E. Reutt-Robey and E.D. Williams, submitted for publication (2003).

SS-WeP8 Using Island Step-Edge Fluctuations to Determine Absolute Step Energies: Application to Pb(111) @footnote 1@, T.J. Stasevich, F. Szalma, T.L. Einstein, University of Maryland, College Park

It is well known that the equilibrium shape of an adatom or vacancy island can be used to extract the step free energy (or line tension) of the island step-edge up to a scale factor. Obtaining the absolute step energy, however, requires a deeper analysis. Recently it has been shown that by analyzing the island step-edge fluctuations about the equilibrium island shape, the desired absolute step energy can be obtained. @footnote 2,3@ We exploit this theoretical framework to analyze the temporal fluctuations of two-dimensional Pb(111) adatom and vacancy islands measured with scanning-tunneling microscopy. @footnote 4@ We report on our ongoing analysis and discuss the degree to which subtle transformations are needed to obtain eigenmodes from the conventional multipole modes. With the aid of movies, we also discuss techniques used to find the equilibrium island shape, as well as tools used to analyze the fluctuations and, thus, determine the absolute step free energies. @FootnoteText@ @footnote 1@ Work at UM supported by NSF Grants MRSEC DMR 00-80008 and EEC-0085604. @footnote 2@ S. Kodambaka et al., Phys. Rev. B 67 (2003) 035409; S.V. Khare et al., Surf. Sci. 522 (2003) 75. @footnote 3@ F. Szalma and T.L. Einstein, submitted to SS1@footnote 4@ K. Thürmer et al., Phys. Rev. Lett. 87 (2001) 186102.

SS-WeP9 Persistence Exponent for Terrace-Diffusion Limited Step Fluctuations: Numerical Simulation @footnote 1@, H. Gebremariam, C. Dasgupta, T.L. Einstein, University of Maryland, College Park

The strength of the step-step repulsion, one of the 3 key parameters of the step continuum model, is known to influence many properties of a vicinal surface. Motivated by experiments at Maryland on Ag(111) and Pb(111) @footnote 2@ and on Al/Si(111), @footnote 3@ we gauge the impact these interactions on the persistence exponent θ . (Here the steady-state persistence probability $p(t) \sim t^{-\theta}$) is the probability that a fluctuating step has not crossed a chosen rough initial position by time t . @footnote 4@ According to simple scaling based on Langevin arguments, θ should be $(1/2)[1+1/z]$ for evaporation-condensation ($z=2$) and $(1/2)[1+3/(4z)]$ for periphery diffusion dynamics ($z=4$). @footnote 4@ To investigate whether either of these relations also holds for terrace-diffusion-limited (TD) dynamics (for which $z=3$), we perform Monte Carlo simulations for an SOS model similar to that used for earlier investigations of step fluctuations. @footnote 5@ @FootnoteText@ @footnote 1@ Work at UM supported by NSF Grants MRSEC DMR 00-80008 and EEC-0085604. @footnote 2@ D.B. Dougherty et al., Surface Sci., in press [doi:10.1016/S0039-6028(03)00017-7]. @footnote 3@ D.B. Dougherty et al., Phys. Rev. Lett. 89 (2002) 136102. @footnote 4@ J. Krug et al., Phys. Rev. E 56 (1997) 2702. @footnote 5@ N. C. Bartelt et al., Surface Sci. 312 (1994) 411.

SS-WeP10 Effects of Thickness Extension Resonance Oscillation of Acoustic Wave on Activity/Selectivity of Metal Catalysts with Two Layer Structures, Y. Oka, Y. Nakajima, N. Saito, H. Nishiyama, Y. Inoue, Nagaoka University of Technology, Japan

We have so far reported that the thickness-extension resonance oscillation (TERO) of acoustic wave generated on a ferroelectric crystal by a piezoelectric effect has the ability to markedly enhance the catalytic activity and to significantly change the reaction selectivity of metal-catalyzed reactions. The catalyst activation by TERO was associated with large and dynamic lattice displacement vertical to the catalyst surfaces. The TERO effects were different among the metal catalysts. In aiming at raising the efficiency of the TERO effects, it is of interest to examine the TERO effects on two-layer structure catalysts combining the different kinds of metal phases. In the present study, a metal catalyst combining Mo with Ag was employed. A ferroelectric z-cut LiNbO₃ single crystal was used as substrate, on which Ag film was deposited at a thickness of 100 nm,

followed by the deposition of Mo with different thickness in the range 20-100 nm. Auger electron spectroscopic measurements showed that the two-layer structures were maintained during catalytic run. In ethanol decomposition on the Mo/Ag catalysts with different thickness of Mo layer, major gas phase products were ethylene and acetaldehyde. With turning TERO on, only the activity for ethylene production remarkably increased. The activation coefficient, defined as the ratio of the activity with TERO-on to that with TERO-off was 16 for 100nm, 17 for 75 nm, 24 for 50 nm, and 27 for 20 nm Mo layer, indicating that the TERO-inducing activation for ethylene production became larger as the thickness of Mo layer was smaller. Lattice displacement of Mo/Ag catalysts increased with decreasing thickness of the Mo layer. There was a correlation between the extent of lattice displacement and catalyst activation by the TERO in the two layer structures. These results have demonstrated that the combination of different metal phases is useful for extending TERO effects to catalyst activation.

SS-WeP11 Chemisorption of Sulfur on Au(111), Au(100) and Au(110) by Means of UHV and Electrochemical Adsorption, Y.W. Yang, L.J. Fan, National Synchrotron Radiation Research Center, Taiwan

Reaching a detailed understanding of the interaction between sulfur and gold surfaces has become more urgent due to their wide usage in constructing self-assembled monolayers in nanoengineering research. Here, we report on a detailed structural and energetic study of molecular S₂ adsorbed on Au(111), Au(100) and Au(110) surfaces by means of LEED, SR-XPS and TPD. A comparative study of sulfur adsorption from electrochemical (EC) deposition is also investigated with ECSTM. For all three surfaces, LEED study reveals the presence of a series of ordered adsorption structures. TDS data show the presence of strong repulsive interaction among sulfur adsorbates and, interestingly, the existence of several unusual binding states on all three surfaces. These binding states are characterized by sharp features of less than 30 K in desorption peak width. The overall change of S 2p core levels is found to be small in spite of a strong variation of adsorption structure and adsorption site among three gold surfaces. The observed S 2p_{3/2} core levels fall between 161.0 and 161.3 eV. The rather constant S 2p_{3/2} binding energy suggests the importance of final-state metallic screening. ECSTM shows the presence of additional ordered structures not observable from UHV adsorption but stabilized by the coadsorbed ions from the solution. UHV and EC adsorption structure data will be discussed together.

SS-WeP12 Structure and Reactivity of Methyl Pyruvate and Butane-2,3-Dione on Pt(111) and Ni(111): Relevance to Enantioselective Hydrogenation at Surfaces, M.-A. Laliberte, S. Lavoie, P.H. McBreen, Universite Laval, Canada

Methyl and ethyl pyruvate are substrates in one of the rare examples of efficient enantioselective heterogeneous catalysis. @footnote 1,2@ The asymmetric hydrogenation of pyruvates to lactates occurs on chirally-modified supported platinum catalysts. Nickel catalysts are, in contrast, not active for the reaction. Data is now available in the literature for the chemisorption of pyruvates on both Ni(111) @footnote 3,4@ and Pt(111). @footnote 5-8@ An intriguing aspect of these results is that they show that the surface chemistry of pyruvates differs greatly between the two metals. We have previously reported a detailed RAIRS study of the coverage dependent orientation, conformation and surface chemistry of methyl pyruvate on Ni(111). @footnote 3,4@ The present study presents extensive new RAIRS data for methyl pyruvate on Pt(111), and butane-2,3-dione on Ni(111) and Pt(111), thereby enabling a detailed comparison to be made between the two surfaces. @FootnoteText@ @footnote 1@ Y. Orito, S. Imai, S. Niwa, N. G. Hung, J. Synth. Org. Chem. Jpn. 37, 173 (1979) @footnote 2@ H. U. Blaser, H. P. Jalett, W. Lottenbach and M. Studer, J. Am. Chem. Soc. 122, 12675 (2000). @footnote 3@ M. Castonguay, J.-R. Roy, S. Lavoie, A. Adnot, and P. H. McBreen, J. Am. Chem. Soc. 123, 6429 (2001). @footnote 4@ M. Castonguay, J.-R. Roy, A. Rochefort, and P. H. McBreen, J. Am. Chem. Soc. 122, 518 (2000). @footnote 5@ T. Burgi, F. Atamny, R. Schlogl and A. Baiker, J. Phys. Chem. B, 104, 5953. (2000). @footnote 6@ J. M. Bonello, R. M. Lambert, N. Kunzle and A. Baiker, J. Am. Chem. Soc. 122, 9864 (2000). @footnote 7@ J.M. Bonello, E.C.H. Sykes, R. Lindsay, F.J. Williams, A. K. Santra and R.M. Lambert, Surf. Sci. 482 207 (2001) @footnote 8@ J. M. Bonello, F. J. Williams, A. K. Santra, and Richard M. Lambert, J. Phys. Chem. B, 104, 9696 (2000).

Wednesday Morning Poster Sessions, November 5, 2003

SS-WeP14 QCM Studies of Phonon and Electron Scattering Effects for Monolayer Octane/Cu(111) and Octane/Pb(111) Interfaces, T. Coffey, J. Krim, North Carolina State University

The surface resistivity and sliding friction of thin films on metal surfaces has been linked to the scattering of conduction electrons from phonons and imperfections in the lattice. It is also believed that the damping of Frustrated Translational (FT) phonon modes are related to friction between adsorbates and substrates. The parallel FT modes are believed to be directly linked to sliding friction, but it is not clear how changes in the damping of perpendicular FT modes affects sliding friction. The perpendicular FT mode of octane adsorbed on Cu(111) has a damping constant that is twice as large as that of octane adsorbed on Pb(111). We are using QCM to study octane sliding on copper and lead surfaces to determine how the damping of perpendicular FT modes affect sliding friction. We have observed an increase in sliding friction as the damping of the perpendicular FT mode increased. B.N.J. Persson, Sliding Friction, Physical Principles and Applications, Springer, Berlin (2000). Fuhrmann and Ch. Woll, Surface Science 368 (1996) 20-26.

SS-WeP15 Photoemission Study of the Oxidation of Cu{111} with Hyperthermal O₂ Molecular Beam, K. Moritani, Japan Atomic Energy Research Institute, Japan; M. Okada, S. Sato, S. Goto, T. Kasai, Osaka University, Japan; A. Yoshigoe, Y. Teraoka, Japan Atomic Energy Research Institute

The oxidation of Cu has been of great interest because of the important role of Cu oxides in material science, for example, high T_c superconductors of cuprates and solar cells. Thus, many experimental and theoretical studies have been performed to understand the oxidation of Cu. However, the oxide-formation processes have been little elucidated from the kinetics and dynamics points of view. In the present work, we studied the oxidation of Cu{111} with a hyperthermal O₂ molecular beam (HOMB) using X-ray photoemission spectroscopy (XPS) in conjunction with a synchrotron radiation (SR) source. All experiments were performed with the surface reaction analysis apparatus (SUREAC 2000) constructed in BL23SU at SPring-8. The kinetic energy of incident O₂ can be controlled by changing the O₂, He and/or Ar gas mixing ratios with the nozzle temperature kept at 1400 K. The incident direction of the HOMB is along the surface normal of the sample kept at 300 K. After the irradiation of a proper amount of HOMB, high-resolution XPS spectra were measured at 300 K using SR. We measured O-uptake curves, determined from the integration of O-1s XPS spectra, in the 2.3- and 0.6-eV HOMB irradiation on the Cu{111} surface. The efficiency of oxidation with HOMB is higher than that with ambient thermal O₂ gas. The kinetics of the dissociative adsorption in the HOMB incidence can be described well using a Langmuir-type adsorption model under $\theta \leq 0.5$ ML. On the other hand, further oxidation occurs rather inefficiently under $\theta > 0.5$ ML even for the 2.3-eV-HOMB irradiation. We found that such slow oxidation process of Cu can be interpreted in terms of a collision-induced-adsorption mechanism. We will discuss possible models of oxidation process of Cu based on the incident-energy dependence of the O-uptake curve.

SS-WeP16 Sulfur-oxygen Interactions on Cu(100) Revealed by Surface Resistivity Measurements, P.M. Baker, R.G. Tobin, Tufts University

Measurements of adsorption-induced changes in the electrical resistivity of thin Cu(100) films show that small amounts of preadsorbed sulfur dramatically reduce the resistivity caused by subsequently adsorbed oxygen. Previous measurements with sulfur and oxygen alone had shown that these two atoms, although chemically very similar, exhibited very different surface resistivity behavior. For oxygen the resistivity increases linearly with coverage, indicating minimal interactions between the oxygen atoms. Sulfur exhibits a strongly nonlinear coverage dependence, suggesting that at high coverages interactions between the adsorbed sulfur atoms reduce their cross section for scattering the metal's conduction electrons. In the present experiments the resistivity induced by oxygen was measured on 50 nm-thick Cu(100) films predosed with varying amounts of sulfur. For all sulfur coverages studied the oxygen-induced resistivity varies linearly with oxygen coverage, but the slope of the resistivity vs. oxygen coverage curve is strongly affected by the sulfur. This slope is a measure of the scattering cross section of each adsorbed oxygen atom. A sulfur coverage as low as 0.03 ML reduces the slope by a factor of two from its value on a sulfur-free surface. Evidently adsorbed sulfur atoms suppress the scattering cross section of coadsorbed oxygen even more strongly than they affect the cross section of other sulfur atoms. The saturation oxygen coverage is not significantly reduced at the sulfur

coverages studied, indicating that site-blocking by sulfur is not involved. Rather the explanation must lie in changes in oxygen's electronic structure due to chemical interactions with the sulfur. @FootnoteText@ @footnote 1@R.G. Tobin, Surf. Sci. 524, 183 (2003).

SS-WeP17 Adsorption and Reaction of NO and CO on CeO₂(111) and Ce_{0.8}Zr_{0.2}O₂(111) Surfaces, S. Azad, M.H. Engelhard, J. Szanyi, C.H.F. Peden, Pacific Northwest National Laboratory

The adsorption and reaction of NO and CO on oxidized and reduced CeO₂(111)/YSZ(111) surfaces have been studied using temperature-programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). NO desorbs molecularly from the fully oxidized and reduced surfaces, when adsorbed at 125 K, in three desorption states at 157, 196 and 300 K. NO reacts non-dissociatively on the fully oxidized surface. Reactivity of the high temperature annealed and sputtered surfaces, is significantly higher compared to the fully oxidized surface. Adsorption of NO on the reduced surfaces is followed by N-O bond dissociation producing adsorbed N and O atoms, which subsequently form a variety of products during TPD. A large fraction of CO molecules, adsorbed on the sputtered ceria surface, is oxidized to CO₂ whereas CO desorbs molecularly from the fully oxidized CeO₂(111)/YSZ(111) surface, when adsorbed at 125 K. These results will be compared with the ongoing studies on adsorption and reaction of NO and CO on Ce_{0.8}Zr_{0.2}O₂(111)/YSZ(111).

SS-WeP18 Electronic Properties of Au Nanoparticles Covalently Attached to Au{111} via 1,10-decanedithiol, D.J. Fuchs, P.S. Weiss, The Pennsylvania State University

1,10-decanedithiol molecules are inserted into a n-decanethiol [CH₃(CH₂)₉SH] self-assembled monolayer (SAM) on Au{111} and are characterized by scanning tunneling microscopy (STM). Bifunctional molecules are inserted into the SAM for the covalent attachment of monolayer protected gold nanoparticles. The gold nanoparticles are synthesized with short chain alkylthiol ligands to promote covalent attachment to the inserted 1,10-decanedithiol molecules and to reduce the probability of steric binding. Electronic properties of isolated gold nanoparticles are compared to proximate pairs and assemblies of gold nanoparticles.

SS-WeP19 The Decomposition of Ethylene on Rhodium(100): Theory and Experiments, A.P. Bavel, D.L.S. Nieskens, D. Curulla Ferre, J.W. Niemantsverdriet, Eindhoven University of Technology, The Netherlands

Hydrocarbon decomposition into C_xH_y fragments is of great importance for understanding catalytic reactions of these species. We investigate the decomposition pathway of ethylene on the rhodium(100) surface, both on a clean surface and on a hydrogen presaturated surface. We use different experimental techniques: Temperature Programmed Desorption (TPD), Static Secondary Ion Mass Spectrometry (SSIMS), Low Energy Electron Diffraction (LEED) and High Resolution Electron Energy Loss Spectroscopy (HREELS). It is known from literature that ethylene decomposition starts already at low temperatures (<200 K) and continues up to 700 K to give C on the surface. The nature of the intermediate species has been shown to depend on the amount of presaturated hydrogen. Several authors have shown, by using HREELS, the presence of CCH₃ species in an upright position and CCH species in a "bent" mode. Our LEED experiments indicate a p(2x2) structure for a saturation dosage of ethylene, implying a saturation coverage of 0.25 ML. The TPD spectra show a complicated pattern for the hydrogen desorption. We can distinguish several decomposition limited desorption processes for hydrogen. SIMS measurements show that CCH and CHCH species are present at relatively low temperatures. Some preliminary HREELS experiments in specular and off-specular mode have already been performed. In addition to the experiments we have used periodic DFT calculations to calculate the energy of all possible C_xH_y species on the Rh(100) surface. We have used a p(2x2) unit cell in the calculations, thus mimicking a saturation coverage of ethylene. The calculations show that CCH₃ and CCH are the most stable species, in accordance with literature. We have also found, however, that the CHCH species is even more stable. At higher temperatures these species will decompose further into CH and finally carbon. @FootnoteText@ @footnote 1@Slavin, A.J., Bent, B.E., Kao, C.T. and Somorjai, G.A., Surface Science 206 (1988) 124-144. @footnote 2@Kose, R., Brown, W.A. and King, D.A., Chemical Physics Letters 311 (1999) 109-116. @footnote 3@Egawa, C., Surface Science 454-456 (2000) 222-226.

Wednesday Morning Poster Sessions, November 5, 2003

SS-WeP20 The Adsorption of Benzene on Zr(0001), N. Stojilovic, R.D. Ramsier, The University of Akron

The adsorption of benzene on Zr(0001) has been studied by temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) methods. Following adsorption at 150 K benzene desorbs at about 720 K. Low energy electron bombardment (500 eV) of adsorbed benzene neither affects the amount of desorbing species nor results in the production of new species. AES and secondary electron emission crystal current (SECC) measurements indicate that carbon remains at the surface after thermal desorption. This work is part of an effort to investigate the possibility of forming zirconium carbide layers for selective surface passivation.

SS-WeP23 Step Edge Diffusion on Ag: Correlations and Persistence as a Function of Temperature*, O. Bondarchuk, M. Degawa, E.D. Williams, D.B. Dougherty, M. Constantin, S. Das Sarma, C. Dasgupta, University of Maryland

The stochastic character of step-edge diffusion can be evaluated in terms of the persistence probability for step edge fluctuation, that is the probability that a fluctuating step does not return to a chosen initial position over a given time interval. Time dependent STM was used to observe temporal step fluctuations on Ag(111) thin film in temperature range from RT up to 450 K. The concept of persistence@footnote 1,2@ as well as the more usual time-correlation function have been used to analyze the step edge fluctuation on the surface in equilibrium and under electrical current stress. Experimentally measured persistence scales as a simple power law that is consistent with scaling predictions,@footnote 1@, and which also agrees with more rigorous tests of persistent behavior.@footnote 3@ The temperature dependence of the persistence prefactor is extremely weak, in contrast with the (diffusion constant dominated) Arrhenius behavior of the prefactor of the correlation function. Numerical calculations using the continuum Langevin equation confirm the weak temperature dependence. The physical significance of the persistence prefactor and the effects of discrete sampling and electrical current stress will be discussed. *This work has been supported by the NSF-NIRT and NSF-MRSEC. @FootnoteText@@footnote 1@J.Krug, H. Kallabis, S.N. Majumdar, S.J.Cornell, A.J. Bray, C.Sire, Phys.Rev. E56(1997)2702. @footnote 2@ D.B. Dougherty, O. Bondarchuk, M.Degawa, E.D. Williams, Surf.Sci. 527(2003)L213. @footnote 3@ M. Constantin, S.Das Sarma, C. Dasgupta, O.Bondarchuk, D.B. Dougherty, E.D. Williams, in press.

