

Monday Afternoon Poster Sessions, October 31, 2005

Surface Science

Room Exhibit Hall C&D - Session SS-MoP

Surface Science Poster Session

SS-MoP2 Probing the Vibrational State-Resolved Gas-Surface Dynamics of CH₄ on Ni(111). V. Campbell, 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 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 the CH₄ vibrational fundamental and incident on clean Ni(111) surface. 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.

SS-MoP3 Alkylidene Functionalization of Molybdenum Carbide Surfaces: Thermal Stability and Chemical Reactivity. H. Oudghiri-Hassani, M. Sijaj, I. Temprano, C. Maltais, P.H. McBreen, Université Laval, Canada

Metal carbides possess a blend of metallic and ceramic properties and are amenable to unique surface modification procedures. In particular, molybdenum carbide surfaces may be functionalized using alkylidene groups. Such groups involve a double bond between the organic component and a single molybdenum atom at the surface, as distinct from bridge-bonded structures. We have previously shown that surface alkylidenes on molybdenum carbide display anomalously high thermal stability. The origins of this thermal stability will be discussed on the basis of extensive synchrotron photoemission, RAIRS and isotope substitution desorption data. The combined data reveal a key role for excess surface carbon in stabilizing the alkylidene groups to temperatures as high as 900 K. Furthermore, it will be shown that the metathesis activity of the surface alkylidene initiating sites may be used to perform add-on functionalization using a variety of olefins and substituted olefins.

SS-MoP4 Sulfur-CO Interactions on Cu(100) Films through Surface Resistivity and Infrared Reflectance Measurements. C. Liu, R.G. Tobin, Tufts University

Interactions between dissimilar adsorbates on Cu(100) thin films have been investigated experimentally through their effects on electrical transport in the metal. We report measurements of surface resistivity induced by CO on 50 nm-thick epitaxial Cu(100) films preadsorbed with different amounts of sulfur, together with temperature-programmed desorption (TPD) and infrared reflectance measurements. Adsorbate-induced surface resistivity arises from the scattering of conduction electrons in the metal from the impurity potential created by the adsorbate. Previous experiments have shown that the scattering cross section of sulfur decreases with increasing coverage, indicating a strong sulfur-sulfur interaction. In the present work, sulfur-CO interactions are explored by measuring the slope of the resistivity vs. CO coverage curve as a function of sulfur precoverage. Effects of sulfur on CO's scattering cross section are revealed as changes in the slope. Sulfur-induced changes in CO adsorption are also monitored with infrared vibrational spectroscopy and TPD. @FootnoteText@ @footnote 1@R.G. Tobin, Surf. Sci. 524, 183 (2003).

SS-MoP5 Adsorption Geometries of Prochiral Molecules on Pt(111): Heterogeneous Enantioselective Hydrogenation. M.A. Laliberté, A. Rouffignat, I. Temprano, S. Lavoie, P.H. McBreen, Université Laval, Canada HREELS and RAIRS were used to study the adsorption of carbonyls and dicarbonyls on Pt(111) with the goal of better understanding the Orito reaction. The Orito reaction describes the enantioselective hydrogenation of the keto-function of alpha-ketoesters on chiral-modified platinum particles. Measurements were performed on acetone, ethyl formate, biacetyl, methyl pyruvate and ethyl pyruvate adsorbed on clean Pt(111), and coadsorbed with toluene, benzene, naphthalene, methyl naphthylene, cyclohexane and naphthylethylamine. Very strong

coadsorption interactions resulting in complete modification of the adsorption geometries of the carbonyl molecules were observed for several of these systems. The results aid in mapping out the range of adsorption geometries available to dicarbonyl substrates in the Orito reaction. The results will be discussed in the context of a proposed new mechanism for the enantioselective reaction.

