

Wednesday Morning Poster Sessions, November 5, 2003

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.¹ ¹F. 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.¹ 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.¹ ¹G. 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.¹ ¹This work supported by the DOE NNSA NA-22 program

SS-WeP7 Modeling Nano-Structure Evolution in the Continuum Step Model: Decay of Pb Crystallites¹, M. Degawa, D.B. Dougherty, K. Thum, 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.¹ 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 quench² and after triggered decay.³ 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).

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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.

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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. Miyamishi, 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.

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