SS-WeP25 Growth and Characterization of Ultra-thin Lattice Matched Multilayers of Cr@sub x@Mo@sub 1-x@ and MgO, I. Meyvantsson, S. Olafsson, University of Iceland; *K. Johnsen,* Biopharmaceuticals, Iceland; *J.T. Gudmundsson,* University of Iceland, Iceland

We report on the preparation of a lattice matched heteroepitaxial system in a magnetron sputtering discharge. Cr@sub x@Mo@sub 1-x@ thin films were grown on MgO(1 0 0) using DC power, and an MgO overlayer was grown on top by reactive sputtering using pulsed power. The composition of the binary metal alloy is chosen so that the interatomic distance along the direction approximates the lattice constant of MgO. Thus the film should exhibit negligible strain. The structure of the films was studied by ex situ X-ray diffraction (XRD) and the morphology by scanning electron microscopy (SEM). Low angle X-ray reflectivity measurements were performed to determine film thickness, and surface and interface roughness. The effect of substrate temperature during growth is discussed based on thermodynamics and kinetics of the growth process. The minimum thickness for continuity of the binary metal alloy film was determined using four point probe resistance measurements. The insulating properties of the MgO film as a function of thickness were assessed by measuring the tunnelling current I-V characteristics of a metal-insulator-metal structure.

SS-WeP26 Substrate Orientation Dependence for Ni Film Growth on Al Single Crystals: Comparisons of Atomistic Simulations with Experiment, R.J. Smith, N. Winward, C.V. Ramana, V. Shutthanandan, N.R. Shivaparan, Y.W. Kim, Montana State University; *G. Bozzolo,* NASA GRC and OAI; *J. Morse,* OAI

The structure and composition of metal-metal interfaces grown at room temperature is strongly dependent on a number of kinetically limited processes. Using ion scattering spectroscopy (LEIS and HEIS), we have studied the evolution of interface alloying for room temperature deposition of Ni on low-index surfaces of Al, and find that the thickness and composition of the Ni-Al interface varies remarkably for Al(100) as compared to Al(110) and Al(111) substrates. In the present work we have used Monte Carlo simulations with embedded-atom potentials to study the

interface evolution of Ni on these three Al surfaces. The results are compared with measurements of interface formation obtained using MeV He ion backscattering and channeling (RBS/c), as well as low-energy He ion scattering (LEIS). Both simulation and experiment show a greater tendency for Ni to remain at the surface of Al(100) when compared to the more open Al(110) and more close-packed Al(111) surfaces. To further understand this unusual behavior the BFS method for alloys is used to calculate the strain and chemical energies associated with a series of Ni-Al surface configurations, and in this manner, to construct a likely scenario for the evolution of the Ni-Al alloy on the three surfaces. Work supported by NSF DMR 00-77534.

SS-WeP27 Theory of Uptakes in Thin-film Growth: Autocatalytic-reaction Model and Kinetic Monte-Carlo Simulation, M. Suemitsu, H. Togashi, Tohoku University, Japan; *T. Abe,* Tohoku Institute of Technology, Japan

In many thin film growth systems, the film grows via nucleation of 2D clusters, their growth, and coalescence. The process occurs with various time and space scales depending on the substrate temperature T and the impinging flux P of the precursors, which determines the uptake and morphology of the film. This T- and P-dependence arises from various T- and P-dependence of the surface processes behind the film growth: precursor adsorption and adatoms' migration and desorption. Migration and desorption are always thermally activated but with different activation energies. Adsorption may or may not be thermally activated but is consistently influenced by P. Reflecting this complication, thin film growth dynamics is a delicate function of both T and P. In high-P-low-T regime the growth proceeds with a random adsorption, which presents a Langmuir-type uptake of the film coverage. In low-P-high-T regime it proceeds with a 2D-island growth, which presents a sigmoid-function-type uptake. We have recently proposed autocatalytic-reaction (ACR) model as a rate equation for thin-film growth,@footnote 1@ which was successfully applied to various modes in dry oxidation at Si(001) up to one monolayer. With only two fitting parameters as it is, ACR bridges the gap between the two extremes of the behavior. To clarify the physics behind the model, we have conducted in this work a kinetic Monte Carlo (KMC) simulation assuming (1)adsorption of precursors only at the bare portion of the substrate, (2)finite residence time for the adatoms before desorption, (3)isotropic migration of adatoms, and (4)minimum stable clusters with two atoms. Quantitative agreement obtained between KMC and ACR allow us to discuss the development of the surface morphology using KMC. It was found that the success of the ACR model lies in its effective inclusion of nucleation, growth, and coalescence of adatoms. @FootnoteText@@footnote 1@ M. Suemitsu, Y. Enta, Y. Miyanishi, N. Miyamoto, Phys. Rev. Lett. 82 (1999) 2334. .

SS-WeP29 Direct Observation of Key Interactions Between the Chiral Modifier, Substrate Molecule and Pt(111) Surface in the Enantioselective Hydrogenation of Methyl Pyruvate, S. Lavoie, M.-A. Laliberte, P.H. McBreen, Universite Laval, Canada

Methyl and ethyl pyruvate are substrates in one of the rare examples of efficient enantioselective heterogeneous catalysis. The asymmetric hydrogenation of these alpha-ketoesters to the corresponding lactates on chirally-modified supported platinum catalysts is known as the Orito reaction. The daunting complexity of this reaction may be appreciated by considering the fact that interactions between the chiral modifier and the metal surface, between the pro-chiral substrate and the metal surface, between the modifier and the pro-chiral substrate, and between the pro-chiral substrate and adsorbed hydrogen, must all be taken into account. A similar list can be made for interactions involving the half-hydrogenated ketoester-and all this ignores the role of the solvent. It then seems improbable that the uhv surface science approach can be used to profitably attack such a complex system. However, we will show that a uhv RAIRS study of methyl pyruvate on chirally modified Pt(111) reveals key information of relevance to any discussion of the reaction mechanism of the Orito reaction. In particular the RAIRS study permits the direct observation of hydrogen bonding between methyl pyruvate and the modifier. Furthermore, it shows how the interaction modifies the geometry and thermal stability of the adsorbed pyruvate. The results also reveal subtle effects due to spectator species, due to the modifier coverage and due to the adsorption conformation of methyl pyruvate. The combined new information on the 1:1 modifier-pyruvate interaction and on the pyruvate adsorption geometry suggests an important revision to the most widely accepted mechanism for the Orito reaction. In addition, data taken in a comparative study of methyl pyruvate on Ni(111) and Pt(111)-systems which display very different surface chemistries-will be used to comment on possible reasons why nickel is inactive for the Orito reaction.

Wednesday Afternoon, November 5, 2003

Surface Science

Room 328 - Session SS+NS-WeA

Perspectives and New Opportunities

Moderator: R.A. Bartynski, Rutgers University

2:00pm **SS+NS-WeA1 The Birth and Evolution of Surface Science: Key Role of AVS, C.B. Duke**, Xerox Wilson Center for R&T **INVITED**

This presentation consists of a description of the birth and evolution of surface science as an interdisciplinary research area. It provides an overview of the themes developed in the Surface Science section of the AVS 50th anniversary issue of The Journal of Vacuum Science and Technology (JVST). The history of Surface science can be traced in terms of four waves of innovation [see e.g., C. B. Duke, Proc. Nat. Acad. Sci. 100, 3858 (2003)]. It was born in the mid 1960s based on the combination of ultra high vacuum technology, the recognition that "low energy" (500 eV) electrons exhibit inelastic collision mean free paths of atomic dimensions, and the commercial availability of single-crystal samples. The founding in 1964 of JVST and Surface Science marks this event. During the 1970s through the turn of the century the evolution surface science was strongly influenced by the microelectronics revolution that in turn was profoundly impacted by the evolving surface analytical capabilities. In the 1980s scanning probe microscopy was invented. It blossomed in the 1990s, launching a new era of digital imaging in surface science. Today, the frontiers of surface science are increasingly in its applications to characterize complex systems, including solid-liquid interfaces and fragile biological systems. Descriptions of these are taken from C. B. Duke and E. Ward Plummer, eds. "Frontiers in Surface and Interface Science", Surf. Sci. 500 (2002). In this presentation I trace the evolution of surface science through these four eras of its evolution with emphasis on how AVS has been instrumental in shaping each era.

2:40pm **SS+NS-WeA3 STM Single Atom/Molecule Manipulation: A New Dimension for Nanoscience and Technology, S.-W. Hla**, Ohio University **INVITED**

The fascinating advances in single atom/molecule manipulations with the STM-tip allow scientists to fabricate artificial atomic scale structures, to study local quantum phenomena or to probe physical and chemical properties of matter at single atom and molecule level on crystal surfaces. The STM-tip is not only used as an imaging tool but also as a manipulating and even, as an engineering tool in these experiments. In this presentation, our recent results of single atom/molecule manipulation experiments conducted by using a low temperature UHV-STM on metallic surfaces will be presented. A variety of cutting-edge STM single atom/molecule manipulation procedures, in combination with complementary tunneling spectroscopy and imaging, are systematically used to develop robust and innovative experimental schemes. Using these schemes, we examine the mechanical stability, electronic properties and chemical reactivity of single molecules at the spatial limit. The presentation will include vibrational spectroscopy/microscopy of single semi-phenyl molecules, electronic spectroscopy examinations of single Ag atoms/vacancies and self-assembled molecular films. Determination of mechanical strengths and internal conformational changes of large single molecules using tip-molecule interaction forces will be shown. Detail single atom movement mechanisms during quantum corral constructions with the STM-tip will be demonstrated. The extraction of single atoms from the native substrate and construction of various atomic scale structures on an atom-by-atom basis using the STM-tip will be presented by showing STM movies. @FootnoteText@ @footnote 1@S.-W. Hla, K.-H. Rieder, Ann. Rev. Phys. Chem. 54, 307-330 (2003). @footnote 2@H.C. Manoharan, C.P. Lutz, D.M. Eigler, Nature 403, 512-515 (2000). @footnote 3@B.C. Stipe, M.A. Rezaei, W. Ho, Science 280, 1732-1735 (1998). @footnote 4@C. Joachim, K. Gimzewski, A. Aviram, Nature 408, 541-548 (2000).

3:20pm **SS+NS-WeA5 Stark-Effect and Two-Electron Photon Emission in Scanning Tunnelling Spectroscopy, R. Berndt, G. Hoffmann, L. Limot, T. Maroutian**, University of Kiel, Germany; **P. Johansson**, University of Årrebro, Sweden; **J. Kroeger**, University of Kiel, Germany **INVITED**

We report a quantitative low-temperature scanning tunnelling spectroscopy (STS) study on the Ag(111) surface state over an unprecedented range of currents (50 pA to 6uA) through which we can tune the electric field in the tunnel junction of the microscope. We show that in STS a sizeable Stark effect causes a shift of the surface state binding

energy $E_{\text{sub S}}$, even at very low currents. Data taken are reproduced by a one-dimensional potential model calculation, and are found to yield a Stark-free energy $E_{\text{sub S}}$ in agreement with recent state-of-the-art photoemission spectroscopy measurements. Next, unusual emission of visible light is observed in scanning tunnelling microscopy of the quantum well system Na on Cu(111). Photons are emitted at energies exceeding the energy of the tunneling electrons. Model calculations of two-electron processes which lead to quantum well transitions reproduce the experimental fluorescence spectra, the quantum yield, and the power-law variation of the intensity with the excitation current.

4:00pm **SS+NS-WeA7 Electrostatic Potential Profile within a Biased Molecular Electronics Device: a Cavity QED Approach, J.W. Gadzuk**, National Institute of Standards and Technology

The fundamental principle behind a molecular electronics (MoleE) device is similar to that driving many resonant electron scattering or transmission processes; initial insertion of an electron into a resonance state, propagation in some manner (coherent, incoherent, or diffusive) that is a controllable characteristic of the resonance-supporting system, and final extraction of the selectively transmitted electron. The stages of a MoleE system responsible for the three-step conduction are often referred to as donor, bridge, and acceptor. The scattering or resonance properties depend amongst other things, upon the electrostatic potential profile along the bridge or molecular wire. Since the molecular wires are packed together within a self-assembled monolayer in real MoleE devices, the present study focuses on the electrostatics and dynamics of such structures, here formulated as a problem in cavity QED of a structured, polarizable continuum film of the bridge material inserted between parallel metallic plates rather than as one in conventional quantum chemistry. The plates (electrodes) and the molecular film are each characterized by their dielectric response functions and the donor/acceptor-electrode interactions by charge redistribution required to satisfy the appropriate electrodynamic boundary conditions. This approach provides fresh insights into the overall features of the electrostatic potential profile and select atomic-scale properties such as electrode-induced shifts in the resonance (aka HOMO and/or LUMO) energies within the molecules which in turn are crucial in determining the current-voltage characteristics of the MoleE device, as will be demonstrated.

4:20pm **SS+NS-WeA8 Quantum Size Effect Induced Modification of CO Chemisorption on Cu/fccFe/Cu(100), A.G. Danese, R.A. Bartynski**, Rutgers University

Nanoscale metal thin films can exhibit quantum size effects (QSE) whereby their electronic, structural, magnetic and chemical properties may differ greatly from those of the bulk. The quantum confinement of electrons due to high reflectivity scattering at the film's interfaces forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. We have studied the role of MQW states in the chemisorption of CO on n ML Cu/fccFe/Cu(100) where $\sim 2 < n < \sim 14$ using inverse photoemission (IPE) and temperature programmed desorption (TPD). IPE results show the unoccupied MQW states in the Cu overlayer increasing in energy as a function of increasing Cu thickness with MQW states crossing the Fermi energy ($E_{\text{sub F}}$) at 5 ML Cu and 11 ML Cu in both the bare and CO covered system. Accordingly the IPE intensity at $E_{\text{sub F}}$ oscillates as a function of Cu well thickness and temperature programmed desorption (TPD) performed on the CO covered Cu films exhibits modulations in the CO peak desorption temperature ($T_{\text{sub des}}$) which are correlated with these IPE modulations. The MQW states are quasi 2 dimensional (2-d) and we attribute this chemisorption QSE to the bottom of a 2-d subband that crosses $E_{\text{sub F}}$ every time a MQW is observed to cross $E_{\text{sub F}}$. This increases the density of states at $E_{\text{sub F}}$ available for the CO-Cu bond, thus strengthening the bond as observed by two $T_{\text{sub des}}$ maxima at 5 ML Cu and 11 ML Cu. Between these $E_{\text{sub F}}$ crossings, the DOS as measured by IPE intensity decreases and we observe that the two quantities oscillate together.

4:40pm **SS+NS-WeA9 Manipulating Single Metal Atoms with the Scanning Tunnelling Microscope, K.-F. Braun, K.H. Rieder**, Freie Universit@um a@t Berlin, Germany; **K. Flipse**, Eindhoven University of Technology, The Netherlands; **S.-W. Hla**, Ohio University

Scanning tunnelling microscopy has been used to manipulate single atoms, small molecules as well as larger molecules and parts of it. Lateral manipulation can be applied to position atoms for the construction of artificial assemblies on desired atomic sites. Although manipulation techniques have been used on a variety of systems only little is known about the interaction forces between microscope tip and adparticle. Here

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we present a detailed study of the lateral manipulation of Au and Ag atoms on Ag(111) and Ni(111) surfaces. We describe a complete picture of how single Ag atoms move on the various potential energy landscapes of a Ag(111) surface during a quantum corral construction by using an STM tip at 6 K. The threshold tunnelling resistance and tip-height to move the Ag atom across the surface are experimentally measured as $210 \pm 19 \text{ k}\Omega$ and $1.3 \pm 0.2 \text{ \AA}$. The experimental atom manipulation signals reveal remarkably detailed atom movement behaviour dependent on the surface crystallographic orientation and offer atomic-level tribology information. @footnote 1@ Manipulation experiments with Au atoms on the same Ag(111) surface show a voltage dependent threshold resistance above $\pm 100 \text{ mV}$. Possible current and field effects will be discussed. Measurements on Au atoms on a Ni(111) surface display even a long-ranged repulsive interaction for voltages below -300 mV . The influence of the electronic surface structure on the manipulation will be discussed. Electrons injected in the antibonding levels of the atom-surface system can weaken the bond to allow lateral manipulation at high voltages as well as desorb the atom. @footnote 2@ @FootnoteText@@footnote 1@S.W. Hla, K.-F. Braun, K.H. Rieder, Phys. Rev. B, Rapid Comm., accepted (2003). @footnote 2@K.-F. Braun, K. Flipse, K.H. Rieder, in preparation (2003).

5:00pm **SS+NS-WeA10 Adsorption and Deprotonation of Dichlorothiophenol on Cu(111): STM-Based Hydrogen Abstraction and Thiolate Formation**, B.V. Rao, K.-Y. Kwon, J. Zhang, A. Liu, L. Bartels, University of California at Riverside

We present low-temperature scanning tunneling microscope (STM) measurements of the initial steps of the adsorption of di-chloro-thiophenol (DCTP), an aromatic thiol, on Cu(111). Upon adsorption of ultra-low coverages at 15 K individual molecules can be found on Cu(111) terraces which appear as large, flower-shaped protrusion in STM images. This is caused by the rotation of the molecule around the sulfur atom which rests at an on-top site of the substrate. Deprotonation to the thiolate may be caused by annealing to nitrogen temperatures or attachment/removal of electrons to/out of the molecule at a bias exceeding 300 mV. Following deprotonation, the sulfur atom shifts to a higher-coordinated substrate site and the molecules is fixed in place. STM-based vibrational spectroscopy reveals a pronounced S-H stretch mode at 320 meV before deprotonation, which is absent from spectra taken after deprotonation. The STM based hydrogen abstraction process can be accomplished reliably at -500 mV with a first-order dependence on the current. Perfect selectivity for the sulfur bound hydrogen is achieved even if the excitation current targets the benzene ring. Adsorption of 1 L of DCTP at nitrogen followed by annealing to ambient temperatures leads to the formation of an ordered structure comprised of pairs of DCTPs of opposite chirality in the adsorbed state. Further increasing the adsorbate coverage, more and more of the molecules do not lie flat on the surface but have the benzene ring pointing up.

Surface Science

Room 327 - Session SS+OF-WeA

Growth and Characterization of Organic Films

Moderator: L.A. Baker, Naval Research Laboratory

2:00pm **SS+OF-WeA1 Electronic and Geometric Structures of Pentacene Molecules Grown on Au(100)**, Y.J. Song, K. Lee, J. Yu, Y. Kuk, Seoul National University, Korea

A pentacene molecule has attracted much interest for its possible application to organic-based electronic devices with its interesting electronic properties. Despite reported semiconducting property of the bulk crystal, it is hard to grow the high-quality film. Here, we report our scanning tunneling microscopy studies on the geometric and electronic structures of pentacene molecular layers on a Au(100) surface. Because of the high diffusivity of the molecule at room temperature, the STM studies were done at low temperature. At submonolayer coverage, the molecules are confined to the troughs of the reconstructed Au(100)-(5x20), forming a chain structure perpendicular to the reconstructed ridges. We resolved the HOMO and LUMO states of pentacene molecules on a Au(100) surface with atomic resolution. The DFT (density functional theory) results of the molecular layer reveal good agreement with the observed geometric and electronic structures. The electronic levels of pentacene molecules are shifted in the presence of metallic substrate. This result can be valuable when one makes metal-pentacene junctions for device applications. The electronic levels are also shifted with pentacene-pentacene interactions. At the coverages higher than 2 monolayers, a single phase was observed. The

pentacene-pentacene interaction plays a important roll to the growth structures. The 5 pentacene molecules work as a base unit for the multilayer film. The correlation between the growth structure and the transport property will be discussed.

2:20pm **SS+OF-WeA2 Pentacene Thin Films on Clean and Chemically Modified Si(001) Surfaces**, K.P. Weidkamp, L. Fang, R.J. Hamers, University of Wisconsin-Madison

We have investigated the microstructural, chemical and electronic properties of pentacene thin films formed on Si(001) surfaces. Using FTIR and valence-band photoemission spectroscopy, we find that the initial pentacene molecules deposited onto the surface undergo a transition from sp² to sp³ bonding and partial dissociation, all indicating the formation of covalent C-Si bonds that inhibit diffusion and thereby result in poor pentacene crystal formation. In contrast films prepared by deposition on to Si(001) surfaces that were initially modified with a monolayer of pentacene molecules show no evidence for dissociation and exhibit highly reversible adsorption and desorption, demonstrating that the pentacene molecules do not form covalent bonds with the underlying organic-modified surface. In order to understand how the molecular structure of the interfacial organic layer affects that structure and electronic properties of the pentacene thin films, we have investigated pentacene thin films deposited onto silicon surfaces that were modified with several different organic molecules including cyclopentene, dodecene, and phenanthrenequinone. These three molecules are expected to differ significantly in thickness, molecular rigidity, and effective molecular conductivity. AFM images show that the each organic molecular layer induces specific changes in the microstructure of the pentacene films deposited on top. Measurements of the electrical properties through the films will also be presented.