SS-MoP6 "Hot Electrons" at Organic-Metal Interface: Photodissociation of Phenol on Ag(111). S. Ryu, J. Chang, S.K. Kim, Seoul National University, Korea

Photodissociation of many organic adsorbates on metal surfaces has been attributed to photoexcited "hot electrons". To address this issue, we have explored the interfacial electronic structure of phenol adsorbed on Ag(111) using time-resolved two-photon photoemission spectroscopy. The photoinduced anion state of phenol was found at 3.1 eV above the Fermi level at one monolayer coverage. The binding energy of this state remained constant at around 0.7 ~ 0.8 eV for all coverages. Polarization dependence of the photoelectron signal revealed mechanistic details for each excitation step. The lifetime of the anion state was found to increase from 33 to 60 fs, indicating its lesser coupling to the bulk as the coverage increased from 1 to 9 ML. These findings demonstrate the role of hot electrons in photodissociation of adsorbates.

SS-MoP7 Interaction of Sulphur-Containing Anions with Copper Single Crystal Electrodes. J. Hommrich, S. Hümann, P. Broekmann, K. Wandelt, A. Spänig, University of Bonn, Germany

Processes at metal/electrolyte interfaces are a promising route to modify and structure surfaces on the nanometer scale. This, because processes at metal/electrolyte interfaces may be easier to control than those in vacuum, and are probably more economic. In this contribution we summarize results for sulphur-containing anion adsorption from solution on single crystal copper electrodes as obtained with in-situ ElectroChemical Scanning Tunneling Microscopy (ECSTM) and Fourier-Transform Infrared Spectroscopy (FTIRS) in combination with ex-situ surface analytical methods like AES, LEED, XPS, ISS etc. Hetero-atoms like, for instance, sulphur are often the anchors through which organic molecules are bound to surfaces. In particular, results will be presented and discussed for the most basic anionic groups, namely SO₄²⁻ and S²⁻, as well as derivatives thereof like sulfonate and thiocyanate anions on Cu(111) and Cu(100) electrodes. Special emphasis will be placed on the adsorbate structure and dynamics, on structural phase transitions, adsorption induced surface reconstruction as well as chemical stability as a function of electrode potential.

SS-MoP8 Electrochemical Formation of a Semiconducting Metal Oxide observed by In Situ Tunneling Spectroscopy. I. Diez-Perez, A. Guell, University of Barcelona, Spain; P. Gorostiza, University of California, Berkeley; F. Sanz, University of Barcelona, Spain

Obtaining tunneling spectroscopic data in electrolytic solutions is fundamental to understand electrode reactivity. Electrochemical scanning tunneling spectroscopy (ECTS) represents a powerful method for the in situ elucidation of the electronic structure on solid-electrolyte interfaces. Its experimental realization has been reported only in a few instances with some limitations. We present tunneling spectra of an Fe electrode immersed in a borate buffer electrolyte while it is reversibly oxidized to different potentials within the three oxidation ranges: Fe(0), Fe(II) and Fe(III). Complete series of ECTS spectra within the entire Fe passivation range allow us the representation of oxide surface conductograms by plotting the e- energy level on the Y-axis (tip potential), the electrode oxidation state on the X-axis (sample potential) and surface conductance represented by the Z gray scale. Our spectra span up to 2.2V using high tip potential scan rates (up to 15V/s). We have developed a new method to prepare and isolate Pt/Ir tips specially for in situ STS applications. Under conditions where the passive film is chemically stable in the working buffer, we found that the different redox transitions at the iron surface result from the availability of free charge carriers controlled by electron energy barriers at the oxide/solution interface. The passivity of iron results from the build-up of an energy barrier in n-Fe(III) and the absence of states available for charge exchange within almost 1.5eV below the CB edge. Increasing the sample potential in the passive plateau results mostly in increasing the band bending inside the oxide and decreasing the electron concentration. @FootnoteText@ @footnote 1@E.Tomita, N. Matsuda, K. Itaya, J. Vac. Sci. Technol., A8(1)534(1990). @footnote 2@I. Diez-

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Perez, P. Gorostiza, F. Sanz. *J. Electrochem. Soc.*, 150: B348 (2003). @footnote 3 @ A. G. Guell, I. Diez-Perez, P. Gorostiza, F. Sanz, *Anal. Chem.*, 76, 5218. (2004).