2:40pm **SS+OF-WeA3 Spectroscopic Measurements on Ultra Thin Highly Ordered Films of Organic Semiconductors**, T. Fritz, TU Dresden, Germany
INVITED

Research activity on molecular solids has gathered pace in recent years as these materials have a wide range of interesting properties, emerging industrial interest with real applications at the horizon, and possible future applications that will enable electronics to move into the nanoscale. High quality samples, precise structural data, and a detailed understanding of the physical properties are essential, with special emphasis on thin films and interfaces. In this respect, the use of highly controlled growth techniques like Organic Molecular Beam Epitaxy (OMBE) is becoming more and more important, aiming at high quality thin films with controlled crystal structure and morphology, and therefore displaying well defined physical properties. In order to investigate those physical properties deeply, spectroscopy methods are required which allow to characterize films with film thicknesses down to even submonolayers. In our contribution two different spectroscopy methods will be discussed in detail. By the first one, called Scanning Tunneling Spectroscopy (STS), one can determine the energetic positions of both filled and empty states of a molecular layer on an inorganic substrate in a single measurement. Due to the high special resolution small domains with different ordering can be electronically distinguished. Despite electron spectroscopies, optical spectroscopy on organic materials is a very powerful tool and can even provide structural information. Given the fact that exciton confinement effects in quasi-one-dimensional organic crystals will become apparent only if the layer is sufficiently thin (usually less than 4 monolayers), a method is required which will allow to measure the optical absorption down to submonolayers coverage with a sufficient signal-to-noise ratio. The method of choice is the Differential Reflection Spectroscopy (DRS, a variant of reflection absorption spectroscopy), carried out in situ, i.e., during the actual film growth.

3:20pm **SS+OF-WeA5 Epitaxial Growth of Pentacene on Bi/Si(111) Films**, G.E. Thayer, IBM T.J. Watson Research Center; J.T. Sadowski, Tohoku University, Japan; R.M. Tromp, IBM T.J. Watson Research Center

Electrical contacts between organics and metals have been known to limit charge injection in organic electronic devices. Thus it is not surprising that there is a considerable amount of current work modifying metal surfaces and interfaces in an effort to align conduction with organic molecular levels. The solution to this problem begins with understanding the fundamental mechanisms that control both the morphology and electronic structure at the interface between metal and organic materials. Although the interfaces of organic films grown on many clean substrates (semiconductors, insulators, and metals) are found to be poorly ordered, our work has revealed that pentacene grows epitaxially on Bismuth (a

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semimetal). Using LEEM, PEEM, LEED, AFM, and STM our efforts have focused on understanding how pentacene molecules order in Pn/Bi/Si(111) thin films (1ML-10MLs). In contrast to the frequently used Pn/Au system, in the first ML of Pn/Bi the pentacene molecules stand up and are highly ordered as seen by the sharp LEED patterns that we observe. Our LEED analysis finds that the structure of Pn/Bi/Si(111) thin films is similar to the bulk structure of Pentacene with lateral 2D cell dimensions of $a=7.8\text{\AA}$, $b=6.2\text{\AA}$, and $\gamma=84.9^\circ$. In one dimension, this structure is 1:1 commensurate in the $\sqrt{3}$ direction of the underlying hexagonal Bi surface structure. However, in the other direction it is rotated by a small angle and is incommensurate with the Bi lattice. Control of Pn crystal orientation on metal electrodes will enable the fabrication of organic FFT's whose electrical characteristics are not degraded by large angle grain boundaries at the source and drain junctions.

3:40pm SS+OF-WeA6 AFM Study of Carboxylic-Acid Functionalized Pentathiophenes on Mica Surfaces, J. Chen, Lawrence Berkeley National Laboratory; A.R. Murphy, University of California; D.F. Ogletree, M. Salmeron, Lawrence Berkeley National Laboratory; J.M.J. Frechet, Lawrence Berkeley National Laboratory and University of California

We studied SAM films of the oligothiophene derivative (D5TBA @footnote 1@) with AFM to determine its growth and structure and its response to mechanical excitations. We found that self-assembled films formed on mica substrates from hydrophilic (THF) and hydrophobic (chloroform) solutions were totally different in their structure and mechanical properties. In one case methyl groups were exposed while in the other carboxylic groups (COOH) were exposed, resulting in very different friction properties. Friction anisotropy was observed between domains of different orientations. Scanning polarization force microscopy (SPFM) was used to obtain contact potential maps (Kelvin Probe mode) to confirm film structures deduced from contact mode imaging. Generally, deposition from THF solutions produced stable monolayer aggregates with exposed methyl groups. Multilayer regions were sometimes observed, with alternate methyl and carbonyl group terminations. During contact AFM imaging the third and higher layers could be progressively peeled off by increasing the load applied to the tip, however the second layer was found to incorporate into the first layer in a densification process. Deposition from chloroform solutions usually produced unstable multilayer films with methyl groups contacting the mica surface. @FootnoteText@ @footnote 1@ D5TBA, or 4-(5''-Decyl-[2,2';5', 2''; 5'', 2'''; 5''', 2'''''] pentathiophen-5-yl)-butyric acid, was prepared by Stille cross-coupling methods using functionalized thiophene monomers.

4:00pm SS+OF-WeA7 Surface Polymerization by Ion Assisted Deposition for Polythiophene Film Growth, S. Tepavcevic, Y. Choi, L. Hanley, University of Illinois at Chicago

Cationic polymerization is induced at the gas-solid interface by hyperthermal organic cations coincident on a surface with a thermal beam of organic monomers.@footnote 1@ This process, termed surface polymerization by ion assisted deposition (SPIAD), produces films that maintain the chemical structure of the monomer.@footnote 2@ A polythiophene film is produced here by SPIAD with 100 eV thiophene ions and terthiophene monomers coincident on Si and indium tin oxide (ITO) substrates held under vacuum. X-ray photoelectron spectroscopy observes enhancement in film growth for SPIAD compared with either thiophene ion or terthiophene exposure alone. Polythiophene films grown by both mass-selected@footnote 1@ and non-mass-selected ions@footnote 3@ with coincident terthiophene dosing both display similar fluorescence intensity at two wavelengths characteristic of emission from films of the terthiophene monomer. Raman spectra of films from non-mass-selected ions display several vibrations also observed in terthiophene films. Ions therefore play a critical role in film growth from non-mass-selected ions, in addition to any radical or photochemically driven processes that may also occur. @FootnoteText@ @footnote 1@L. Hanley and S.B. Sinnott, Surf. Sci. 500 (2002) 500. @footnote 2@S. Tepavcevic, Y. Choi, and L. Hanley, J. Amer. Chem. Soc. 125 (2003) 2396.@footnote 3@L. Hanley, Y. Choi, E.R. Fuoco, F.A. Akin, M.B.J. Wijesundara, M. Li, A. Tikhonov, and M. Schlossman, Nucl. Instr. Meth. Phys. Res. B 203C (2003) 116.

4:40pm SS+OF-WeA9 Molecular Dynamics Simulation Study of Continuous C@sub 3@F@sub 5@@@super +@ and CF@sub 3@@@super +@ Ion Depositions on Polystyrene Surfaces, I. Jang, S.B. Sinnott, University of Florida

Fluorocarbon plasma treatment is widely studied and used to change surface properties and to grow thin polymer films. However, it is difficult to determine the detailed mechanisms responsible for the surface reactions

that lead to thin film growth due to the complexity of plasma systems. Computer simulations of the deposition of mass selected fluorocarbon ions have been used to isolate the effects of polyatomic ions in low energy plasma deposition of thin films. In this study, the continuous deposition of a beam of polyatomic fluorocarbon ions (C@sub 3@F@sub 5@@@super +@ and CF@sub 3@@@super +@) on polystyrene surfaces is performed using classical molecular dynamics simulations. The forces are determined using the reactive empirical bond order method for short-range interaction and Lennard-Jones potential for long-range van der Waals interaction. The incident energy of the ions is 50 eV/ion and they are deposited normal to polystyrene surface. The simulations allow us to determine the mechanisms responsible for thin-film growth and surface modification by the ion beam deposition. Specifically, they show how fluorocarbon polymer precursors are formed and react with one another. Overall, the simulations predict that CF@sub 3@@@super +@ depositions are more effective in fluorination of polystyrene surface than C@sub 3@F@sub 5@@@super +@ depositions. This work is supported by the NSF under grant CHE-0200838.

5:00pm SS+OF-WeA10 Exploring the Reactivity of Atomic Oxygen with Organic Surfaces, G.M. Wolfe, A.J. Wagner, J. Torres, C.C. Perry, D.H. Fairbrother, Johns Hopkins University

Atomic oxygen is a major component in oxygen and air-based plasmas and also plays a major role in the erosion and degradation of polymeric coatings in spacecrafts as they pass through Low Earth Orbit (LEO). Through the use of self-assembled monolayers and well-defined polymeric substrates an understanding of the fundamental molecular level surface reactions of atomic oxygen with organic surfaces can be determined. Our work explores the interactions of O radicals, with a series of self-assembled monolayers (SAMs), employed as models for polymer surfaces. In situ X-ray photoelectron spectroscopy (XPS) is used to elucidate the mechanism of radical reactions occurring with dodecane, hexadecane, and X-ray modified hexadecane SAMs, as well as a semi-fluorinated SAM (CF-SAM). In the hydrocarbon SAMs, the reaction with atomic O progresses through three stages. Initially, reactions at the vacuum/film interface generate a steady state concentration of C-O, C=O and O-C=O groups. Sustained atomic oxygen exposure on hydrocarbon-based SAMs promotes the formation of volatile oxygen-containing carbon species, e.g. CO@sub 2@, leading to the development of a steady state etch front. Ultimately, oxygen penetrates to the film/substrate interface to form sulfonate and Au@sub 2@O@sub 3@ species. Experiments on the CF-SAM reveal an induction period of ~90 minutes prior to oxygen incorporation, an effect ascribed to the inertness of C-F and C-C bonds towards atomic oxygen and the well-ordered structure of the CF-SAM. In contrast to the hydrocarbon SAMs, reactivity within the CF-SAMs are initiated by O atom reactions at the film/substrate interface leading to desorption of intact adsorbate chains. Results on the interaction of atomic O with phosphorous ion-implanted poly(ethylene) will also be presented.

Surface Science

Room 310 - Session SS1-ThM

Patterned Growth and Etching of Semiconductors

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

8:20am **SS1-ThM1 Self-Assembly of Atomic Chains on Stepped Silicon**, *F.J. Himpsel*, University of Wisconsin, Madison **INVITED**

It is now possible to systematically engineer one-dimensional chain structures of metal atoms on silicon using self-assembly. Stepped Si(111) templates offer the opportunity to vary the chain spacing with atomic precision and to control the electron count, including fractional band filling. Two applications of chain structures are explored: 1. An atomic scale memory is constructed using self-assembled, 5-atom wide tracks that form on Si(111)5x2-Au. Extra Si atoms in lattice sites on top of the tracks are used to store data, one bit per atom with an empty buffer space of 5x4 atoms. The density is comparable to that in DNA (32 atoms/bit). This memory serves as test structure for finding the fundamental limits of data storage density and readout speed. They are given by the correlation between adjacent atoms and the shot noise in STM. 2. One-dimensional electrons in metallic chains are characterized by mapping their band structure and Fermi surface. While metallic surface electrons are completely decoupled from the Si substrate, the metal atoms are locked into Si lattice sites which makes a Peierls transition to an insulator unfavorable. The dimensionality is varied between 1D and 2D via the chain spacing. R. Bennowitz, et al., Atomic scale memory at a silicon surface, *Nanotechnology* 13, 499 (2002). A. Kirakosian, et al., Correlations in a one-dimensional lattice fluid on Si(111)5x2-Au; *Phys. Rev. B*, in press. R. Losio, et al., Band splitting for Si(557)-Au: Is it spin-charge separation?, *Phys. Rev. Lett.* 86, 4632 (2001); K. N. Altmann, et al., Electronic structure of atomic chains on vicinal Si(111)-Au, *Phys. Rev. B* 64, 035406 (2001); J. N. Crain, et al., Fermi Surfaces of Surface States on Si(111) + Ag, Au, *Phys. Rev. B* 66, 205302 (2002); J. N. Crain, et al., Fractional band filling in an atomic chain structure, *Phys. Rev. Lett.*, in press.

9:00am **SS1-ThM3 Length Scale Dependence of Evolution of Corrugations During Sublimation from Patterned Vicinal Si(111) Surfaces***, *T. Kwon, H.C. Kan, R.J. Phaneuf*, University of Maryland

We describe the results of a combinatorial approach toward controlling the evolution of topography during sublimation from silicon. Arrays of lithographically-patterned cylindrical pits on vicinal Si(111) surfaces interfere with the motion of "straight" steps at temperatures near 1200C. On each substrate, pit diameters are varied from 0.7 microns to 8 microns, with the pit-spacing equal to twice the diameter. Within this range, a critical length scale is found, above which straight steps wrap around pits, leaving a pronounced corrugation within the surface plane, but beneath which the evolution is quickly to straight step bunches, with a pronounced corrugation perpendicular to the surface plane. In the simplest model, this critical length scale is set by the competition between the sublimation induced spreading pressure on the steps and their intrinsic stiffness. Preliminary observations on vicinal Si(111) surfaces also indicate the importance of step-step interactions in the evolution of the topography, with a pronounced inward relaxation of the pit wall on the "uphill" side, and an inward bowing of otherwise straight steps on the "downhill" side. *Work supported by the Laboratory for Physical Sciences and an NSF-MRSEC.

9:20am **SS1-ThM4 Current-Induced Pattern Formation on Vicinal Surfaces**, *T. Zhao, J.D. Weeks*, University of Maryland

Vicinal surfaces can exhibit a number of different morphological instabilities that may be important in crystal growth and nano-scale device fabrication. Particularly interesting step bunching and step wandering patterns arise from electromigration on Si(111) surfaces; these patterns are observed depend on both the current direction and the temperature. We develop a new two-region diffusion model where adatoms in a small region near a step are assumed have different diffusion rates from those on terraces due to different surface reconstruction or bonding configurations near the step. A linear stability analysis of this theoretical model yields both the bunching behavior and the most unstable wavelength for in-phase wandering. We find good agreement with existing experiments. Moreover, to account for the long time behavior of such surfaces, we use a geometric representation of the interface to derive a nonlinear

evolution equation for a step in the presence of anisotropic diffusion arising from the electric field. The evolution of the step resulting from fields oriented with different angles off the z-axis bears strong resemblance to the experiments. See M. Degawa, K. Thürmer, I. Morishima, H. Minoda, K. Yagi, and E.D. Williams, "Initial stage of in-phase step wandering on Si(111) vicinal surfaces," *Surf. Sci.* 487, 171 (2001). See M. Degawa, H. Minoda, Y. Tanishiro, and K. Yagi, "In-phase step wandering on Si(111) vicinal surfaces: Effect of direct current heating tilted from the step-down direction," *Phys. Rev. B* 63, 045309/1 (2001).

9:40am **SS1-ThM5 Effects of Diffusion and Chemical Reactivity on Step Bunching: The Formation of Macrosteps During Etching**, *S.P. Garcia, H. Bao, M.A. Hines*, Cornell University

The chemical production of macroscopic features on etched silicon surfaces was investigated using scanning tunneling microscopy and atomistic, kinetic Monte Carlo simulations. Macroscopic features arise when atomic steps bunch together into enormous macrosteps with heights on the order of microns. In aqueous silicon etching, step bunching is driven by spatial inhomogeneities in the etchant, as demonstrated by experiments in which diffusive transport is controlled. Under conditions of step-flow etching, inhomogeneities can be enhanced when random fluctuations bring some steps close together. The inhomogeneities can influence the etch rate locally. For example, etchant depletion can lead to local deceleration of step etching, whereas heat released by the etching reaction can lead to local acceleration. This coupling of chemical reactivity to diffusion-controlled processes may cause closely spaced steps to speed up or slow down. To understand how atomic-scale chemical processes and mesoscale diffusion produce step bunching, we have developed a simulation that combines an atomically realistic, two-dimensional model of etching with a continuum model of diffusion. Simulations generated by this technique show that step bunching can give rise to a variety of etch morphologies, all of which are strongly affected by the site specificity of etching and by the effect of diffusion on local reactivity.

10:00am **SS1-ThM6 Equilibrium Morphologies for Cl-roughened Si(100) at 700 - 750 K: Experiments and Monte Carlo Modeling**, *G.J. Xu, K.S. Nakayama, B.R. Trenhaile, C.M. Aldao, J.H. Weaver*, University of Illinois at Urbana-Champaign

Adsorbed halogen atoms on Si(100)-(2x1) can induce roughening at temperatures where material removal (etching) is minimal. Variable temperature scanning tunneling microscopy was used to follow roughening at 700 - 750 K for surfaces with 0.1 - 0.99 ML of Cl. Dimer vacancies and Si adatoms were observed at short times, and at longer times the progression toward a state of dynamic equilibrium was traced. Once dynamic equilibrium was reached, the appearance of individual pits and regrowth islands changed but their densities and mean sizes did not. The results show that the roughness depends non-linearly on Cl coverage with surfaces having 0.3 ML being nearly ten times rougher than those with 0.1 ML. The importance of Cl-free dimers is stressed, and the role of Cl as an impediment for vacancy and adatom diffusion is demonstrated. Roughening is attributed mainly to adsorbate-adsorbate repulsive interactions. Further insight can be gained from Monte Carlo simulations, where the consequences of adsorbate-adsorbate interactions are explored and the resulting morphologies are compared with those experimentally observed. While adsorbate-adsorbate interactions may be the main driving force responsible for roughening, contributions from other interactions cannot be ruled out.

10:20am **SS1-ThM7 Adsorbate Interactions and Roughening of Sub-monolayer Halogenated Si(100) Surfaces**, *D. Chen*, University of North Carolina at Chapel Hill; *J.J. Boland*, Trinity College Dublin, Ireland

Spontaneous roughening of halogen terminated Si(100) surfaces was previously shown to arise from steric repulsions between adsorbates. However, more recent studies have shown that significant roughening occurs even for coverages that are substantially below a monolayer and calls into question the role of steric repulsions. Here, we present a comprehensive study of the roughening process on a sub-monolayer chlorinated Si(100) surface, and in particular its correlation with both the surface coverage and spatial distribution of adsorbates. We find the roughening is due to steric repulsions and this interpretation is supported by DFT calculations. A new model is developed to describe the dependence of roughening on halogen coverage. C.F.Herrmann, D.Chen, J.J.Boland, *Phys. Rev. Lett.* 89, 096102 (2002)

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10:40am **SS1-ThM8 Atomistic Modeling of Morphological Evolution During Active and Passive Oxidation of Si(100)**, *M.A. Albao, D.-J. Liu*, Iowa State University; *C.H. Choi*, Kyungpook National University, South Korea; *M.S. Gordon, J.W. Evans*, Iowa State University

Prolonged exposure of Si(100) surfaces to oxygen produces: etching at high temperatures (T) characterized by the formation of monolayer-deep elliptical etch pits in successive layers (active oxidation); simultaneous etching and formation of oxide-capped Si-nanoprotuberances at moderate T (transition regime); and coverage of the substrate by an oxide layer at low T (passive oxidation). We develop a simple atomistic model with the goal of describing evolution of the complex far-from-equilibrium surface morphology for a broad range of temperatures across the transition regime. Model development is guided by experimental observations, by general concepts from nucleation theory for the formation of etch pits and oxide islands, and by input from ab-initio quantum chemistry (e.g., indicating different SiO desorption barriers for perfect and defective surfaces).

11:00am **SS1-ThM9 Oxygen Etching of Low- and High-Index Si Surfaces**, *J.L. Skrobiszewski, A.A. Baski*, Virginia Commonwealth University

When Si surfaces are exposed to O@sub 2@ at elevated temperatures, both oxide nucleation and etching can occur, with etching dominating at higher temperatures. We have used scanning tunneling microscopy (STM) to study the transition regime where both processes occur on the low-index (001) and (111) surfaces, as well as on the high-index (5 5 12) and (113) surfaces. All of these surfaces were exposed to O@sub 2@ at sample temperatures of 675 to 750°C, pressures on the low 10@super -7@ Torr scale, and exposures of 5 to 400 Langmuirs. On the low-index surfaces, the surface morphology can be significantly disrupted in this transition regime by etch pits, as well as monoatomic height islands caused by etching around oxide-induced pinning sites. The original terrace-plus-step morphology is only maintained for temperatures above 750°C, where only step-flow etching occurs. For the transition regime on the high-index Si(5 5 12) surface, no etch pits are found on the terraces, but three-dimensional pyramidal or linear islands are observed on terraces and along step edges. These islands presumably form at oxide nucleation sites and grow in size as the surrounding surface is etched away. Interestingly, both the pyramidal and linear islands incorporate (113) facet planes, indicating an enhanced stability of this orientation against etching. When the Si(113) surface is exposed to O@sub 2@ under similar conditions, the resulting morphology also shows no etch pits and incorporates 3D islands, but without any well-defined facet planes. The etching behavior of the high-index surfaces in the transition regime is therefore qualitatively different from that observed for the low-index planes.