SS-MoP9 Interaction of Water Vapor with Clean and Contaminated Ru Surfaces, B.V. Yakshinskiy, N.S. Faradzhev, T. Graber, T.E. Madey, Rutgers, The State University of New Jersey

We compare the interaction of water vapor (H_{2O} and D_{2O}) with two important surfaces of hcp Ru: the atomically-rough (10-10) and the smooth close-packed (0001) surfaces. Several methods, including temperature programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and low energy ion scattering (LEIS) were used to study adsorption/desorption processes of water on the clean surfaces, as well as on carbon-dosed, oxygen-dosed and air-exposed surfaces. Both H_{2O} and D_{2O} undergo partial dissociation upon adsorption/desorption on Ru(10-10), which is in contrast to Ru(0001), where there is a striking isotope effect: D_{2O} is adsorbed molecularly, without dissociation, whereas H_{2O} dissociates partially. The data show non-wetting behavior of water on the air-exposed or the carbon-covered surfaces, but water becomes more strongly bonded to an oxygen-dosed substrate. We also report on the electron-induced dissociation and the electron-stimulated desorption (ESD) of water adsorbed on these surfaces at low temperature. The data provide insights into recent controversy concerning the interaction of water with Ru surfaces.

SS-MoP10 XPS and Sulfur K-edge NEXAFS Characterization of Isotope Effect for Coadsorption Systems (H_{2O} or D_{2O})/L-Cysteine/Cu(100), S. Yagi, D. Tomihara, T. Nomoto, Nagoya University, Japan; G. Kutluk, JST, Japan; M. Taniguchi, Hiroshima University, Japan; K. Soda, Nagoya University, Japan

Adsorption structure and chemical property of a sulfur-containing amino acid molecule of L-Cysteine on transition metal surface has been interested in a bio-compatibility, a bio-catalysis and a bio-materials fields. XPS (X-ray Photoelectron Spectroscopy) and NEXAFS (Near edge X-ray Absorption Fine Structure) techniques have established themselves as a powerful tool to characterize both a local molecular adsorption structure and a chemical condition of the adsorbates at adsorption sites. In the present study, we have paid attention to the isotope effect for coadsorption systems (H_{2O} or D_{2O})/L-Cysteine/Cu(100) studied by coupling of (S_{2p} , C_{1s} , O_{1s} and N_{1s}) XPS and sulfur K-edge NEXAFS measurements. There are some dominant differences in the experimental results of XPS and NEXAFS spectra for coadsorption systems of (H_{2O} or D_{2O})/L-Cysteine/Cu(100).

SS-MoP11 Covalent Attachment of Pt-Dendrimer Encapsulated Nanoparticles to 11-Mercaptoundecanoic Acid Thin Films, T.J. Black, K.A. Perrine, Y. Gu, H.J. Ploehn, D.A. Chen, University of South Carolina

Polyamidoamine dendrimers represent a diverse tool for chemical and biological research due to their functionality and highly tunable properties. The work presented here takes advantage of the dendrimer's ability to act as a nanoscale template for controlling the size distribution of metal particles formed in solution. Specifically, amine-terminated, generation 4 polyamidoamine dendrimers (G_4-NH_{20}) are treated with K_2PtCl_6 in a metal:dendrimer ratio of 40:1 to coordinate approximately 40 Pt^{2+} ions inside each dendrimer. Subsequent reduction with $NaBH_4$ is believed to form metallic Pt particles ~2 nm in diameter according to transmission electron microscopy studies. We have optimized a procedure that covalently links the dendrimer encapsulated nanoparticles onto a self-assembled monolayer of 11-mercaptoundecanoic acid (MUA) on Au(111) surfaces; this robust dendrimer film allows for various mechanical and chemical treatments that would not otherwise be possible. After the MUA monolayer is exposed to EDC (1-[3-(diethylamino)propyl]-3-ethylcarbodiimide hydrochloride) and an NHS (hydroxysuccinic acid)catalyst followed by treatment with the dendrimer solution, infrared reflection absorption spectroscopy (IRAS) experiments suggest that amide bonds are formed between the SAMs and the dendrimer by the disappearance of the carboxylic acid mode at 1722 cm^{-1} from the MUA accompanied by the appearance of amide modes at 1670 cm^{-1} and 1556 cm^{-1} . X-ray photoelectron spectroscopy also confirmed the presence of Pt- G_4NH_{20} on the SAMs since nitrogen and platinum signals were detected. The next step of this project will be to remove the dendrimer templates and SAM from the Au(111) surface by oxidation-reduction cycles, leaving behind the Pt nanoparticles. The ultimate goal of this work is to study the surface chemistry of the supported, well-characterized Pt particles in model catalytic reactions, such as CO oxidation.