11:20am **SS1-ThM10 Growth of Gd on the High-Index Si(113) and Si(5 5 12) Surfaces**, *E. Morris, J.W. Dickinson, A.A. Baski*, Virginia Commonwealth University

The growth of rare earth metals on the low-index Si(001) surface has been of recent interest due to the appearance of silicide "nanowires."@footnote 1@ This nanowire formation is presumably due to a close lattice match between the rare earth silicide and Si lattice along the [1bar10] row direction, and poor match perpendicular to it. In this study, we have used scanning tunneling microscopy (STM) to examine the growth of the rare earth metal Gd on two high-index Si surfaces: Si(113) and Si(5 5 12). These two surfaces are oriented 25.2° and 30.5° down from (001) towards (111), respectively. When very low coverages of Gd are deposited onto these surfaces and annealed at 600°C, (113) terraces with a well-ordered 2x2 reconstruction are formed. In the case of Si(5 5 12), the reconstructed (113) terraces are opposed by other facet orientations. When the coverage is increased to approximately 0.5 ML, isolated nanowires nucleate at step edges and extend along the [1bar10] direction. These nanowires are 5 to 15 nm wide, 1 to 2 nm tall, and grow up to 0.5 micron in length. Because the lattice periodicity along the nanowire direction is identical for the (001), (113), and (5 5 12) surfaces, the appearance of such nanowires on the high-index surfaces provides further evidence for a lattice mismatch mechanism. Interestingly, the anisotropic structure of these high-index surfaces results in nanowire growth that causes fewer disruptions to the initial step morphology than observed for (001). @FootnoteText@ @footnote 1@ C. Ohbuchi, J. Nogami, Phys. Rev. B 66, 165323 (2002) and references therein.

11:40am **SS1-ThM11 Attempts on Synthesizing Linear Atomic Metal Chains on GaN(0001)**, *C. Lung, C. Chang*, National Taiwan University, R.O.C. The continuing advances in miniaturization of semiconductor devices have seriously challenged the fields of materials processing and circuit designs.

This work explores the chemical reaction involved in the possible formation of nanowires using a pyridylamino chelate that contains a linear atomic chain of chromium for CVD. The adsorption, surface reaction, and thermal pyrolysis of this metal string chelate on GaN(0001) were characterized using synchrotron radiation-induced core-level photoelectron spectroscopy, secondary ion mass spectrometry, and temperature-programmed desorption. Secondary ion mass spectrometric studies showed that pyridylamino trinuclear chromium complex may react with the GaN(0001) surface to produce pyridine and pyridylamino fragments even at a very low substrate temperature of less than 150 K. Upon increasing exposure of the trinuclear chromium metal-chain complex on GaN(0001), the Cr3p photoelectron profile altered substantially, revealing an evolution in bonding configuration of the chromium metal-chain chelate on the surface. At low exposures, the Cr3p profile contained three features, peaked at different binding energies, of equal areas. The number of distinguishable features in the Cr3p spectrum increased to five as the chelate coverage on GaN(0001) was increased to more than one monolayer. Increasing the substrate temperature not only caused a change of the bonding geometry of the chromium string on the surface but also induced decomposition of the chromium chelate in two different stages. Desorption of the dipyridylamino ligand took place at a substrate temperature of 340 K, while disruption of the chromium string occurred at about 540 K. Results of this work point to the possibility of forming chromium nanospecies on the semiconductor surface through vacuum chemical deposition using organometallic metal strings. The fundamental aspects and the formation of nanowires involved in the nano-contact technology will be discussed.

Surface Science Room 327 - Session SS2-ThM

Catalysis III: High vs. Low Pressures

Moderator: J.N. Russell, Naval Research Laboratory

8:20am **SS2-ThM1 Oxide Nucleation Kinetics on Al(111): The Role of Short-range and Long-range Interactions between Chemisorbed O Atoms**, *D.E. Oner, B. Kasemo, I. Zori@aa c@*, Chalmers University of Technology and Göteborgs University, Sweden

Experimental work indicates that oxide nucleation on Al(111) takes place in a heterogeneous surface phase, at an average coverage of chemisorbed O atoms of about 0.15ML, specifically at the edges of chemisorbed O islands containing 10-15 O atoms. The former observation was based on spectroscopic evidence while the latter was directly observed in STM experiments. In this contribution we suggest that the rate for oxide nucleation is strongly influenced by a combination of a long-range repulsive (elastic) interaction in competition with a short-range (nearest neighbor) attractive interaction between O adatoms. The model used to describe oxide formation is an extension of an earlier kinetic model that in addition to the oxide nucleation step also includes adsorption/chemisorption step. In the pure chemisorption phase O@sub 2@ dissociative adsorption takes place that leads to an O island size distribution in agreement with the STM observations. Chemisorbed O atoms interact via superimposed short-range attractive and long-range repulsive interactions. The oxide nucleation is simulated via a place exchange step. The latter step is the rate-limiting step for oxide nucleation. The short-range interaction stabilizes the chemisorbed phase, while the repulsive long-range interaction promotes oxide formation, i.e. it enhances the place exchange jump rate. Our Monte Carlo simulations, based on the transition theory approach, can account for: a) the observed threshold in O island size needed for oxide nucleation to occur, b) the total oxygen uptake kinetics and c) the oxide formation kinetics, reported in recent STM-surface spectroscopic experiments. The two important parameters in the model are the strengths of the long-range and short-range interactions, respectively. Agreement between simulation predictions and experimental data is achieved for a unique and reasonable choice of model parameters.

8:40am **SS2-ThM2 Chemical Inhibition of Aluminum Surface Oxidation**, *V.J. Bellitto*, Naval Surface Warfare Center; *J.N. Russell, Jr.*, Naval Research Laboratory

Aluminum powders are used to tailor the energetic content of propulsion and explosive systems. As the size of aluminum particles approach the nano-scale, the performance of the energetic materials may be enhanced by providing greater surface to volume ratios, but not if the nano-particle is largely comprised of aluminum oxide. Therefore, we are examining chemical methods for passivating aluminum surfaces and inhibiting

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oxidation. We report the surface chemistry of a series of perfluoro- and perhydro- carboxylic acid compounds on an Al(111) surface and their ability to inhibit aluminum surface oxidation. Using x-ray photoelectron spectroscopy and infrared reflection absorption spectroscopy we established the compounds chemisorb on the atomically clean Al(111) surface through scission of the O-H bond and formation of carboxylate species. We monitored the temperature dependent chemistry of the adsorbates, demonstrating the greater thermal stability of the fluorinated surface species. The oxidation rates of the clean, partially functionalized (0.5 ML) and fully functionalized (1ML) Al(111) surfaces were compared. The fully functionalized surface did not exhibit spectroscopic features characteristic of O@sub 2@ chemisorption or Al@sub 2@O@sub 3@ formation even after being exposed to > 1 x 10⁵ L of O@sub 2@ at room temperature. The thermal dependence of the oxidation inhibition is under investigation.

9:00am **SS2-ThM3 Methane Dissociative Chemisorption on Ni(100): Closing the Non-equilibrium Gap between Surface Science and Catalysis, H.1 Abbott**, Unaffiliated; A. Bukoski, D. Kavulak, I. Harrison, University of Virginia

A simple, 3-parameter microcanonical unimolecular rate theory of gas-surface reactivity is shown to predict experimental dissociative sticking probabilities for methane dissociative chemisorption on the Ni(100) surface over roughly 10 orders of magnitude variation in both pressure and sticking - even at quantum state resolved levels of detail. Facile energy randomization within the transiently formed gas-surface collision complexes is postulated to make the pooled energy from 15 local degrees of freedom statistically available to surmount the barrier to dissociation. The apparent threshold energy for C-H bond cleavage of CH@sub 4@ incident on Ni(100) is 65 kJ/mol, down from 432 kJ/mol in the gas phase. Interestingly, this threshold energy is in quantitative accord with ab initio quantum chemistry calculations, but 15-45% smaller than calculations based on generalized gradient approximation density functional theory. More generally, some of the difficulties faced when interpreting non-equilibrium surface science experiments and comparing them with equilibrium catalysis experiments will be discussed.

9:20am **SS2-ThM4 High Pressure STM Studies of Metal and Alloy Surfaces: Adsorption Induced Phase Separation, E.K. Vestergaard, R.T. Vang, F. Besenbacher**, University of Aarhus, Denmark

A major issue in the catalytic community concerns the validity of applying surface science data obtained under Ultra-High Vacuum (UHV) conditions to "real" catalytic processes occurring at atmospheric pressure and above. Using high-pressure scanning tunneling microscopy (HP-STM) we have studied the adsorption structures on Pt(111) and Ni(111) at 1 bar of CO, and for these simple systems we demonstrate that the CO adsorption structures at high pressures are similar to structures formed under low pressure and low temperature conditions. Furthermore, we present results concerning the influence of high CO pressures on the stability of a Au/Ni surface alloy. Exposing the Au/Ni(111) surface alloy to 1 bar of CO results in a Ni(111) surface covered with small Au clusters, showing that high CO pressures induce a phase separation of the alloy. When scrutinizing this process at slightly lower pressures (10-20 torr), we have been able to follow the phase separation in real time. STM movies show that the Au cluster formation starts at the step edges of the Ni surface. Ni atoms are removed from the steps, and as the steps thus move over the surface Au clusters are nucleated and left behind in the wake of the moving steps. We propose that the removal of Ni-atoms is caused by Ni-carbonyl formation; CO is known to react with Ni surfaces at elevated pressures to form Ni-carbonyls, which are volatile at room temperature and therefore leave the surface. This latter study provides an example of a pressure gap, where model systems studied under UHV conditions certainly lack important aspects of the processes found at more realistic conditions.

9:40am **SS2-ThM5 STM Observation of Model Catalysts in Action: from Vacuum to High Pressures, J.W.M. Frenken, B.L.M. Hendriksen, M. Ackermann, S. Bobaru**, Leiden University, The Netherlands **INVITED**

Surface-science research in the field of catalysis is plagued by the presence of a large disparity between the gas pressures acceptable in most surface-sensitive instruments and the pressures used in practical catalysis. This so-called 'pressure gap' can easily be as large as ten orders of magnitude. One may expect that there are several phenomena that behave non-linearly over this enormous pressure range, which makes it difficult, and in some cases even impossible to simply extrapolate the results of low-pressure experiments to the high-pressure reality of catalysis. In order to bridge the pressure gap, we have recently constructed a special-purpose STM, which

is integrated with a tiny flow reactor cell. Only the tip of the STM is inside the reactor. With this new instrument, we have obtained a first atomic-scale look at 'live' (model) catalysts, while they were active under semi-realistic conditions, namely high pressures and elevated temperatures. Simultaneously with the STM-observation, the instrument can analyze the composition of the gas leaving the reactor. Results will be shown for CO-oxidation on Pt(110), Pt(111), and Pd(001). These results reveal a new reaction mechanism, the so-called 'Mars-van-Krevelen'-mechanism, which is only active at high pressures. On each of these surfaces, the surface structure and the chemical reactivity are observed to switch simultaneously at a specific pressure ratio between O@sub 2@ and CO. In each case, the most active structure is identified as a thin surface oxide, which takes part in the reaction with CO. @FootnoteText@ @footnote 1@ B.L.M. Hendriksen and J.W.M. Frenken, Phys.Rev. Lett. 89 (2002) 046101. @footnote 2@ STM movies of catalysts in action can be viewed on our website: <http://www.physics.leidenuniv.nl/sections/cm/ip>.

10:20am **SS2-ThM7 Universality in Heterogeneous Catalysis, J.K. Nørskov**, Technical University of Denmark, Denmark **INVITED**

Electronic structure methods based on density functional theory have reached a level of sophistication where they can be used to describe complete catalytic reactions on transition metal surfaces. This gives an unprecedented insight into these processes, and it allows us to pinpoint the origin of the catalytic activity of a metal in terms of its electronic structure. The ammonia synthesis is used to exemplify the approach. It will be shown that by combining density functional calculations with kinetic modelling we can now predict relative catalytic activities of different metals. The generality of the approach is illustrated by including a number of other catalytic reactions into a universal property-activity scheme, which identifies the surface properties that determine the catalytic activity for a whole class of reactions.

11:00am **SS2-ThM9 Lateral Interactions in the Kinetics of Surface Reactions, D.L.S. Nieskens, D. Curulla Ferre, A.P. van Bavel, J.W. Niemantsverdriet**, Eindhoven University of Technology, The Netherlands

The rate of a chemical reaction on a surface depends strongly on the presence of neighboring adsorbate species. As lateral interactions between adsorbates are predominantly repulsive, their effect becomes notable at highly covered surfaces. Lateral interactions can change the kinetic parameters (the activation energy and the pre-exponential factor) of a reaction. A change in these kinetic parameters can cause a reaction to occur at a different temperature or pressure. Lateral interactions can even enable a certain reaction pathway which otherwise would be inaccessible. Our goal is first to quantitate these lateral interactions, and second to make good use of them in enabling new reaction pathways. For this we do experiments on single crystal surfaces. We use a combination of techniques: Temperature Programmed Desorption (TPD), Static Secondary Ion Mass Spectrometry (SSIMS), Low Energy Electron Diffraction (LEED) and High Resolution Electron Energy Loss Spectroscopy (HREELS). Using this combination of techniques we obtain a complete picture of the concentration of species, both in the gas phase as well as on the surface. Furthermore we can detect any ordering that occurs on the surface. In addition to the experimental work we also performed Density Functional Theory (DFT) calculations on the same kind of systems. Our strategy for determining lateral interactions is to find ordered structures of an adsorbate A on the surface, then co-adsorb a species B and determine the effect of A on the desorption of this species B. By using an ordered structure of adsorbate A, we are able to "count" the number of "A-neighbors" of the desorbing species B and thus assign the total interaction energy to a known number of neighbors. This enables us to quantify the lateral interaction energy between adsorbate A and B. The energies acquired by the experiments are quite consistent with the ones determined by the computational approach.

11:20am **SS2-ThM10 Strategies for the Study of Methanol and CO Electrocatalysis on Nanometer-Scale Catalysts, C. Korzeniewski**, Texas Tech University

The electrochemical oxidation of methanol and related small molecules has been of special interest in relation to fuel cell research. The development of fuel cells that operate below 100 °C on methanol, or H₂ has stimulated interest in the reaction steps involved in methanol and carbon monoxide oxidation at metal electrodes. In addition to being a by-product of methanol oxidation, carbon monoxide can also be present as an impurity in H₂. Adsorption of carbon monoxide on the anode catalyst generally degrades its performance. We have approached the study of methanol and carbon monoxide oxidation with the use of electrochemical techniques in

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combination with in situ infrared spectroscopy and wet-analytical methods. This presentation will focus on the surface electrochemistry of methanol and carbon monoxide at nanometer scale Pt and bimetallic Pt materials. Catalysts are adsorbed onto smooth gold and highly ordered pyrolytic graphite (HOPG) electrodes. Gold enables infrared sampling in a standard reflectance geometry, while HOPG allows particle characterization with respect to size distribution and spatial arrangement by atomic force microscopy. Properties of nanometer-scale metal particles in relation to CO oxidation and methanol oxidation pathways will be discussed.

11:40am SS2-ThM11 The Water Formation Reaction on a Palladium and Platinum Catalysts, Studied with Laser-induced Fluorescence and Kinetic Modelling. *A. Johansson, M. Forsth, A. Rosen, Goteborg University and Chalmers University of Technology, Sweden*

The noble metals palladium and platinum are widely used as catalysts where the most important application is said to be the cleaning of exhaust gases. In addition, high-temperature data, especially for palladium are very scarce. In this study we have studied water formation on the palladium metal at high temperatures (1300 K) and moderate pressures (13-26 Pa). The OH desorption was studied with laser-induced fluorescence and the water production with microcalorimetry as a function of the hydrogen mixing ratio, α_{H_2} . With basis on the experimental data a theoretical model was also obtained using Chemkin. The result was compared with similar experiments for platinum. The following differences were observed. The maximum in OH desorption occurs at the same α_{H_2} for both platinum and palladium, however the maximum in water production is measured to be at different α_{H_2} ; at 20% for platinum and 40% for palladium. From the model the initial sticking coefficients for hydrogen and oxygen are found to be about a factor of ten larger on Pd than for Pt. The OH desorption was also seen to have a first order coverage dependence on palladium, no such behaviour was found for platinum. The main route for water formation on a platinum surface is the hydrogen addition reaction however, the main water forming reaction on palladium is not straightforward to determine because of the coverage dependent OH desorption. The reverse of the hydrogen addition reaction was found to be more important for the OH formation on Pd than on Pt. The apparent desorption energy as a function of α_{H_2} was also measured for palladium. It was seen that it is increasing with α_{H_2} to a maximum and then stays constant. It is interesting to note that the maximum in apparent desorption energy occurs at the same α_{H_2} as the maximum in water production. The same phenomenon is also observed on platinum, but at a different α_{H_2} .

Surface Science

Room 328 - Session SS3-ThM

Oxide Structure, Growth, and Defects

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

8:20am SS3-ThM1 Effect of Atomic Polarization on Adsorption on Ferroelectric Surfaces: BaTiO₃ (100). *J. Garra, D.A. Bonnell, University of Pennsylvania*

Ferroelectric surfaces have become the focus of recent interest as templates for directed assembly and as thin film devices, yet the surface properties are largely unknown. It has been shown, however, that the local chemical reactivity on ferroelectric surfaces depends on the orientation with which the polarization vector intersects the surface. For example photo reduction (electron donation) occurs over domains with positive surface termination, while photo oxidation (hole donation) occurs over domains with negative surface termination. In order to determine how atomic polarization affects reaction mechanisms, we compare LEED and TPD measurements of desorption from BaTiO₃ (100) single crystals. Samples are poled in UHV above the Curie temperature and cooled in the electric field in order to achieve homogeneous and predefined polarization orientation before adsorption. Domain structure is confirmed with Piezo Force Microscopy. Water, methanol, and ammonium are used as probe molecules. Adsorbate bond energies above and below the ferroelectric-to-paraelectric phase transition will be discussed in the context of the magnitude of local electric fields.

8:40am SS3-ThM2 Sodium Segregation and Morphology on Co₃O₄ Single Crystal Surfaces. *S.C. Petitto, M.A. Langell, University of Nebraska-Lincoln*

The Co₃O₄(110) single crystal surface was characterized in its clean and sodium covered states using Low Energy Electron Diffraction (LEED), X-Ray Photoelectron Spectroscopy (XPS), and Auger Electron Spectroscopy (AES). Annealing Co₃O₄(110) at T = 650K results in sodium segregation from the bulk material, quantified here by the AES I_{Na}/I_{Co} intensity ratio. LEED analysis of the clean Co₃O₄(110) surface shows a well-ordered pattern with sharp diffraction features, whereas the Co₃O₄(110)-Na surface presents a more poorly ordered structure with a hexagonal superimposed pattern due to the sodium oxide overlayer. Concurrent with sodium segregation, the Co₃O₄(110) surface is reduced and the surface cannot be fully reoxidized as long as sodium remains present even upon extended oxygen annealing. XPS of the clean Co₃O₄(110) is characteristic of the spinel structure with Co³⁺ occupying the octahedral sites within the lattice and Co²⁺ in tetrahedral sites. Co₃O₄(110)-Na cobalt XPS, however, shows the cobalt chemical environment is closer to that in CoO with Co²⁺ in octahedral sites. Upon flashing to T_o = 800K, sodium desorbs from the surface, primarily as NaOH. Pre-dosing with H₂O does not appear to catalyze NaOH desorption but rather suppresses it, and the hydrogen is assumed to come from the ambient background in the UHV chamber.

9:00am SS3-ThM3 Resonant Photoemission of Cobaltite Perovskites and Double Perovskites. *W.R. Flavell, A.G. Thomas, D.T. Tsoutsou, A.K. Mallick, M. North, UMIST, UK; E.A. Seddon, C. Chacho, A.E.R. Malins, CLRC Daresbury Lab, UK; R. Stockbauer, R.L. Kurtz, P.T. Sprunger, Louisiana State U.; S.N. Barilo, S.V. Shiryayev, G.L. Bychkov, Belarus Academy of Sciences* **INVITED**

Double perovskites based on Co(III), e.g. GdBaCo₂O_{5.5}, show GMR behaviour and a range of poorly understood spin-state transitions. Whereas the Co(III) ion occupies only octahedral sites in perovskites such as LaCoO₃, in double perovskites, Co is present in two environments, octahedral and pyramidal. In order to investigate the electronic structure of these oxides, resonant photoemission of single crystals of the double perovskites GdBaCo₂O_{5.5} and DyBaCo₂O_{5.5} and of the perovskite HoCoO₃ has been carried out at the UK Synchrotron Radiation Source. Co 3p → 3d resonance photoemission has been shown to be a powerful diagnostic of the LS (low spin) state of d⁶ Co(III) in cobaltites. The resonance onset position of features associated with the LS state lies typically around 2.5 eV higher than those associated with Co(III) in HS (high spin) or IS (intermediate spin) states. This is thought to be because the t_{2g} states are full in the LS state so the Co 3p → 3d transitions are delayed until the e_g states, which lie ~2-3 eV higher, can be occupied. This diagnostic test is used to explore the Co spin fluctuations in double perovskites with temperature. In contrast with previous data for LaCoO₃, we see no delayed resonance for GdBaCo₂O_{5.5} or DyBaCo₂O_{5.5} at temperatures as low as 50 K, consistent with the idea that the Co spin in the pyramidal sites does not fluctuate with temperature. However, a delayed resonance is observed at temperatures up to 400 K in HoCoO₃. This resonance delay disappears as the temperature is raised, as does a low binding energy feature of the valence band associated with LS Co(III). These observations are consistent with a LS to IS transition in octahedral Co(III) in HoCoO₃. The giant RE 4d → 4f resonances are also probed, and used to identify the 4f DOS. We show that the DOS closest to the Fermi energy for all materials is of TM 3d/O₂p character, with no RE 4f contribution. Comparison is made with recent LDA+U calculations.