SS-MoP12 Adsorption and Hydrogenation of 1,3-butadiene on Pd(111) and Pd-Sn/Pd(111) Surface Alloys, Chr. Breinlich, J. Haubrich, C. Becker, K. Wandelt, University of Bonn, Germany

The selective hydrogenation of dienes into mono-olefines is an important industrial reaction. Industrial processes are usually carried out with supported catalysts containing transition metals such as palladium or platinum. Palladium shows a high activity and selectivity for these reactions. Therefore we have studied the adsorption and hydrogenation of 1,3-butadiene on Pd(111) and Sn-modified Pd(111) surfaces. The Pd-Sn surface alloys were produced by annealing of tin layers of various thicknesses. Depending on the amount of deposited tin this procedure actually resulted in ordered surface alloys of ($Sn_{3x}Pd_{3-3x}$) R_{30} or $p(2 \times 2)$ superstructure, which were characterized by LEED, AES and UPS. The adsorption and reaction of 1,3-butadiene was investigated by TPD. After 1,3-butadiene adsorption at 55 K the desorption of the multilayer was found near 120 K on all surfaces. Further heating lead to the complete dehydrogenation of the butadiene on the Pd(111) surface. On the surface alloys only a part of the butadiene dehydrogenates while the rest desorbs at 200 - 230 K. By preadsorbing either hydrogen or deuterium the 1,3-butadiene can be partially hydrogenated to butene on the surface alloys. The partial hydrogenation is highly selective since no desorption of butane has been found. The branching ratio of desorption vs. hydrogenation on the surface alloys is clearly a function of the amount of tin, which was deposited and, hence, the surface stoichiometry. HREELS investigations reveal the adsorption modes of 1,3-butadiene and butene on these surfaces.

SS-MoP13 Oxygen-induced Faceting of NiAl(111), E. Loginova, W. Chen, N.M. Jisrawi, T.E. Madey, Rutgers University

We report the adsorption of oxygen and oxygen-induced faceting of NiAl(111), as studied by means of LEED, AES and high-resolution soft XPS (HRSXPS, using synchrotron radiation at NSLS). The atomically rough NiAl(111) surface remains planar at room temperature when exposed to oxygen. However, the surface changes its morphology and becomes faceted upon annealing at 1100K and higher; nucleation and growth of facets are studied. The adsorption and reaction of oxygen are characterized by HRSXPS measurements of Al 2p and Ni 3p core levels for the faceted and planar surfaces. The data indicate that a well-ordered thin aluminum oxide film can be formed on the faceted NiAl surface. Our work is motivated by the possibility that self-organized alumina thin-film-covered NiAl facets might be used as templates for uniform growth of metallic nanostructures with controlled size and spacing. The $Al_{2O_3}/NiAl(111)$ system is a good model material for studying catalytic reactions over Al $_2$ O $_3$ -supported metal catalysts.

SS-MoP14 Adsorption of Sulfur Dioxide on Zircaloy-4, N. Stojilovic, R.D. Ramsier, The University of Akron

The adsorption of sulfur dioxide on Zircaloy-4 surfaces is investigated using Auger electron spectroscopy. We find that both surface oxidation and saturation with sulfur and oxygen occur at low coverages at 300 K. Heating above 800 K results in oxygen dissolution into the bulk whereas sulfur stays in the near surface region. We examine effects of this residual sulfur on subsequent sulfur dioxide and oxygen adsorption. In both cases the adsorbates oxidize the sulfur-contaminated surface. Sulfur dioxide exposures at 300, 600 and 900 K all result in similar amounts of surface sulfur, indicating similar sticking coefficients in this temperature range. However, 900 K adsorption does not result in a shift of the Zr(MNN) feature that would signify surface oxidation. Thus this system can either adsorb or absorb oxygen from sulfur dioxide depending on the temperature, and the sulfur remains trapped near the surface without poisoning it with respect to subsequent oxidation.

SS-MoP15 Surface and Bulk Electronic Structures of Heusler-type Fe@sub 2@Al, M. Miyazaki, K. Soda, S. Yagi, M. Kato, T. Takeuchi, Nagoya University, Japan; U. Mizutani, Toyota Physical and Chemical Research Institute, Japan; Y. Nishino, Nagoya Institute of Technology, Japan

Surface and bulk electronic structures of Heusler-type Fe@sub 2@Al have been studied by both surface- and bulk-sensitive photoelectron spectroscopy, in particular, for the valence band and V 2p core level regions, in order to elucidate the changes in the valence band electronic structures for the surface and bulk regions and to clarify the mechanisms of its unusual transport properties@footnote 1@ and of the large enhancement of its thermoelectric power on a small deviation in the chemical composition.@footnote 2@ The valence band spectrum reveals fairly large intensity at the Fermi level E_F for the surface-sensitive low photon energy excitation but considerably small E_F intensity

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for the bulk-sensitive high photon energy excitation. This intensity reduction implies that a pseudogap is formed around E_F in the bulk electronic structure, as predicted by band calculations.² The intensity between the binding energy of 0.4 eV and E_F is relatively increased for the large photoelectron takeoff angle (measured from the surface normal). These facts indicate that the pseudogap is destroyed in the surface layers. The V 2p core level spectrum shows a surface-derived satellite structure in the low binding energy side of the main bulk band. This suggests that the valence electron concentration around V may be large in the surface region in comparison to the bulk. We will discuss the surface and bulk electronic structures with use of a DV-X α local electronic structure calculation. ¹ Y. Nishino et al., Phys. Rev. B71, 094425 (2005). ² Y. Nishino, Materials Trans. 42, 902 (2001).

SS-MoP16 Growth and Oxidation of Ultrathin Films of Zirconium on the Au(111) Surface, T.J.Z. Stock, Queen's University, Canada; A.J. Slavin, Trent University, Canada

The growth and oxidation of ultrathin zirconium films (to 5 atomic layers) on the gold(111) surface in ultrahigh vacuum have been studied as a function of substrate temperature and oxygen pressure. The oxide films are of interest as a possible replacement for SiO₂ in the gate of field-effect transistors. The study has used Auger electron spectroscopy, electron energy-loss spectroscopy, low energy electron diffraction and work function measurements. The evolution of the chemical composition of the oxide layer has been followed using a high-stability quartz-crystal microbalance.¹ ² L. Bouzidi, S.S. Narine, K.G. Stefanov and A.J. Slavin; A high-stability quartz-crystal microbalance for investigations in surface science. Rev. Sci. Instrum. 74, 3039-3044 (2003).

SS-MoP17 Adsorption of Acetic Acid on Zn_xNi_{1-x}O, H.G. García Flores, University of Nebraska-Lincoln and Los Alamos National Laboratory; A. Starace, M.A. Langell, University of Nebraska-Lincoln

Zinc can be dissolved in rocksalt NiO to produce solid solutions of Zn_xNi_{1-x}O over an approximate composition range of 0 \leq x \leq 0.35. Both metals are formally M²⁺, typically the stable oxidation state in oxides, but the octahedral coordination site of the cations in the rocksalt structure is unusual for zinc, which is typically tetrahedral as is found in wurtzite ZnO. The unique chemical environment of the zinc-nickel oxide solid solution can potentially result in new and interesting surface reactivity. Solid solutions of the zinc-nickel oxide over the range of 0.05 \leq Zn \leq 0.35 were prepared by calcination at 1200 K and were characterized using powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). The Auger parameter for zinc in these homogeneous solid solutions increases indicating stronger ionic character. Acetic acid (CH₃COOH) was then used to examine the surface reactivity of the mixed-metal solid solution in a series of adsorption experiments that were carried out as a function of zinc concentration and surface pretreatment. At 250 K, the primary adsorbate observed is bidentate acetate and, once formed, the species is stable on the substrate to approximately 500 K.