9:40am SS3-ThM5 Growth Modes in a System Requiring Bulk Mass Transport: Step Motion and Island Nucleation on TiO₂ (110) Exposed to Oxygen. *K.F. McCarty, J.A. Nobel, N.C. Bartelt, Sandia National Laboratories*

We use low-energy electron microscopy (LEEM) to systematically investigate how the (110) surfaces of oxygen-deficient rutile crystals grow when exposed to oxygen. This growth is interesting because it requires a combination of bulk and surface diffusion -- as established by Onishi and Iwasawa (1996) using scanning tunneling microscopy, growth occurs as titanium interstitials from the bulk react with ambient and adsorbed oxygen. If the reaction only occurred at step edges, then one might expect to observe only step-flow growth. Instead, we find that distinct growth processes occur, depending primarily on temperature and oxygen pressure. The temperature/pressure dependence of these growth regimes has been

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systematically determined for a slightly reduced crystal. At high temperature, TiO@sub 2@ growth occurs by pure step flow without the nucleation of new islands. At low temperatures, however, crystal growth proceeds by two-dimensional islands nucleating and spreading laterally. In this layer-by-layer growth regime, the surface periodically oscillates between structures with 1x1 and 1x2 periodicity. The threshold temperature above which island nucleation does not occur depends upon the local terrace width and pressure. For a range of temperatures around the threshold, nucleation occurs on wide terraces but not on narrow terraces. In the regime of pure step flow, we analyze the rate at which isolated islands and interacting island arrays grow. Comparison of the experimental data to numerical simulations of island growth allows us to discuss the relative importance of Ti transport through the bulk and oxygen-containing species on the surface.

10:00am **SS3-ThM6 The Effect of Nitrogen Doping on Rutile Single Crystals - A Photochemical Surface Science Study**, *O.E. Diwald, T.L. Thompson, J.T. Yates Jr.*, University of Pittsburgh

A major goal in the development of new materials for photocatalysis and photo electrochemistry is to shift the solid's photoresponse into the visible light region, in order to utilize solar light more efficiently. Recently, doping of polycrystalline TiO@sub 2@ with non metal ions such as nitrogen@footnote 1@ has attracted much attention, as these materials have shown activity under visible light irradiation (@lambda@ @<=@ 550 nm). In order to investigate the effect of nitrogen doping on the photoactivity of TiO@sub 2@(110) single crystals, nitrogen incorporation into the rutile lattice was achieved either by sputtering with mixtures of N@sub 2@@super +@ and Ar@super +@ ions or by thermal treatment in ammonia (NH@sub 3@). Secondary Ion Mass spectroscopy and X-ray photoelectron spectroscopy were employed to measure depth distribution and chemical state of the implanted nitrogen. For rutile single crystals, these two doping methods result in different chemical states of the incorporated nitrogen. Ion implantation by sputtering produces substitutionally bound nitride species N@super -@, whereas NH@sub 3@ treatment leads to the formation of a N-H bonded dopant in the rutile lattice. For investigation of the photoactivity, the photodesorption of O@sub 2@ was measured as a function of excitation energy and photon flux.@footnote 2@ Compared to the undoped TiO@sub 2@ (110) rutile crystal, the action curve of the crystal that was doped with substitutionally bound nitride exhibits an unexpected blueshift. These findings will be related to changes in the electronic structure of rutile TiO@sub 2@ due to the different dopant species. This work was supported by the DoD Multidisciplinary University Research Initiative (MURI) program administered by the Army Research Office under Grant DAAD-19-01-0-0619. @FootnoteText@@footnote 1@ R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science, 293, 269 (2001),@footnote 2@ G. Lu, A. Linsebigler, J. T. Yates Jr., J. Chem. Phys., 102, 4657, (1995).

10:20am **SS3-ThM7 STM Study of Defect Production on the TiO@sub 2@(110)-(1x1) and TiO@sub 2@(110)-(1x2) Surfaces Induced by UV-light**, *P. Maksymovych, S. Mezheny, D.C. Sorescu, J.T. Yates, Jr.*, University of Pittsburgh

The photoinduced hydrophilicity of the TiO@sub 2@ surface has been the subject of extensive research due to its technological importance in the development of antifogging and self-cleaning coatings. The phenomenon has been postulated to be due to structural changes of TiO@sub 2@; however, the exact mechanism of the process is unknown. The effect of broadband UV radiation on the stoichiometric TiO@sub 2@(110)-(1x1) and the reduced TiO@sub 2@(110)-(1x2) surfaces was observed using the scanning tunneling microscope (STM) in ultra-high vacuum. It was found that the TiO@sub 2@(110)-(1x1) surface is not affected by UV radiation within the statistical error of the experiment. The majority of defect sites on the surface are the bridging oxygen vacancies, and their surface density remains unchanged after UV irradiation. In contrast, production of line defects in the direction was observed on the TiO@sub 2@(110)-(1x2) surface. The overall defective area of the surface was found to increase linearly with UV-exposure, the estimated cross section of the defect formation being $10^{-23.5 \pm 0.2} \text{ cm}^2/\text{photon}$ ($h\nu \geq 3.0 \text{ eV}$). The origin of the defects is attributed to collective removal of oxygen from the surface. In order to determine whether the UV-induced defects can cause hydrophilicity of TiO@sub 2@, adsorption of H@sub 2@O on the TiO@sub 2@(110)-(1x2) surface was studied by STM. At 300K adsorption of H@sub 2@O occurred preferentially on the crosslinks of the TiO@sub 2@(110)-(1x2) surface. However, cooling the surface to 110K during H@sub 2@O exposure led to more efficient adsorption, which took place on the added rows of the TiO@sub 2@(110)-(1x2) surface in addition to

the crosslinking sites. No changes in the topology of the UV-induced defects were observed after H@sub 2@O exposures.

10:40am **SS3-ThM8 The Oxygen Chemistry of Rutile TiO@sub 2@(110) - A Comprehensive STM Study**, *R. Schaub, E. Wahlström, A. Ronnau, E.K. Vestergaard, F. Besenbacher*, Interdisciplinary Nanoscience Center, Denmark

The detailed understanding of the oxygen chemistry on titanium oxide is an important issue for chemical and photo-chemical processes on this material. We present a thorough high resolution variable temperature STM investigation of the interaction of oxygen molecules with the (110) surface of TiO@sub 2@. Single oxygen molecules interact with oxygen vacancies, mediating their diffusion through a simple oxygen atom exchange mechanism. Surprisingly, this mechanism does not account for healing of the vacancies as speculated in the literature until now. The adsorption of molecular oxygen leads also to the creation of different oxygen-related species, which are readily distinguishable by their contrast in STM images and their dynamics in time-resolved STM experiments. The subtle interaction of these different species present on the surface accounts for the healing of the vacancies through an unanticipated and complex mechanism discussed in detail.

11:00am **SS3-ThM9 Measuring Defect Sites on TiO@sub 2@(110): The CO@sub 2@ Probe**, *T.L. Thompson, O.E. Diwald, J.T. Yates, Jr.*, University of Pittsburgh

Defect sites govern the chemical and photochemical behavior of TiO@sub 2@ rutile surfaces. We have found that CO@sub 2@ binds more strongly (54.0 kJ/mol) to oxygen-vacancy Ti@super +3@ defect sites made by thermally reducing TiO@sub 2@(110) than to the fully-oxidized 5-fold coordinated Ti@super +4@ surface sites (48.5 kJ/mol). Enhanced surface reduction at temperatures up to 1000K causes an increase in the relative amount of the strongly-bound CO@sub 2@.

11:20am **SS3-ThM10 Surface Structure and Properties of Vanadia Supported on Anatase TiO@sub 2@(001)**, *W. Gao, E.I. Altman*, Yale University

We have successfully grown epitaxial anatase TiO@sub 2@(001) thin films on LaAlO@sub 3@(001) substrates using oxygen plasma assisted molecular beam epitaxy (OPA-MBE). A two-domain (1x4)/(4x1) reconstruction was observed by reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED). With OPA-MBE, monolayer to multi-layer vanadia was deposited on the reconstructed anatase (001) surface. Photoelectron spectroscopy (UPS and XPS) was used to characterize the chemical state of the vanadia. XPS results showed that the vanadia was predominantly in the 5+ oxidation state after deposition of a monolayer at 525 K, while UPS showed a small peak in the TiO@sub 2@ bandgap consistent with a small amount of V@super 4+@. After 1 ML vanadia was deposited on anatase (001), the anatase (1x4)/(4x1) LEED and RHEED patterns were replaced by (1x1) patterns indicating that the vanadia lifts the reconstruction and suggesting that the monolayer is pseudomorphic. The reducibility of the monolayer was studied by monitoring XPS peak shifts as a function of annealing temperature. At temperatures between 625 K to 875 K, the vanadia was reduced to the 3+ oxidation state; these results were very similar to vanadia on SiO@sub 2@. XPS results also showed a decrease in the intensity of the V peaks with increasing temperature. At ~875 K, nearly no vanadium was detected by XPS and the (1x4)/(4x1) pattern of the bare surface was restored suggesting that V migrated into the bulk. Vanadia growth beyond the first monolayer caused the RHEED pattern to fade and produced no discernible LEED patterns suggesting that pseudomorphic growth cannot be continued beyond 1 ML. The structural evolution of the surface as vanadia was deposited was also characterized by scanning tunneling microscopy (STM).

11:40am **SS3-ThM11 Initial Stages of Cu@sub 2@O Nano-Clusters Formation on SrTiO@sub 3@(100)**@footnote 1@, *I. Lyubinetzky, S. Thevuthasan, A.S. Lea, D.E. McCready, D.R. Baer*, Pacific Northwest National Laboratory

Self-assembled crystalline cuprous oxide (Cu@sub 2@O) nano-clusters have been grown on the SrTiO@sub 3@(100) substrate using oxygen plasma assisted molecular beam epitaxy. The growth mechanism, composition and structure were examined by x-ray photoelectron spectroscopy, x-ray induced Auger electron spectroscopy, scanning probe microscopy, scanning Auger microscopy, and x-ray diffraction. Growth parameters for the formation of pure Cu@sub 2@O nano-clusters have been optimized accordingly to the surface phase diagram of the Cu-O system, which has been determined for temperature versus oxygen

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pressure. Unlike typical semiconductor systems, e.g. Si-Ge, initial stages of the growth for studied here metal oxide system proceed without formation of the wetting layer, with formation of the 3D truncated square $\text{Cu}_{2\text{O}}$ dots starting already at sub-monolayer coverages. At following stages of the growth, nano-dots underwent shape/structure transformation similar to the semiconductor systems. Under different surface conditions of the $\text{SrTiO}_3(100)$ substrate (high temperature annealed, perfect TiO_2 -terminated surface vs. original mixed-terminated surface) significant differences in the uniformity of the nano-clusters distribution have been observed. Complications due to the re-growth of the Sr-rich nanostructures in addition to the $\text{Cu}_{2\text{O}}$ nano-dots formation at the certain substrate conditions will be also discussed.

@FootnoteText@
@footnote 1@ This work has been conducted as part of the PNNL Nanoscience and Nanotechnology Initiative supported by the U. S. Department of Energy.

Biomaterial Interfaces

Room 318/319 - Session BI+SS-ThA

Biodiagnostics

Moderator: G. Leggett, University of Sheffield, UK

2:00pm BI+SS-ThA1 Engineered DNA and RNA Molecules as Biochemical Tools, *R. Breaker*, Yale University **INVITED**

RNA and DNA molecules can be engineered to perform as precision allosteric enzymes, or "molecular switches", that are modulated by specific effectors. These designer sensor elements have numerous applications ranging from the construction of biosensors to the development of novel genetic switches. We have embarked on a program to establish effective molecular engineering strategies for switch construction, and to establish the fundamental principles that dictate the performance characteristics of these molecules. In pursuing our objectives, we have created a variety of RNA molecular switches that are modulated by specific target molecules that range from nucleotides and oligonucleotides to drug compounds, metabolites and toxins. In addition, we have begun to explore the use of immobilized RNA switches for the construction of advanced biosensor arrays. Our findings suggest that RNA and DNA have a significant untapped potential for functioning as precision molecular switches in both industrial and natural settings.

2:40pm BI+SS-ThA3 Base-dependent Competitive Adsorption of DNA on Gold, *D.Y. Petrovykh*, University of Maryland and Naval Research Laboratory; *H. Kimura-Suda, M. Tarlov*, National Institute of Standards and Technology; *L.J. Whitman*, Naval Research Laboratory

We characterize the room-temperature adsorption of single-stranded DNA (ssDNA) homo-oligonucleotides from solution onto polycrystalline Au films, including competitive adsorption between all possible pairs of unmodified oligomers. Although recent studies have shown that different DNA bases and homo-oligonucleotides interact differently with Au surfaces, competitive interactions among the bases - which will occur in most practical applications - have not been systematically addressed. We use Fourier transform infrared (FTIR) and X-ray photoelectron (XPS) spectroscopy to characterize the resulting films, and observe that oligonucleotides adsorb with a strongly base-dependent affinity, adenine (A) > cytosine (C) >= guanine (G) > thymine (T). In competitive adsorption experiments on Au, oligo(dA) strongly dominates over the other oligonucleotides. The relative adsorption affinity of oligo(dA) is so great that it competes effectively against adsorption of thiolated oligomers, and even causes hybridized oligo(dA)*oligo(dT) duplexes to denature in the presence of Au. The asymmetric adsorption affinities of the oligonucleotides must be carefully considered in systems using gold substrates, electrodes, or nanoparticle labels, and are likely to also occur on other substrates of practical importance.

3:00pm BI+SS-ThA4 MALDI MS of Proteins Separated on a Chemical Gradient Modified Open Channel Microchip, *G.R. Kinsel, X. Li, R.B. Timmons*, University of Texas at Arlington

Efficient methods for protein separation and characterization are critical to the success of a wide array of biological and biomedical research activities. Current methods involve electrophoretic separation of proteins, followed by staining, excision, digestion and analysis of isolated proteins by Matrix-Assisted Laser Desorption / Ionization Mass Spectrometry (MALDI-MS). This approach is both time consuming and subject to significant protein loss resulting from the various manipulations of the sample. Research in our laboratory is directed at circumventing these limitations through the incorporation of the sample separation process directly on the surface of the MALDI-MS sample stage. In our approach substrates suitable for use as the MALDI sample stage are modified to incorporate open electrophoretic separation channels. Substrates that have been employed include PMMA chips, which are patterned using heat-imprinting methods, and silicon wafers, which are patterned using conventional plasma etching methods. A chemical gradient is developed along the separation channel by masking adjacent areas and sequentially depositing thin films on the channel via pulsed RF plasma polymerization of allyl alcohol at various duty cycles. Control mixtures of peptides having varying hydrophilicity are electrokinetically injected into the gradient chemically modified open channel, electrophoretically separated and then analyzed by rastering the MALDI desorption laser across the channel while acquiring MALDI mass spectra. Successful results obtained to date, demonstrate the potential

value of this approach for improving sensitivity and specificity in MALDI MS analysis.

3:20pm BI+SS-ThA5 Pb@super 2+@ Sensitive Catalytic DNA Assay Integrated into Microfluidic Channels, *R.A. Zangmeister, M. Tarlov*, National Institute of Standards and Technology

Advances in microchip technology coupled with innovative bioassays are advancing the field of biosensors. We previously reported a method for immobilizing single-stranded DNA (ss-DNA) probe molecules in polyacrylamide hydrogels within plastic microfluidic channels. Spatially defined plugs are formed by photopolymerization of a solution containing 19:1 polyacrylamide/bisacrylamide and ss-DNA modified at the 5' end with an acrylic acid group. Low concentrations of fluorescent-tagged ss-DNA targets can be captured and detected in the hydrogels. We aim to couple this technology with a novel bioassay based on the response of catalytic DNA to Pb@super 2+@ ions in solution. It is reported to show > 80-fold selectivity for Pb@super 2+@ over other divalent metal ions, and with fluorescent tag modifiers can be used to detect Pb@super 2+@ ions over a large concentration range (10 nmol to 4 mmol).@footnote 1@ Our goal is to immobilize the enzyme strand sequence of the catalytic DNA duplex into the hydrogel plugs immobilized in microfluidic channels. Our strategy is to electrophorese fluorescently tagged substrate strands into the hydrogel plug where they hybridize with the immobilized enzyme strand to form the catalytic DNA system. Then Pb@super 2+@ is electrophoresed into the hydrogel plug resulting in the catalytic cleavage of the substrate strand and the release of the fluorescent-tagged sequence fragment that is detected using a fluorescence microscope. The combination of these two technologies results in a Pb@super 2+@ detection system with enhanced sensitivity due to the high loading of DNA probes in the hydrogel plug, the spatially confined, directed mass transfer characteristics of the microfluidic channels, and the inherently low fluorescent background of the hydrogels. The immobilization, retention of catalytic DNA activity, and current limits of detection will be discussed. @FootnoteText@ @footnote 1@ Li, J.; Lu, Y., J. Am. Chem. Soc. 2000, 122, 10466-10467.

3:40pm BI+SS-ThA6 Monitoring Neurotransmitters with Voltammetry, *R.M. Wightman*, University of North Carolina **INVITED**

Carbon-fiber microelectrodes can serve as chemical sensors for the detection of easily oxidized chemical messengers such as dopamine, serotonin, and histamine in biological systems. The electrodes have micron dimensions and can be used on millisecond time scales. Thus, they can be used to measure neurotransmitter release at the level of single cells or in the brain of intact, behaving animals. Such measurements are giving new insights into the complex chemical interactions that regulate behavioral states.

4:20pm BI+SS-ThA8 Adsorption Behavior of Proteins in Microcapillaries, *A. Bhattacharyya, K. Lenghaus, D. Halagowder, J.J. Hickman*, Clemson University; *J.W. Jenkins, S. Sundaram*, CFD Research Corporation

The dynamics of protein adsorption, desorption and denaturation are important factors in determining the efficacy of a microfluidic device for biotechnology applications. When a protein solution is passed through a microcapillary, the protein molecules can adsorb onto the surface of the capillaries and can often subsequently denature. Hence an understanding of the adsorption behavior of a protein is very important in order to determine the basic parameters for fabrication of a microfluidic based MEMS device. Most of the research on protein adsorption characteristics is based on static systems. However, the adsorption behavior of proteins in static and flow systems is not necessarily the same. Our research focuses on investigating the difference in the adsorption behavior of proteins under flow and static conditions, using enzymatic proteins as probes. We have used enzymes such as alkaline phosphatase, glucose oxidase and horseradish peroxidase in our studies. The microcapillaries used were PEEK (Poly-Ether-Ether-Ketone) and PTFE (Polytetrafluoroethylene). A total protein assay (MicroBCA) was used to quantitate the amount of protein adsorbed to the surface and enzymatic assays were used to estimate the activity of the proteins. A statistical model based on the Langmuir equation was used for extracting the kinetic binding constants and the protein coverage on the surface. Our results indicate that there is a significant difference in the surface affinities and binding site densities observed in static and flow conditions. These results will enable us to improve existing protein adsorption and fluid dynamics software and eventually create design rules for biocompatible MEMS devices.

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4:40pm **BI+SS-ThA9 Micro- to Nanofluidic Systems for Bioanalysis**, *G.P. Lopez*, University of New Mexico; *S.S. Sibbett*, Intel Corp.; *D. Petsev*, University of New Mexico; *C.F. Ivory*, Washington State University; *M. Piyasena*, *A. Garcia*, *L.K. Ista*, *M.J. O'Brien*, *P. Bisong*, *S.R.J. Brueck*, University of New Mexico

This talk will present an overview of efforts at the University of New Mexico to develop chip based micro- and nanofluidic systems for biosensing and bioseparations. Microfluidic systems to be described include microchip countercurrent electroseparation (in collaboration with Intel Corp.) and affinity microcolumns with fluorescence detection. New methods for fabrication of nanofluidic systems based on interferometric lithography will also be described. These methods are especially well suited for manufacture of bioanalytical systems that incorporate large scale integrated nanofluidic components. Characterization and modeling of fluidic properties of the bioanalytical systems will be emphasized.

5:00pm **BI+SS-ThA10 Chitosan - A Biomaterial Interface that can be Selectively Deposited onto Micropatterned Surfaces and Conjugated to Sensing Biomolecules**, *L.-Q. Wu*, *H. Yi*, University of Maryland Biotechnology Institute; *M.J. Kastantin*, *S. Li*, *D.A. Small*, *J.J. Park*, University of Maryland; *T. Chen*, University of Maryland Biotechnology Institute; *G.W. Rubloff*, *R. Ghodssi*, University of Maryland; *W.E. Bentley*, *G.F. Payne*, University of Maryland Biotechnology Institute

We are examining the amino-polysaccharide chitosan as a biomaterial interface. Chitosan's pH-dependent electrostatic properties allow it to be selectively deposited (i.e. "templated") onto micropatterned electrodes in response to an applied voltage. Deposition of chitosan, or chitosan-containing conjugates, is rapid (about 2 minutes) and can be performed under mild conditions. After neutralization, the films are retained without the need for an applied voltage. These films can also be removed from the electrode using mildly acidic conditions (pH<6). Chitosan's amine groups are also nucleophilic and can readily react with a variety of reagents. In particular, standard coupling chemistries can conjugate proteins and oligonucleotides with chitosan. We are exploiting glutaraldehyde coupling chemistries to anchor nucleic acids and proteins onto chitosan surfaces. In one study, we tethered oligonucleotide probes onto an electrochemically deposited chitosan surface and examined the bio-detection of mRNA by a hybridization-based assay. In a second study, we selectively deposited chitosan on an electrode surface embedded in the base of a microfluidic channel. The green fluorescent protein (GFP) was subsequently anchored to this chitosan surface. In summary, chitosan is unique interface biomaterial - it can be templated onto a microfabricated surface and conjugated to bio-molecules. We are currently exploiting these capabilities in biosensor and bio-MEMS applications.

Surface Science

Room 327 - Session SS+OM-ThA

Self-Assembled Monolayers

Moderator: L. Hanley, University of Illinois at Chicago

2:00pm **SS+OM-ThA1 Non-dissociative Chemisorption of Methanethiol on Ag(110)- A Critical Result for Self-assembled Layer Formation**, *J.-G. Lee*, *J. Lee*, *J.T. Yates, Jr.*, University of Pittsburgh

Three definitive experiments have been performed which show that CH@sub 3@SH does not dissociate upon chemisorption on clean Ag(110). On the clean Ag(110) surface, the adsorption in the first layer occurs at 0.5 ML, producing a (2x1) LEED structure. The undissociated molecule desorbs at ~140 K. Using a 50%-50% mixture of CH@sub 3@SD and CD@sub 3@SH, no evidence of S-H or S-D bond scission by isotope mixing between these molecules is found upon desorption. And finally, when the CH@sub 3@SH molecule is incident on clean Ag(110) surface in the temperature range from 240 K to 400 K, less than 1% of the incident molecules dissociate to produce adsorbed S. In contrast, when a sulfur-poisoned Ag(110) surface is exposed to CH@sub 3@SH, autocatalytic dissociation occurs below 240 K, producing CH@sub 4@, H@sub 2@S and adsorbed S atoms. These results are in striking contrast to the behavior of Cu(110) where CH@sub 3@SH dissociation occurs below 320 K leaving S. These results are of importance in understanding the self assembly of alkanethiol layers on silver where it has been commonly assumed that S-H bond scission occurs at room temperature. This work was supported by DOE-BES.

2:20pm **SS+OM-ThA2 Spectroelectrochemical Studies of Self-Assembled Monolayers of Thiols**, *I. Thom*, St Andrews University, Scotland; *M. Buck*, St Andrews University, Scotland, UK

Thiol SAMs provide a convenient route to modify electrodes and to serve as templates for directing electrochemical processes. Towards a rational design of thiol SAMs for electrochemical applications the electrochemically induced desorption and adsorption of thiols are studied in-situ using the combination of electrochemistry and non-linear optical techniques. Potential dependent capacitive and faradaic currents are correlated with the second harmonic signal which probes the S-Au bond formation. Studies of alkane thiols and biphenyl based thiols reveal that this correlation is strongly dependent on the electrolyte, i.e. both the penetration of ions into the layer and the desorption mechanism are affected by the electrolyte. In the ethanol case, a change in the desorption mechanism during multiple potential cycling is observed. While the current continuously decreases with increasing number of cycles, the change of the SHG signal remains essentially unaltered and indicates a change in the faradaic process. This change is explained by a transition from thiolate to disulfide formation upon the desorption of thiols.

2:40pm **SS+OM-ThA3 Photoemission Study of Dodecanethiol on Ag(111) and Au(111)**, *H. Geisler*, Xavier University; *J.M. Burst*, *S.N. Thornburg*, *C.A. Vetrice*, University of New Orleans; *Y. Losovyj*, *P.T. Sprunger*, Louisiana State University

Self-assembled monolayers show great promise for use in many technological applications such as in chemical and biological sensing, chemical resists in lithography, corrosion protection, and molecular electronics. However, there are several fundamental properties of these systems that are not well understood. For instance, the adsorption of alkanethiols on Au(111) results in a (@sr@3 x @sr@3)R30° overlayer; whereas, adsorption on Ag(111) results in an incommensurate overlayer even though Au and Ag are isoelectronic and are lattice matched to 0.3%. Although there have been several studies of the geometric structure of thiols on Au(111) and to a lesser extent on Ag(111), there have been very few studies of the electronic structure of these films. Angle-resolved ultraviolet photoelectron spectroscopy studies of the growth of dodecanethiol on Au(111) and Ag(111) have been performed in UHV by vapor deposition. By using vapor deposition, the submonolayer striped phase, full monolayer upright phase, and the multilayer phase can be studied. The monolayer coverage of thiol results in peaks at binding energies of 20 eV, 14 eV, 10 eV, and 7 eV. By comparing the dispersion of the Ag(111) d-band emission for the clean surface to the surface after deposition of a monolayer of thiol, it was determined that there is a loss of order of the Ag surface atoms. Similar measurements for Au(111) reveal that the Au(111) surface remains in an ordered state. This result provides a mechanism for the different adsorption geometries of alkanethiols on Au(111) and Ag(111). Since there is no ordered template of Ag atoms after thiol adsorption, the van der Waals interaction between the CH@sub 2@ chains dominates, resulting in an ordered, incommensurate overlayer. Measurements of the thiols in the multilayer regime reveal a uniform shift of the thiol peaks to higher binding energy, presumably due to sample charging effects from the insulating nature of these films at 150 K.

3:00pm **SS+OM-ThA4 Short Aromatic Thiols on Cu(111): Initial Adsorption Configuration and the Formation of an Ordered Monolayer**, *B.V. Rao*, *K.-Y. Kwon*, *J. Zhang*, *A. Liu*, *L. Bartels*, University of California at Riverside

We present low-temperature scanning tunneling microscope (STM) measurements of the initial orientation of di-chloro-thio-phenol (DCTP) and S-phenyl-thio-acetate (SPTA), a thio-phenol whose sulfur-bound hydrogen is replaced by an acetyl group. The latter is a common practice in order to protect the thiol group during the synthesis of poly-functional organic molecules. This poster compares the impact of the acetyl substitution on the initial steps of the molecules interaction with a Cu(111) surface. DCTP adsorbs at low temperatures (15K) with the sulfur atom at an on-top site and is able to rotate around it. This results in the observation of a flower shaped species on STM images. There are two chiral adsorption configurations which can be distinguished by STM. In contrast, SPTA adsorbs in a position in which both the phenyl and the second carbon of the acetyl group point upward resulting in a double protrusion in STM images. While tunneling electrons of less than 500meV of either bias can cause the abstraction of hydrogen from the thiol group of DCTP, SPTA is stable beyond 1V in tunneling bias. Increasing the coverage by adsorption at nitrogen temperatures, DCTP forms an ordered monolayer consisting of dimers, both of which have the phenyl group lying flat on the surface. The formation of extended islands of the ordered monolayer requires annealing of the sample beyond liquid nitrogen temperatures. Further increase of the

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coverage results in pronounced protrusion at defect sites of the ordered monolayer, which we interpret as molecules that point the phenyl ring away from the surface. STM resolution on a film consisting entirely of such species is poor; however, it can confirm that an ordered film is formed.

3:20pm SS+OM-ThA5 Balance of Structure-building Forces in Monomolecular Films: Terphenyl-substituted Alkanethiolates on Noble Metal Substrates, A. Shaporenko, Universität Heidelberg, Germany; M. Brunnbauer, A. Terfort, Universität Hamburg, Germany; L.S.O. Johansson, Karlstad University, Sweden; M. Zharnikov, Universität Heidelberg, Germany

The design of versatile monomolecular films relies on detailed knowledge of basic rules governing the packing density and exact arrangement of the molecular constituents in these systems. The most important issue in this connection is the understanding of the interplay between the structure-building headgroup-substrate and intermolecular interactions. To address this issue we have studied self-assembled monolayers (SAM) formed from terphenyl-substituted alkanethiols $C_{60}H_{14}S_2$ ($C_{60}H_{14}S_2$) on Au and Ag substrates. In these systems, strongly interacting terphenyl backbones force a dense molecular packing, which does not fit to the geometry of the metal-S-C bond at certain length of the aliphatic part. We used several complementary experimental techniques such as x-ray photoelectron spectroscopy (XPS), high-resolution XPS, near edge X-ray absorption fine structure spectroscopy, infrared absorption spectroscopy, ellipsometry, and water contact angle measurements to characterize the TPN SAMs. Odd-even changes in the packing density, the tilt angle of the terphenyl moieties, etc have been observed and considered in detail. These changes could be clear correlated with the geometry of the metal-S-C bond, which assumed to be different on Au and Ag. The results imply a predominant role of the headgroup-substrate interaction in the balance of structure-building forces in the aliphatic SAMs and give a practical tool for the fabrication of monomolecular films with desired properties.

3:40pm SS+OM-ThA6 Pronounced Odd-Even Changes in the Molecular Arrangement and Packing Density of Biphenyl-Based Thiol SAMs: A Combined STM and LEED Study, P. Cyganik, M. Buck, University of St Andrews, UK; W. Azzam, G. Witte, Ch. Woell, Ruhr Universitaet Bochum, Germany

Self-assembled monolayers (SAMs) of thiols are promising candidates for nanolithographic applications. Towards a rational design and control down to the length scale reaching molecular dimensions we study SAMs a particular type of thiols which is characterized by a biphenyl unit and an alkane spacer of varying length (CH_3 (C_6H_4) $_2$ CH_2 (CH_2) $_n$ SH, BPN, $n = 2, 3, 4, 5$). SAMs adsorbed on Au(111) substrates were studied using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Our results demonstrate that preparation at elevated temperature results in highly ordered layers with large domains. Whereas the (2×3) structure of the BP3 and BP5 SAMs is similar to that reported previously for other aromatic thiols, SAMs made from BP2 and BP4 exhibit a very different structure. A (5×3) unit cell containing 8 molecules is found which corresponds to a packing density reduced by 25 % compared to BP3 and BP5. The odd-even effect observed in the molecularly resolved STM images of BPN, therefore, confirms the pronounced influence of the spacer chain on the structure of these biphenyl based SAMs.

4:00pm SS+OM-ThA7 Mechanism of Nanomolecular Motion Induced by Polarity Change of the Electric Field in the Self-Assembled Monolayers, T. Ishida, AIST, Japan; H. Fukushima, TPRC, SEIKO EPSON Corporation, Japan; T. Tamaki, AIST, Japan

We have successfully observed the nanoscale molecular motion induced by polarity change of the electric field by STM, when small amounts of asymmetrical disulfides containing mobile terphenyl moieties were embedded into pre-assembled dodecanethiol SAMs. Taking the direction of the dipole moment into account, the thickness of embedded molecular protrusions became larger at the positive bias. However, STM experiments revealed that the thickness of the molecular protrusions was larger at the negative bias, contrary to this prediction. STS revealed the higher rectification property at the area of the terphenyl terminated monolayer where also showed the higher electrical conduction at the negative tip bias compared to positive one. The higher electrical conduction at the negative tip bias was likely to retract the STM tip, showing the apparent nanomolecular motion by the polarity change. Next, we investigated the relationship between the higher rectification property and real conformational change. When symmetric

disulfide which is not easy to change molecular conformation are embedded into pre-assembled dodecanethiol SAMs for the comparison, both the rectification property and apparent molecular motion were not observed. In addition, when the STM tip was directly attached to asymmetric disulfides, rectification property was not observed in STS. Thus, we concluded that the conformational change is the influential factor to induce the higher rectification property. T. Ishida, H. Fukushima, T. Tamaki and H. Tokumoto, Jpn J. Appl. Phys. in press. H. Fukushima and T. Tamaki J. Phys. Chem. B106 7142(2002).

4:20pm SS+OM-ThA8 The Reaction of Tetrakis(dimethylamino)titanium with Self-Assembled Monolayers Possessing -OH, -NH₂ and -CH₃ Terminal Groups, A.S. Killampalli, P.F. Ma, J.R. Engstrom, Cornell University

Organic materials are playing an increasing role in modern microelectronic devices—beyond their traditional role as photoresists. New areas include their application as low- ϵ dielectrics. Interfaces between organics and metals are also of interest, including in fields such as molecular electronics. To date, almost all work concerning the formation of organic-metal interfaces on pre-existing organic layers has involved metal thin films deposited by (elemental) evaporation. In the work described here we examine an alternative approach to the formation of inorganic-organic interfaces, namely, via the use of organo-transition metal complexes. Here we study the reaction of the titanium precursor, tetrakis(dimethylamino)titanium (TDMAT), with model organic surfaces [self-assembled monolayers (SAMs) terminated by -OH, -NH₂ and -CH₃ groups] using X-ray photoelectron spectroscopy (XPS). Trichlorosilane self-assembled monolayers have been formed on SiO₂ surfaces that, in selected cases, were subjected to additional chemical conversion steps. Prior to insertion into vacuum these layers were characterized using AFM, ellipsometry and contact angle measurements. Exposure of these surfaces to TDMAT was carried out in a custom-designed ultrahigh vacuum chamber equipped with facilities for XPS and quadrupole mass spectrometry (QMS). In selected cases, angle resolved XPS (ARXPS) was used to probe the spatial extent of reaction of the precursor. Among the SAM surfaces studied, the -OH terminated SAM exhibits the highest reactivity, followed by the -NH₂ and -CH₃ terminated SAMs, in that order. ARXPS results reveal that TDMAT reacts primarily at the top of the -OH terminated SAM, while the reaction on the -CH₃ terminated SAM is actually with underlying reactive regions at the SAM/SiO₂ interface. Additional results concerning the reaction of TDMAT with these monolayers, including modeling of the adsorption kinetics, will be presented.

4:40pm SS+OM-ThA9 Characterization of Carboxyl Functionalized SAMs and Surface-Attached Interlocking Molecules Using Near-Edge X-ray Absorption Fine Structure, T.M. Willey¹, University of California, Davis and Lawrence Livermore National Lab; A.L. Vance, T. van Buuren, C. Bostedt, B.R. Hart, R.W. Meulenberg, A.J. Nelson, L.J. Terminello, Lawrence Livermore National Laboratory; C.S. Fadley, Lawrence Berkeley National Laboratory

Self-Assembled Monolayers (SAMs) and other organo-thiol compounds on Au(111) have become increasingly important to achieve surface attachment of complex molecules. In order to produce useful films, one needs to understand the orientation, order, and substrate bonding of the molecules. Carboxyl and amino terminated SAMs are useful in functionalizing surfaces for surface attachment and immobilization of proteins, DNA, viruses, as well as using the charged state of the endgroups in switchable surfaces. We are also using such functionalization in surface attached interlocking molecules to attempt to induce and measure reorientation (switching) within interlocking molecules. However, functionalization often (adversely!) affects the synthesis, order, packing, and formation of these films. With proper synthetic protocol, many of these issues can be overcome. Here, NEXAFS results probe the orientation of molecules while XPS is used to determine the attachment and chemical nature of the films. We present NEXAFS spectra to compare and contrast the ordering and between SAMs from mercaptohexadecanoic acid (HS(CH₂)₁₅COOH) a long-chain molecule with strong chain-chain interactions and thioctic acid (S(CH₂)₂(CH₂)₂CH(CH₂)₄COOH) with a large base hindering strong interactions between its short chains. Stark conformational differences occur in these films of the endgroups with deprotonation (COO⁻ vs. COOH.) In addition, we will present initial results on ordering and attachment in

¹ Morton S. Traum Award Finalist

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amino-terminated alkanethiols on gold, and preliminary results using functional groups in switching interlocking molecules on surfaces.

5:00pm **SS+OM-ThA10 Self Assembled Monolayers on Microelectronic Copper Thin Film for Prevention of Corrosion**, *Y.S. Tan*, National University of Singapore, Singapore; *M.P. Srinivasan*, *S.O. Pehkonen*, National University of Singapore; *Y.M. Chooi*, Chartered Semiconductor Manufacturing Ltd., Singapore

Abstract: Self-assembled monolayers of dodecanethiol (DT), Mercaptobenzothiazole (MBT), Benzotriazole (BTA) and Imidazole (IMD) were formed by adsorption on the surface of copper thin film used in the ultra large-scale integrated circuits. The films were characterized by X-Ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared (FTIR) Spectroscopy and contact angle measurements. The corrosion inhibitive behaviours of these organic monolayers were investigated in aerated 0.5 mol/dm³ H₂SO₄ solutions by means of Electrochemical Impedance Spectroscopy (EIS) and polarization techniques. The presence of the monolayers reduced corrosion by blocking the copper surface from the dissolved oxygen in the acid medium. The relative inhibition efficiencies of these inhibiting agents in preventing copper oxidation is found to be in the order of: DT > MBT > BTA > IMD. The effectiveness of the inhibitors increased with temperature, concentration of the inhibitors and immersion time in the solution. An adsorption model was proposed on the basis of the variation of impedance with inhibitors' concentration.

Surface Science

Room 328 - Session SS-ThA

Oxide Reactions and Catalysis

Moderator: A. Klust, Tulane University

2:00pm **SS-ThA1 Atomic Understanding of Strong Nanometer-Thin Metal/Alumina Interfaces and the Making of Nanoscale Island and Film Catalysts**, *D.R. Jennison*, *T.R. Mattsson*, Sandia National Laboratories Chambers, Droubay, Jennison, and Mattsson [Science 297 (2002) 827] recently reported room temperature laminar growth of Co deposited in vacuum from an evaporation source on fully hydroxylated but otherwise clean $\alpha\text{-Al}_2\text{O}_3$ (0001). We extend this work to a number of metals using density functional (DFT) calculations. The exothermicity of the suggested core reaction, $2\text{OH}^- + \text{M} \Rightarrow \text{H}_2\text{O} + \text{M}^{2+} + 2\text{O}^{2-}$, where M represents any metal, is investigated for Cr, Fe, Ni, Cu, Mo, Ru, Rh, Pd, and Al. We find that this reaction is strongly exothermic for most metals. However, while Rh is slightly endothermic, it has a sufficient heat of adsorption to react immediately upon contact. The behavior of Cu cannot be determined within the current accuracy of DFT. Pd is strongly endothermic, suggesting noble metals will not react. By first-principles molecular dynamics simulations of Rh, we confirm a substantial likelihood for direct "hot" reactions driven by the heat of adsorption, as originally proposed. However, Rh has two reaction barriers, indicating more complex kinetics than with Co. Now 1-2 ML films may be made and also nano-islands with steps, both having potential catalysis applications. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

2:20pm **SS-ThA2 Potassium Adsorption on Thin Film Cerium Oxide and Its Effect on Supported Rhodium Activity**, *D.R. Mullins*, Oak Ridge National Laboratory

We have examined the adsorption of K on CeO₂ thin films and its effect on the adsorption of CO on Rh supported on the CeO₂. The K saturation coverage, i.e. the maximum coverage achievable before the onset of multilayer desorption, is ca. 1×10^{15} cm⁻². This is about twice what has been observed on Rh(111). It is similar to the CeO₂(111) surface density of 0.8×10^{15} cm⁻². The K exhibits three distinct desorption states near 450K, 600 K and 700 K. The K 2p core-level photoemission does not indicate a significant change in binding energy or the presence of multiple K states as a function of annealing temperature and coverage. CO dissociates when adsorbed on Rh on reduced CeO₂. It is of interest to determine whether charge transfer from K to CeO₂ will also cause CO dissociation on Rh supported on K/CeO₂. CO desorbs from Rh on fully oxidized CeO₂ below 500 K and shows little evidence of O exchange with the ceria. The desorption is similar to CO on Rh(111). When K is present,

the CO desorption occurs between 600 K and 700 K and shows considerable O exchange with the support. The high temperature desorption is similar to what was observed on K/Rh(111) which was ascribed to an interaction between the K and the CO. The high temperature desorption and O exchange are also similar to what has been observed for dissociated CO on Rh supported on reduced CeO₂. For the system CO/Rh/K/CeO₂, there is no evidence of CO dissociation as indicated by the C 1s photoemission. The C 1s photoemission does indicate the formation of surface carbonates. Carbonates were not observed on either K/Rh(111) or Rh/CeO₂. @FootnoteText@ @footnote 1@Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

2:40pm **SS-ThA3 The Interaction of Methyl Iodide with Surface Defects on UO₂(100)**, *J. Stultz*, *S.A. Joyce*, *M.T. Paffett*, Los Alamos National Laboratory

Actinide materials undergo thermal and non-thermal reactions with adsorbed molecules resulting in chemical transformations leading to degradation and gas generation. In most handling and processing scenarios actinide materials readily oxidize forming an actinide oxide interface. Evidence suggests that unique chemistry occurs and may possibly be driven by surface defect sites at these oxide interfaces. To characterize these interactions and possibly quantify surface defect sites, the thermal reactivity of CH₃I with a well annealed and sputter defected UO₂(100) surfaces was investigated. XPS results indicate CH₃I undergoes dissociative adsorption on UO₂(100) at 300K in which I reacts and adsorbs selectively at defect sites leaving little or no residual carbon on the surface. Semi-quantification of surface defects was achieved by analysis of the XPS results for moderately high surface defect densities. Low temperature TPD results indicate mono and multilayer CH₃I desorption characteristics similar to that seen for other metal oxide systems. Additionally, low intensity features in the TPD data suggest trace levels of oxidation of residual surface carbon to form formic acid. LA-UR-03-2698.