SS-MoP18 Adsorption and Reaction of CO and CO₂ on Oxidized and Reduced SrTiO₃(100) Surfaces, L. Wang, Pacific Northwest National Laboratory; S. Azad, Rice University; M.H. Engelhard, Pacific Northwest National Laboratory

The adsorption and reaction of CO and CO₂ on oxidized and reduced SrTiO₃(100) surfaces have been studied using temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). XPS results indicate that the oxidized SrTiO₃(100) surfaces are nearly defect-free with predominantly Ti⁴⁺ ions whereas the sputter-reduced surfaces contain substantial amounts of defects. Both CO and CO₂ are found to adsorb weakly on the oxidized SrTiO₃(100) surfaces. The desorption activation energies of CO and CO₂ from the oxidized SrTiO₃(100) surfaces are 38 and 32 kJmol⁻¹, respectively, following adsorption at 110 K. On sputter-reduced surfaces, enhanced reactivity of CO and CO₂ is observed due to the presence of oxygen vacancy sites that are responsible for dissociative adsorption of these molecules. Our studies indicate that CO and CO₂ molecules exhibit relatively weaker binding to SrTiO₃(100) compared with TiO₂(110) and TiO₂(100) surfaces. These differences can be attributed primarily to the influence of the Sr cations on the electronic structure of the Ti cations in the mixed oxide of SrTiO₃.

SS-MoP19 Molecular Dynamics Study of the Aluminum/Alumina Interface Using an Efficient Charge-Transfer Potential, B.D. Devine, University of Florida; A.J.H. McCaughey, University of Pittsburgh; S.B. Sinnott, S.R. Phillpot, University of Florida

Many of the properties that make aluminum a desirable commercial material are attributable to it rapidly forming a passivating oxide layer. In studying the properties of such active metals, the nucleation of the oxide phase, its structural evolution, and the resulting interfacial effects must be considered. Mechanistic exploration of oxide formation is challenging at the atomistic level due to length and time scale limitations, and the complexity of simultaneously modeling a metal and its oxide. Here, the aluminum/alumina interface is investigated using classical molecular dynamics simulations. The empirical, charge-transfer Streitzi-Mintmire¹ potential is coupled with an efficient direct pairwise summation of the Coulombic interactions.² The merits of the computational approach will be critically evaluated with the intent of applying the techniques to a large scale MD simulation of oxide formation and microstructure evolution. This work is supported by the National Science Foundation (grant no. DMR-0426870). ¹ F. Streitzi, J. Mintmire, J. Phys. Rev. B 1994, 50, 996 ² Wolf et al., J. Chem. Phys. 1999, 110, 8254.

SS-MoP21 Investigation of sp² Carbon in Nanodiamond, J. Hu, J. Foord, University of Oxford, UK, United Kingdom

Diamond electrodes have wide application in electroanalysis, electrolysis, waste water treatment etc. due to superior properties, such as chemical inertness, high overvoltage, and resist to electrode fouling. The sp² carbon inclusion in microcrystalline and nanodiamond is believed to make a major contribution to the performance of diamond electrodes. We investigate this in the present paper. Microcrystalline and nanodiamond films are grown on Si (100) and polished Ti sheet with different methane concentrations by MWCV. The samples are characterized by Raman Spectroscopy, SEM, XPS, Voltammetry and conductivity. With increasing concentration of methane from 1% to 4%, the grain size decreases slightly and becomes more homogeneous. With further higher concentration of methane, the samples are nanocrystalline with typical grains of around 200 nm. XPS and EELS indicate that only a trace amount of sp² carbon is present on sample surface. About 1% percent of sp² carbon in microcrystalline diamond is etched away in electrochemical polarization at 2.2V in 1M HNO₃ solution, and more sp² carbon can be etched away for nanodiamond. This shows that most of the sp² carbon inclusions are present in grain boundaries instead of embedded into diamond grains or present as graphite grains at the electrode surface. Electrochemical etching protocols are examined, to minimize unwanted effect of sp² carbon on the performance of diamond electrode.