3:00pm **SS-ThA4 Thermal and Radiation-Induced Chemistry of Water on Uranium Dioxide Surfaces**, *J. Stultz*, *M.T. Paffett*, *S.A. Joyce*, Los Alamos National Laboratory

Most plans for the disposition of surplus nuclear materials involve storage in sealed containers where the evolution of gases from reactions of adsorbed water could present both pressure and flammability hazards. In order to better understand the relative importance of the thermal- and radiation-induced chemistry, we have studied the interactions of water on single crystals of uranium dioxide. Temperature programmed desorption and electron stimulated reaction/desorption are used to examine the chemistry. In the absence of radiation, water adsorbs/desorbs molecularly on nominally pristine oxide surfaces with a binding energy of only a few kcal/mole greater than water with itself. The strength of this interaction is large enough to indicate that UO₂ surfaces handled outside the driest of environments will be covered with water. External low energy electron irradiation is used to simulate the effects of radiolytic chemistry induced by decay particles. The principle neutral gaseous radiolytic products are H₂, O₂, and water. The relative yields are strongly dependent on temperature and coverage. Ion desorption, which is often sensitive to minority species, indicates that surface hydroxyls, presumably formed at defect sites, are stable up to high temperatures (~ 600K).

3:20pm **SS-ThA5 Gas Sensing Mechanism of SnO₂**, *M. Batzill*, *B. Katsiev*, Tulane University; *A. Chaka*, National Institute of Standards and Technology; *U. Diebold*, Tulane University

Stannic oxide is widely used as a gas sensing material for reducing and oxidizing gases. Variations in the surface oxygen concentration of metal-oxide gas sensors play an important role for explaining their response to a change in the surrounding gas phase. Here we show for different low index SnO₂ surfaces that non-stoichiometric surface terminations are favored at a low oxidation potential of the environment (e.g. UHV conditions). Under such conditions the low-energy (110) surface forms complex surface reconstructions in order to accommodate the loss of surface oxygen. The (101) and (001) surfaces, on the other hand, retain bulk terminations for both stoichiometric and reduced surfaces. The stability of these surfaces is explained on ground of the dual valency of Sn (SnII and SnIV) and the rutile-structure of SnO₂ that allow the (001) and (101) surfaces to attain a Sn²⁺O²⁻

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stoichiometry by removal of bridging oxygen atoms. The surface structures have been determined by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). For reduced surfaces, angle resolved UPS was employed to characterize the dispersion of the surface electronic states. The variation of the surface composition has been measured by temperature programmed ion scattering spectroscopy. The experimental results are verified by density functional theory calculations that show the stability of different surface phases as a function of the oxygen chemical potential. This variable surface composition accompanied by a change in the electronic structure is proposed to be the fundamental process of the gas sensing mechanism for SnO₂.

3:40pm SS-ThA6 Photoinduced Reaction Dynamics of Halocarbon Adlayers on the Fe₃O₄ (111)-(2x2) Selvege of Fe₂O₃ (0001), G.G. Totir, Y. Le, R.M. Osgood, Jr., Columbia University

Electron transfer reactions on surfaces play a key role in electrocatalysis and in photoinduced processes in surface-adsorbate systems. More recently, interest in understanding the reactivity of iron oxides toward halogenated hydrocarbons has been stimulated by applications in catalysis and environmental decontamination procedures. We used time-of-flight (TOF) and temperature programmed desorption (TPD) to study the electron transfer reaction dynamics and photochemistry of halocarbons on surface reconstructed single crystal hematite, Fe₂O₃ (0001). For example, TPD spectra recorded at various coverages of methyl iodide adsorbed at 100 K on the magnetite, Fe₃O₄, termination of single crystal hematite, indicate a rich surface chemistry, with multiple desorption events, similar to results previously obtained for other adsorbates on the same surface. Furthermore, angle-resolved TOF results for monolayer coverage of methyl iodide on Fe₃O₄ (111)-(2x2) indicated that the methyl fragments produced from dissociative electron attachment were ejected at an angle of ~ 0° with respect to the surface normal. Post-irradiation desorption spectra for methyl iodide and carbon tetrachloride on the magnetite surface, and results discussing adsorbate orientation and coverage dependence will be presented.

4:00pm SS-ThA7 Photo-oxidation of Trimethyl Acetic Acid on the Surface of TiO₂(110), M.A. Henderson, J. Szanyi, Pacific Northwest National Laboratory; J.M. White, University of Texas, Austin

TiO₂ has received considerable attention for its use as a photocatalyst in the destruction of organics. Complexities associated with microcrystalline TiO₂ (e.g., identification of surface active sites and intermediates) often hamper mechanistic study of the step-by-step conversion of organics into CO₂. In an attempt to address mechanistically the photo-oxidation of organics on TiO₂, we employ rutile TiO₂(110) as a model photocatalyst and trimethyl acetic acid (TMAA) as a model organic. A saturation exposure of TMAA at 300 K results in dissociation of the acid O-H bond to form bidentate trimethyl acetate (TMA) and OH groups at the bridging anion sites. In TPD, recombination of TMA and OH to form parent occurs between 300 and 550 K, along with water from OH combination and some TMA decomposition to isobutane and isobutene. However, the majority of the TMA adlayer decomposes to CO and isobutane/isobutene at 650 K. UV exposure was performed at 110 K in order to capture intermediates during photolysis, subsequently analyzed in TPD. UV exposure in the absence of O₂ results in rapid conversion of the species responsible for the 300-550 K TPD states into acetate groups. In contrast, the TMA species responsible for the 650 K TPD states are converted into isobutene/isobutene and CO₂ by cleavage of the C-COO bond. Inclusion of O₂ does not affect the rate of acetate formation, but accelerates the conversion of the 650 K TMA into isobutene/isobutane. Evidence has been found for the continued photo-oxidation of the C₄ daughter products into C₃ species. These reactions do not appear to be wavelength dependent for photons with energies in excess of the TiO₂ bandgap. Based on these results, we propose that products of hole trapping on TMA depend on the structural environment of the adlayer, and that a limited amount of electron trapping permits some degree of photochemistry in the absence of O₂.

4:20pm SS-ThA8 The Origin of Photo-induced Hydrophilicity on TiO₂ Surfaces: Photo-generation of Surface Oxygen Vacancies or Photo-oxidation of Adsorbed Organics?, J. Szanyi, M.A. Henderson, Pacific Northwest National Laboratory; J.M. White, University of Texas, Austin

Since the discovery of the photocatalytic nature of TiO₂ in the 1970s, significant efforts have been made to understand both the properties of the oxide material itself and the catalytic processes that occur on its surfaces. In recent years the photo-induced hydrophilic nature of

TiO₂ has been discovered and studied. The hydrophilic behavior continues after removal of the light, but gradually degrades to the pre-irradiation conditions. Most of the original work from Japan suggests that hydrophilicity and photo-oxidation of surface organic contaminants are unrelated properties of TiO₂. They propose UV generated oxygen defect sites on the TiO₂ surface as the origin of hydrophilicity. In turn, the oxidation of oxygen vacancies by O₂ in the air has been proposed as the mechanism for the slow degradation of hydrophilicity of a TiO₂ surface. In order to understand the origin of photo-induced hydrophilicity of TiO₂, we have studied the adsorption of water on a clean and trimethyl acetic acid covered TiO₂(110) surface under carefully controlled experimental conditions. TPD of H₂O suggests that irrespective of the presence or absence of vacancies, water wets the TiO₂ surface as evidenced by the sequential filling of monolayer, second layer and multilayer states as a function of increasing coverage. On the other hand, the monolayer water TPD state is absent for water adsorbed on a TiO₂(110) surface pre-saturated with trimethyl acetate (TMA) species, formed from decomposition of the acid. Exposure of the TMA adlayer to UV light in 5x10⁻⁶ torr O₂ results in nearly complete photo-oxidation of the organic and restoration of the ability of the surface to directly bind water. In this presentation, based on these molecular-level UHV studies, we propose that the origin of photo-induced hydrophilicity on TiO₂ surfaces is likely due to photo-oxidation of adsorbed organics that create a hydrophobic monolayer.

4:40pm SS-ThA9 The Adsorption and Reaction of NO on Single Crystal Titanate (TiO₂ 2@ and SrTiO₃ 3@) Surfaces, C.H.F. Peden, S. Azad, M.H. Engelhard, M.A. Henderson, J. Szanyi, L.-Q. Wang, Pacific Northwest National Laboratory

The control of NO_x (NO and NO₂) emissions from combustion processes, including vehicle engines, remains a challenge particularly for systems operating at high air-to-fuel ratios (so-called 'lean' combustion), where the need is to selectively reduce NO_x with a reductant in a large background of the competing oxidizing species, O₂. A wide variety of oxide materials, including zeolites, are known to be effective for selective catalytic reduction of NO_x from the exhaust of 'lean-burn' engines. As such, there has been much interest for some time in determining the kinetics of adsorption and surface reactions of NO and NO₂, as well as identifying the composition and structure of the mechanistically important adsorbed NO_x species on this class of catalytic materials. In this presentation, we will discuss selected results from our ongoing studies aimed at addressing some of the considerable remaining uncertainties about these processes. In particular, we will compare and contrast the results of our temperature programmed desorption (TPD) and x-ray photoemission spectroscopy (XPS) studies of NO adsorption on single crystal TiO₂ 2@ and SrTiO₃ 3@ surfaces. Both weakly adsorbed NO and the reaction product, N₂O, were observed in TPD from TiO₂(110). The N₂O is formed from an 'NO-like' species identified with XPS. However, NO is the only desorption product from a SrTiO₃(100) surface. @FootnoteText@ @footnote 1@M. Shelef and R.W. McCabe, Catal. Today 62 (2000) 35. @footnote 2@The work was carried out at Pacific Northwest National Laboratory (PNNL) and funded by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Divisions of Chemical Sciences and Materials Sciences. Experiments were performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility located at PNNL and supported by the DOE's Office of Biological and Environmental Research.

5:00pm SS-ThA10 An FTIR Study of Methanol, Water and Acetic Acid on MgO(100) Under Ambient Conditions, M.C. Foster, University of Massachusetts

We have investigated the interactions occurring between the MgO(100) surface and a series of small molecules, namely water, methanol and acetic acid. A sample cell has been constructed such that many of these infrared transparent surfaces are investigated while the volume of gas phase molecules probed is minimized. A number of crystals, obtained by cleaving with a hammer and chisel a larger single crystal boule under a nitrogen purge, are placed in this cell, which is essentially a hollow stainless steel tube with IR windows on either side. The adsorbate of interest is introduced at the desired pressure and allowed to establish a dynamic equilibrium with the MgO(100). The adlayer formed on the crystal faces is observed by transmission Fourier transform infrared (FTIR) spectroscopy. Any IR absorption stemming from molecules in the gas phase in the resulting spectrum is easily subtracted out. Photometry then allows for the quantitative determination of adlayer coverages from absorbance measurements using a modified Beer-Lambert Law. The substrates have

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also been inspected with atomic force microscopy (AFM) both before and after each series of experiments. The interactions of these adsorbates with MgO(100) under room temperature conditions and pressures on the order of 10 Torr vary from physisorbed, as is the case with methanol all the way up to dissociatively chemisorbed, as is the case with acetic acid resulting in the formation of magnesium acetate under these experimental conditions.

Surface Science

Room 327 - Session SS1-FrM

Catalysis IV: Reactivity of Complex Systems

Moderator: S. Semancik, National Institute of Standards and Technology

8:20am SS1-FrM1 Surface Chemistry of Carburization and Embrittlement of Fe, *D.E. Jiang¹, E.A. Carter*, University of California, Los Angeles

High temperature and pressure, as well as reactive gases such as CO and H₂, erode steel. Experimental observations of eroded steel show that carburization and embrittlement are potential causes for the erosion. We investigate the surface chemistry behind this problem via spin-polarized periodic density functional theory. In this talk, we will discuss C and H adsorption on Fe(110) and C and H diffusion into and through bulk Fe. Static properties including site preference, solution enthalpies, and adsorption energies, are predicted with increasing system size and compared with experiment. For adsorption, different 2-dimensional structures will be compared. Barriers for diffusion of C and H into and through bulk Fe will be presented. Our predictions generally agree very well with experiment, though we do make some predictions which suggest further experimental studies. C and H show very different behavior both in bulk Fe and on Fe(110). For example, H prefers the tetrahedral site in bulk Fe, while C prefers the bulk octahedral site. H prefers the quasi three-fold site on Fe(110), while C prefers the long bridge site. Our study provides a clear picture of structures and energetics of C and H in bulk Fe and on Fe(110).

8:40am SS1-FrM2 Surface Science Studies of Tungsten Carbides as Potential Electrocatalysts, *M.B. Zellner, H.H. Hwu, J.G. Chen*, University of Delaware

The purpose of this research is to examine the feasibility of tungsten carbides as direct methanol fuel cell (DMFC) and hydrogen fuel cell electrocatalysts. The motivation to study tungsten carbides stems from the fact that current fuel cells require the use of Pt/Ru anodes, which are expensive and easily poisoned by CO. The successful development of tungsten carbide electrodes as Pt/Ru substitutes can therefore positively influence the commercialization of DMFC and hydrogen fuel cell systems. The reactions of CH₃OH, H₂O, H₂ and CO over tungsten carbide surfaces are studied with temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Thus far, investigations on the C/W(111) and Pt/C/W(111) have been completed. The results show that the carbide surfaces possess characteristics critical to the potential application as DMFC and hydrogen fuel cell anodes. In particular, these surfaces are highly active toward the decomposition of CH₃OH and H₂O, and are able to desorb CO at relatively low temperatures. In order to bridge the materials gap from model surfaces to realistic systems, thin films of WC and W₂C have been deposited on carbon paper and glassy carbon substrates by means of PVD to be tested as electrocatalysts for hydrogen oxidation. Electrochemical testing on the PVD electrocatalysts is currently underway.

9:00am SS1-FrM3 Chemical Properties of Bimetallic and Metal Carbide Surfaces by Theoretical and Experimental Studies, *J.R. Kitchin, M.A. Barteau, J.G. Chen*, University of Delaware

The optimal catalyst balances the adsorption energies of all surface species involved, ensuring adequate concentrations of important intermediates, while preventing poisoning by strongly bound intermediates. Multi-component catalysts, such as transition metal carbides and bimetallic catalysts, are one solution to these problems, as the adsorption properties of molecules can be tuned by the composition of the catalyst. However, it is difficult to know a priori how the chemical properties of a particular carbide or bimetallic catalyst will be modified relative to the parent metals. Advances in Density Functional Theory (DFT) now allow many of these systems to be explored from first principles with desktop computers. We have used DFT to calculate electronic properties and adsorption energies of small molecules and atoms on idealized bimetallic and carbide catalyst surfaces. These electronic properties were then used to establish correlations with experimental data and the calculated adsorption energies. For example, we calculated the electronic structure and adsorption energy of H atoms (HBE) on 13 different monolayer, bimetallic catalyst surfaces and showed a near linear correlation between the calculated HBEs and the surface d-band center of the catalyst. We have

calculated the surface d-band centers of more than 25 other monolayer, bimetallic combinations and some carbide surfaces. Using the HBE/d-band correlation established above we could use these calculations to predict promising new bimetallic catalysts with desirable H and CO binding energies. These correlations, along with a growing database of calculated d-band centers for bimetallic and carbide catalysts, should be considered a starting point for the rational design of bimetallic and carbide catalysts with desired chemisorption properties.

9:20am SS1-FrM4 HREELS Measurements of Iodine Vibrations on Cu(111) and Cu(221), *D. Sung, A.J. Gellman*, Carnegie Mellon University

Density functional theory calculations have shown that iodine atoms adsorb at the tops of the step edges on stepped Cu single crystal surfaces. In order to try to corroborate this prediction, we have measured and compared vibrational frequencies of iodine atoms adsorbed on the flat Cu(111) surface and the stepped Cu(221) surface using High Resolution Electron Energy Loss Spectroscopy (HREELS). Energy losses at 136 cm⁻¹ and 235 cm⁻¹ are observed on both surfaces. We assign these two frequencies to in-plane and out-of-plane vibrations of iodine on the (111) terrace sites. On a stepped surface one would expect the in-plane mode perpendicular to the step edge to be higher in frequency than the in-plane mode on the Cu(111) surface, if the atom is adsorbed at the bottom of the step edge. It would be expected to appear at a lower frequency if the atom is adsorbed at the top of the step edge. On the Cu(221) surface, an additional peak appears at 80 cm⁻¹, corresponding to the vibration of iodine adsorbed on the step edges of Cu(221). The fact that this new mode is at a lower frequency than the in-plane mode on the Cu(111) surface is consistent with the expectation that the iodine atom is adsorbed at the top of the step edge. The experimental results are consistent with the theoretical prediction that iodine atoms adsorb at the top of the step edges on the Cu(221) surface.

9:40am SS1-FrM5 Elucidating the Origin of Low-Temperature Reactivity of the Ni-Pt Bimetallic System, *N.A. Khan, J.G. Chen*, University of Delaware

Bimetallic surfaces possess unique physical, chemical and electronic properties unlike those of either parent metal. These surfaces have generated considerable interest as novel catalytic materials with higher reactivities and selectivities. As catalysts, they are used in numerous applications, such as fuel cells, hydrotreating (bimetallic sulfides and carbides) and hydrogenation catalysts. In our research, we have studied the Ni/Pt(111) and Pt/Ni(111) model bimetallic systems. We have found that the 1 ML Ni/Pt(111) surface demonstrates a low-temperature hydrogenation reaction pathway not present on either pure metal surface. DFT and LEIS studies indicate that this reaction pathway may be a result of Ni diffusing into the Pt(111) subsurface layers. In order to further study the interaction between Pt and Ni and the chemical properties of these bimetallic surfaces, we have also investigated the low-temperature reaction pathway on Pt/Ni(111). TPD studies reveal that the hydrogenation chemistry on the 1 ML Pt/Ni(111) surface is almost identical to that of the 1 ML Ni/Pt(111), revealing that the chemistry is independent of the order of metal deposition, i.e. Ni/Pt(111) or Pt/Ni(111). We will also demonstrate the strong correlation between model Ni-Pt surfaces and supported Ni-Pt bimetallic catalysts.

10:00am SS1-FrM6 Surface Reactions of Co-Adsorbed CH₂I and CF₃I on Ag (111), *K. Adib, H. Piao, J. Hrbek*, Brookhaven National Laboratory; *W. Huang, J.M. White*, University of Texas at Austin

Synchrotron X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) have been used to study the surface reactions of sequentially coadsorbed CH₂I and CF₃I on Ag (111). When adsorbed separately on Ag (111), CH₂I and CF₃I molecules undergo C-I bond cleavage at temperatures as low as 100 K to produce adsorbed CH₂ and CF₃, respectively, as well as I adatoms. In the case of CH₂I, upon subsequent thermal annealing of the surface, the dissociatively adsorbed CH₂ fragments may subsequently recombine and desorb primarily as C₂H₄. In the case of sequential co-adsorption in the submonolayer regime, the CF₃ and CH₂ fragments recombine to desorb as CF₂CH₂. Synchrotron XPS results indicate the presence of a surface bound species formed recombinatively in the temperature range of 200-250 K confirming that the CF₂CH₂ desorption is a two-step process. The first step involves methylene insertion to produce a surface bound species (CF₂CH₂) that can be detected by XPS. The second step involves fluoride elimination and the desorption of CF₂CH₂ as detected by TPD.

¹ Morton S. Traum Award Finalist

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10:20am **SS1-FrM7 Probing the Chemistry of CH₃I on Pt-Sn alloys**, E.C. Samano, CCMC-UNAM, Mexico; C. Panja, N.A. Saliba, B.E. Koel, USC
Adsorption and reaction of CH₃I (methyl iodide) on Pt(111) and the (2x2) and (√3x√3)R30° Sn/Pt(111) surface alloys was investigated primarily by using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). CH₃I adsorbs molecularly on Pt(111) at 100 K, and 34 % of the adsorbed CH₃I monolayer decomposes during heating above 200 K in TPD. Competition occurs during heating within the chemisorbed layer between hydrogenation to produce methane and dehydrogenation that ultimately leads to adsorbed carbon. Alloying Sn into the Pt(111) surface decreases the heat of adsorption and the amount of decomposition of CH₃I. Alloyed Sn slightly reduces the CH₃I adsorption bond energy from 13.4 kcal/mol on Pt(111) to 11.4 kcal/mol on the (2x2) alloy with θ_{Sn} = 0.25 and 9.3 kcal/mol on the (√3x√3)R30° Sn/Pt(111) alloy with θ_{Sn} = 0.33. More notably, the Sn-Pt alloy surface strongly suppressed CH₃I decomposition. Only 4% of the adsorbed CH₃I monolayer decomposed on the (2x2) Sn/Pt(111) surface, and no decomposition of CH₃I occurred on the (√3x√3)R30° Sn/Pt(111) surface during TPD. Methane was the only hydrocarbon desorption product observed during TPD. These results point to the importance of adjacent "pure Pt" three-fold hollow sites as reactive sites for CH₃I decomposition. Finally, we note that CH₃I, and presumably the other short-chain alkyl halides, are not reactive enough on Pt-Sn alloys to serve as convenient thermal precursors for preparing species small alkyl groups such as CH₃(a) for important basic studies of the reactivity and chemistry of alkyl groups on Pt-Sn alloys. Another approach is required such as the use of a CH₃-radical source or non-thermal activation of adsorbed precursors via photodissociation or electron-induced dissociation (EID).

10:40am **SS1-FrM8 A Model Catalyst with Selectivity Controllable Functions: the Effects of Thickness Extensional Resonance Oscillation on the Catalytic Activities for Ethanol Decomposition of Thin AgAu Film Alloy Deposited on a Ferroelectric z-cut LiNbO₃ Crystal**, N. Saito, Y. Sato, Y. Yukawa, H. Nishiyama, Y. Inoue, Nagaoka University of Technology, Japan

In an attempt to design a heterogeneous catalyst that has artificially controllable functions for catalytic reactions, we have employed the resonance oscillation (RO) of acoustic wave generated on a poled ferroelectric crystal and demonstrated that the thickness extension mode resonance oscillation (TERO) has the ability to change the reaction selectivity over thin metal catalysts deposited on a z-cut LiNbO₃ crystal. The effects of TERO are suggested to have strong influences on the electronic states of metal catalysts, and it is particularly interesting to apply the TERO for alloy catalysts consisting of more than one component surface metal atom with different electronic structures. In the present study, we investigated the TERO effects on catalytic ethanol decomposition on AgAu alloy catalysts. The AgAu alloy catalysts were prepared by consecutive deposition of Au and Ag, followed by heat treatment at high temperature enough to allow the metal phases to diffuse and to uniformly mix each other. In catalytic run on a Ag catalyst, the TERO increased ethylene activity without changes in acetaldehyde, indicating that the TERO activate only ethylene production on a single Ag metal surface. On the other hand, the TERO with AgAu catalysts increased the activity for acetaldehyde significantly. The activity enhancement increased with increasing Au content, passed through a maximum at 80% and decreased sharply. Laser Doppler measurement showed that lattice displacement generated by the TERO became the smallest at the same Au content (80%) as that where the TERO effect on the activity for acetaldehyde was the highest. This indicates that the nature and strength of Ag-Au bonds plays in an important role in the TERO-induced activity enhancement. Similar results were also observed for AgCu alloys. The mechanism of different TERO effects between Ag and Ag-based metal alloys is discussed. * supported in part by NASA/ footnote 1 @ N.Saito and Y.Inoue, J.Phys.Chem.B, 107/9, 2040(2003).

11:00am **SS1-FrM9 Different Changes in Work Function of Low- and High-index Cu Surfaces with Lattice Displacement in Surface Acoustic Wave Propagation**, H. Nishiyama, N. Saito, Y. Inoue, Nagaoka University of Technology, Japan

Surface acoustic wave (SAW) generated on a poled ferroelectric crystal by applying rf electric power has been demonstrated to markedly enhance the catalytic activity of thin polycrystalline metal (Ag, Pd, Ni, Cu) films for different kinds of the metal-catalyzed reactions such as ethanol decomposition, ethanol and CO oxidation. The enhancement of the

catalytic activity and the changes in the selectivity with SAW suggest that the SAW could affect the work function of the catalyst metal surfaces. To confirm the view, in the present study, photoelectron emission spectroscopy (PEEM) was employed, since photoemission characteristics are directly related to the work function of the metal surfaces. Thin Cu metal films treated by either annealing or sputtering have been used, and their atomic scale surface structures were inferred by the characteristic CO stretch frequency obtained in infrared reflection absorption spectroscopy (IRAS). It was shown that annealing gave rise to a Cu(111)-like low index plane mainly, whereas sputtering produced a large density of step sites and high index planes such as (311) and (211). The different SAW effects on the low- and high-index Cu surfaces were observed: the SAW propagation decreased the PEEM intensity for the low-index plane such as Cu(111), whereas it increased the PEEM intensity for the high index planes and step sites. The results indicated that the SAW enhanced the work function of a densely packed Cu surface and reduced that of a less packed Cu surface with coordinatively-unsaturated metal atoms. Dynamic and vertical lattice displacement by SAW was proved to have prominent structure-sensitive effects enough to change the electronic structures of the metal surface.

Surface Science

Room 328 - Session SS2-FrM

Oxide Surfaces and Interfaces

Moderator: R.L. Kurtz, Louisiana State University

8:20am **SS2-FrM1 Desorption Induced by Electronic Transitions (DIET) from a Lunar Sample and a Model Mineral Surface***, B.V. Yakshinskiy, T.E. Madey, Rutgers University

We report recent results on an investigation of source mechanisms for the origin of alkali and alkaline earth atoms in tenuous planetary atmospheres, with focus on non-thermal processes (photon stimulated desorption (PSD), electron stimulated desorption (ESD), and ion sputtering). Whereas alkaline earth oxides (MgO, CaO) are far more abundant in lunar samples than alkali oxides (Na₂O, K₂O), the atmosphere of the Moon contains easily measurable concentrations of Na and K, while Ca and Mg are undetected there; traces of Ca have recently been seen in the Mercury's atmosphere (10⁻³ of Na). Our experiments have included ESD, PSD and ion sputtering of alkali atoms from model mineral surface (amorphous SiO₂) and from a lunar basalt sample obtained from NASA. A comparison is made between ESD and PSD efficiency of monovalent alkalis (Na, K) and divalent alkaline earths (Ba, Ca). We find that bombardment of the alkali covered surfaces by ultraviolet photons or by low energy electrons (E > 4 eV) causes desorption of "hot" alkali atoms. This results are consistent with the model developed to explain our previous measurements of sodium and potassium desorption from a silica surface: 1,2 electron- or photon-induced charge transfer from the substrate to the ionic adsorbate causes formation of a neutral alkali atom in a repulsive configuration, from which desorption occurs. A two-electron charge transfer to cause desorption of divalent alkaline earth atoms is a less likely process. A striking reversible temperature-dependent variation of PSD and ESD yields of alkalis from the lunar sample is found; these data have important implications for models of tenuous planetary atmospheres. The data support the suggestion that PSD by UV solar photons is a dominant source process for alkalis in the tenuous lunar atmosphere. * supported in part by NASA/ footnote 1 @ BVY TEM, Nature (1999) 400, 642/ footnote 2 @ BVY TEM, Surf. Sci.(2003) 528, 54.

8:40am **SS2-FrM2 Temperature Dependence of the Noncommutative Valence Band Offset at α-Cr₂O₃/α-Fe₂O₃ Epitaxial Heterojunctions**, J.R. Williams, S.A. Chambers, Pacific Northwest National Laboratory

The valence band discontinuity at α-Cr₂O₃/α-Fe₂O₃ interfaces in epitaxial heterojunctions grown on α-Al₂O₃ (0001) substrate has been measured as a function of deposition temperature. A prior study, conducted at a given temperature, showed a noncommutative band offset of -0.3 ± 0.1 and +0.7 ± 0.1 eV in this system when the top layer is Fe₂O₃ and Cr₂O₃ respectively. This was attributed to an interface dipole that presumably depends on the growth sequence. In this study deposition temperatures of 500°C to 850°C have been investigated, and preliminary results show that this noncommutative band offset is largely independent of deposition temperature. This is an unexpected result, as the interface dipole is

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expected to change with deposition temperature due to interfacial mixing. Specifically we find that the binding energy difference between the Cr 3p and Fe 3p shallow core levels remains at 11.85 ± 0.08 eV (12.36 ± 0.20 eV) for structures with Fe@sub 2@O@sub 3@ (Cr@sub 2@O@sub 3@) as the top layer, and that these values are independent of deposition temperature. RHEED analysis of these structures shows that in all cases the Fe@sub 2@O@sub 3@ layer is unstrained, while the Cr@sub 2@O@sub 3@ layer is strained to match the lattice parameter of Fe@sub 2@O@sub 3@. This work was supported by U.S. DOE BES Department of Chemical Sciences.

9:00am **SS2-FrM3 Electronic Structure at the Fe@sub 3@O@sub 4@/NiO Interface@footnote 1@**, *H.Q. Wang, W. Gao, E.I. Altman, V.E. Henrich*, Yale University

The interfacial electronic structure between the metallic ferrimagnet Fe@sub 3@O@sub 4@ and the insulating antiferromagnet NiO has been investigated in the heteroepitaxial system Fe@sub 3@O@sub 4@ (100)/NiO (100) by growing from submonolayer to multilayer films of NiO (100) on single-crystal Fe@sub 3@O@sub 4@ (100) substrates. The lattice mismatch in this system is only 0.55 %, and excellent superlattice structures have been grown previously by other groups. The presence of tetrahedral Fe@super 3+@ ions lying above the plane of O anions and octahedral Fe cations on Fe@sub 3@O@sub 4@ (100) results in unusually short Fe-Ni cation-cation distances in the stoichiometric interface structure with rocksalt NiO. The Fe@sub 3@O@sub 4@ surface prior to growth is characterized by LEED, RHEED and STM; both the (1x1) and (@sr@2x@sr@2)R45° surface reconstructions have been studied. The NiO growth morphology is measured with STM. The electronic structure is monitored versus overlayer thickness by using UPS, XPS, Auger and EELS spectroscopies, which were chosen because they sample several monolayers (ML) into the substrate/overlayer structure. The overlayer thickness dependence of spectral features is then used to separate interfacial states from those of the substrate and the overlayer film. The evolution of the density-of-states in the O 2p-Fe 3d-Ni 3d band has been observed during the first few ML of NiO deposition. Changes occur across the entire band (from E@sub F@ to about 12 eV below E@sub F@). For NiO layers thicker than about 3 ML, the overlayer electronic structure is essentially that of bulk NiO. @FootnoteText@ @footnote 1@This research was partially supported by U.S. Department of Energy Grant DE-FG02-00ER45844; and NSF equipment grant DMR-0075824.

9:20am **SS2-FrM4 Understanding Fermi Level Pinning of SiO on GaAs(001)-(2x4)**, *D.L. Winn, M.J. Hale, A.C. Kummel*, University of California, San Diego
Scientists have been trying to develop a metal oxide semiconductor field-effect transistor (MOSFET) with GaAs in an effort to reduce standby power and gate leakage. In order to fabricate this device, it is important to understand the chemistry and physics at the oxide/semiconductor interface. It has been reported that a common cause of Fermi level pinning is the liberation of As, resulting from oxides bonding to Ga atoms on the surface. This has been directly observed using STM to monitor the reactions of O and O@sub 2@ on GaAs(001)-(2x4). In contrast, we have shown that SiO pins the Fermi level but does not liberate As when it is deposited on the GaAs(001)-(2x4) surface. Scanning tunneling microscopy (STM) images show that SiO inserts into the As dimers. SiO bonds in both trough and row dimers with a very small minority of the SiO molecules inserting into As-Ga backbonds. Using scanning tunneling spectroscopy (STS), we have observed that ~5% of a monolayer of SiO pins the Fermi level on GaAs(100)-(2x4) at mid-band gap. This is consistent with the SiO adsorbates withdrawing charge from the surface As atoms, causing charge on the As atoms to grossly deviate from the charge on bulk As atoms.

9:40am **SS2-FrM5 Surface Phase Transitions Upon Reduction of WO@sub 3@(100) Thin Films**, *M. Li, E.I. Altman, A. Posadas, C.H. Ahn*, Yale University
The evolution of surface morphology and reconstructions induced by reducing epitaxial WO@sub 3@(100) thin films grown on LaAlO@sub 3@(100) was studied using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). When the WO@sub 3@(100) surface was annealed in either O@sub 2@ or NO@sub 2@ at 620 K, the surface was predominantly covered by a p(2x2) reconstruction with a low density of elongated (1x1) islands. Raising the annealing temperature to 800 K led to a net reducing environment even in the presence of O@sub 2@ or NO@sub 2@. Under these conditions, the surface was dominated by a two domain p(4x2)/p(2x4) reconstruction, although a few small patches of the p(2x2) surface could still be detected. Further annealing at 800 K in oxygen led to the appearance of p(3x2) domains on the p(4x2) dominated surface and a more diffuse p(4x2) LEED pattern. The surface was exclusively

populated by a p(3x2) reconstruction upon annealing in UHV above 800 K while a p(3x2) LEED pattern could also be observed. After further annealing in UHV above 800 K, (1x1) islands appeared on the surface and the p(3x2) LEED pattern became more diffuse. The (1x1) area increased with annealing time in UHV and eventually exclusively (1x1) terminated terraces with straight steps due to crystallographic shear planes were observed. The STM images of the p(4x2) and p(3x2) surfaces were dominated by 0.1 nm deep troughs separating bright rows with 4x and 3x spacings respectively between rows. The appearance of the rows was sensitive to the imaging bias with a 2x periodicity along the rows seen at high biases and a 1x periodicity at low biases. These results could be explained by a structural model based on incomplete (1x1) terraces that form as reduced W@super 3@ ions migrate from the surface into the bulk.

10:00am **SS2-FrM6 First Principles Calculations of the ZrO@sub 2@(100)/Ni(111) Interface**, *J. He, S.B. Sinnott*, University of Florida; *E.C. Dickey*, Pennsylvania State University

We report on first principle calculations of the equilibrium geometries, interfacial energies, and work of separation for the O- and Zr-terminated Ni(111)/cubic-ZrO@sub 2@(100) interfaces. The approach is density functional theory using the generalized gradient approximation combined with nonlocal, norm-conserving and ultrasoft pseudopotentials. The polar ZrO@sub 2@ surface slab is non-stoichiometric to remove artificial electric fields. Consequently, while the work of separation is relatively straightforward to calculate, determination of the interfacial energies depends on the chemical potentials of the system. The manner in which the oxygen and zirconium chemical potentials are calculated will be discussed. The results show the way in which the preferred termination, and thus the interfacial structure, depends on oxygen partial pressure. These results are helpful to better understand the nature of the bonding at metal-ceramic interfaces and to predict the atomistic structure and stoichiometry of the equilibrium interface at various environmental conditions. This work is supported by the NSF (DMR-9976851).

10:20am **SS2-FrM7 In situ-STM Experiments at Elevated Temperature (475K) on Growth, Atomic and Electronic Structure of Thin NiO Films on Ag(001)**, *Ch. Hagendorf, H. Neddermeyer*, Martin-Luther-University, Germany

New results will be presented on the growth behaviour as well as atomic and electronic structure of thin NiO films on Ag(001) by using scanning tunneling microscopy (STM) and spectroscopy (STS) at elevated temperatures. NiO films were deposited with a thickness of up to 3 monolayers by evaporation of Ni in an O@sub 2@ atmosphere of 10@super -6@ mbar. Deposition and heating of the NiO films were followed by in situ-STM measurements which allowed us to identify the various stages of the growth mode. A (1x2) reconstruction is observed at substrate temperatures of less than 475 K and submonolayer coverages. They show a transition to (1x1) double layer NiO(001) after completion of the first monolayer. Only the latter one exhibits a pronounced bias dependent contrast reversal.@footnote 1@ The electronic structure of Ag(001), NiO(001) and the NiO precursor has been mapped using I(V)-STS at elevated temperatures and will be discussed in reference to results obtained on CoO /Ag(001).@footnote 2@ At coverages of more than one double layer areas with metallic behaviour are identified using STS. This indicates the formation of Ag islands in a height of several monolayers by segregation. @FootnoteText@@@footnote 1@ Th. Bertrams et al., J. Vac. Sci. Technol. B 14 (1996), 1141.@footnote 2@ Ch. Hagendorf et al., Surf. Sci. (2003), in press.

10:40am **SS2-FrM8 Low Temperature Oxidation of Nitrided Surfaces**, *J. Torres, C.C. Perry, S.J. Bransfield, D.H. Fairbrother*, Johns Hopkins University

The oxidation of transition metal nitride coatings is an important process because the resultant oxidized interface plays a crucial role in determining the interfacial properties of these materials as well as their durability in extreme environments. The oxidation of iron nitrides, in particular, has received little attention despite its importance as a magnetic coating in the recording industry. In the present study, X-ray Photoelectron Spectroscopy (XPS), Reflection Absorption Infrared Spectroscopy (RAIRS) and Mass Spectrometry (MS) were used to probe the low temperature (< 150 K) oxidation of nitrided iron surfaces exposed to oxygen and water. By carrying out the reactions at these low reaction temperatures, new pathways and intermediates have been identified. During the exposure of nitrided iron surfaces to oxygen, iron oxynitride (Fe@sub x@N@sub y@O@sub z@), nitrosonium ions (NO@super +@) as well as nitrite(nitrito) and iron oxide(hydroxide) species were observed. Upon prolonged oxygen exposures, nitrate species were formed in the oxidized overlayer indicative

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of an O-insertion mechanism into the iron nitride lattice, a process that has not been observed in previous studies of nitride oxidation. In contrast to oxygen, the reactivity of nitrated iron surfaces towards water was limited to the production of adsorbed N-O species and iron oxide(hydroxide). No molecular nitrogen was produced during reactions with oxygen or water in contrast to oxidation studies on other transition metal nitrides. Upon annealing the oxidized overlayer from 150 K to 600 K, nitrogen desorbs exclusively as nitric oxide (NO) between 250-400 K, leaving a surface film of iron oxide on top of the iron nitride.

11:00am **SS2-FrM9 Surface Characteristics of the Remote Plasma-treated ITO**, *S. Kim*, *H. Seo*, Hanyang University, Korea; *Y. Kim*, Pusan National University, Korea; *K. Kim*, *Y. Tak*, LG Electronics; *H. Jeon*, Hanyang University, Korea

Indium tin oxide (ITO) is an essential material in fabrication of organic light emitting devices (OLEDs). ITO functions as a hole injector into organic material and the injection efficiency is influenced by the work function of ITO anode surface. Work function of the ITO surface primarily depends on carbon and oxygen concentration. Particularly, carbon contaminants of ITO surface should be removed as much as it could be, because it results in the defect of bonding structure and increases in the sheet resistance of ITO. We investigated the removal of surface carbon contaminants using the oxygen and hydrogen plasma and examined the change of chemical composition and electrical properties of ITO after plasma treatments. ITO film was coated on glass to a thickness of about 1600 Å, and had a sheet resistance of about 10 Ω/□. And these ITO glass specimens were not pre-cleaned before plasma cleaning to demonstrate effects using plasma treatments only. The remote RF plasma cleaning chamber and the surface analysis system were connected each other by an ultra-high vacuum transfer system for the in-situ analysis. The carbon residues were almost removed below the detection limit of XPS after remote plasma cleaning at 50W. In XPS analysis for Sn 3d_{5/2}, Two peaks were completely resolved. These resolved peaks indicated respectively Sn²⁺ and Sn⁴⁺. The peak intensity of Sn⁴⁺ was reduced on ITO surfaces which was treated by plasma. Work function on ITO surface increased by oxygen plasma treatment and decrease by hydrogen plasma treatment. It also showed that the oxygen concentration affected much more than carbon contamination at the work function of the ITO surfaces. @FootnoteText@ @footnote 1@H. Y. Yu, X.D. Feng, D. Grozea, and Z. H. Lu, R. N. S. Sodhi, A-M. Hor and H. Aziz, Appl. Phys. Lett., 78, 2595-2597 (2001).

11:20am **SS2-FrM10 Temperature Dependent Water Adsorption on BSCCO Single Crystal**, *X.F. Hu*, *D.A. Human*, *C.J. Hirschmugl*, University of Wisconsin-Milwaukee

Infrared Reflection adsorption spectroscopy and Temperature Programmed Desorption studies of water adsorption on the surface normal to ab-plane of BSCCO single crystal reveal the molecular adsorption of water. The monolayer and multilayer desorption temperature is approximately 167 K. The absorption bands occur between 3200-3500 cm⁻¹ for the OH stretching, suggesting hydrogen bonding. The OH stretching bands change their absorption signatures as a function of temperature. For 2 L exposure, one asymmetric broad band is observed at approximately 3350 cm⁻¹ at 80 K, and becomes symmetric at 140K. At 150K, less water is adsorbed, exhibiting a sharper feature at 3250 cm⁻¹ with both high and low frequency shoulders. Below 140K, the adsorbed water forms clusters, and above 150K, it forms clusters with more bulk-like character.

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