SS-MoP22 Imaging the Structure of Natural Organic Matter Adsorbed onto Carbonaceous Surfaces with Atomic Force Microscopy, J. Gorham, H. Fairbrother, Johns Hopkins University

Developing a microscopic understanding of the adsorbate layers formed by Natural Organic Matter (NOM) on carbonaceous surfaces is useful in developing more realistic models under environmental conditions. This information could also have important technological ramifications for water treatment strategies where NOM reduces the adsorptive capacity of activated carbons. In this study, the adsorption of NOM (obtained from the Great Dismal Swamp, VA) on Highly Ordered Pyrolytic Graphite (HOPG) has been studied at the liquid-solid interface using Atomic Force Microscopy (AFM). In these studies HOPG was used to model the extended graphene sheets that characterize the exposed surface of activated carbons. Under low pH conditions (pH 4.0), NOM particles were observed to cover the entire HOPG surface with a layer thickness of \sim 2 nm. Evidence of ordered adsorbate structures involving NOM were observed at low pH. As the pH of the NOM solution increased, the surface concentration of NOM decreased systematically; at pH 10, <10% of the HOPG was covered by adsorbed NOM. Particle size was also influenced by pH with the average size of adsorbed structures being greater at higher pH. The structure of adsorbed NOM was significantly modified by drying with "ring like" structures and larger NOM aggregates observed. Results will also be presented on the effect of ionic strength on the structure of the adsorbate layer.

SS-MoP23 Selective Reduction of MoO₃ Nanostructures on Au(111), D.S. Pinnaduwage, X. Deng, M.M. Biener, C.M. Friend, Harvard University

Well-ordered MoO₃ nanostructures on Au(111) have been prepared using iterative dosing of Mo(CO)₆ and NO₂. A

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c(4x2) unit cell is observed for these nanostructures in scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). The presence of Mo@super 6+@ is confirmed by X-ray photoelectron spectroscopy (XPS). Selective reduction of MoO@sub 3@ nanostructures has been achieved by annealing at 650 K for varying times. Sheer planes are observed in STM due to the formation of Mo@super 5+@. Based on XPS data, ultimately, thermal reduction results in Mo@super 6+@ and Mo@super 5+@ at a 1:1 ratio on the Au surface. However, Mo@super 4+@ is absent in all thermal treatments, indicating the existence of a kinetic barrier for the reduction of either Mo@super 6+@/Mo@super 5+@ to Mo@super 4+@.

SS-MoP24 LEED and XPS Study of the Oxidation Process on Cu(111), K. Moritani, JAERI, Japan; *M. Okada*, Osaka University, Japan; *Y. Teraoka*, A. Yoshige, JAERI, Japan; *T. Kasai*, Osaka University, Japan

The oxidation of Cu has been of great interest because of the important role of Cu oxides in material science. Thus, many experimental and theoretical studies have been performed to understand the oxidation of Cu. However, the oxide-formation processes and the oxygen induced reconstruction on Cu(111) is far less clear. It is advantageous to control oxidation processes and structure in order to understand the chemical reactions and oxide formation processes on the nanoscale. In this work, we studied the oxidation of Cu(111) surface with a hyperthermal O@sub 2@ molecular beam (HOMB) and thermal O@sub 2@ gas using low energy electron diffraction (LEED) and high-resolution 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 O@sub 2@ can be controlled by changing the O@sub 2@, He and/or Ar gas mixing ratios and the nozzle temperature. After the irradiation of a proper amount of HOMB or thermal O@sub 2@ gas, high-resolution XPS spectra were measured at ~300 K using SR and then LEED pattern was observed. We measured O-uptake curves, determined from the integration of O-1s XPS on the surface, after the HOMB irradiation or the exposure to the oxygen atmosphere. The oxidation with under 0.23 eV HOMB at room temperature saturated at 0.3 ML, when only (1x1) and diffused background LEED pattern was observed. The additional incident energy above 0.5 eV promoted the further oxidation above 0.3 ML and induced the reconstruction to c(8x8) phase where the O-1s peak sifted the low binding energy side. This reconstruction and peak shift were observed after thermal gas exposure at the higher temperature. We discuss possible models of oxidation process on the basis of the incident-energy and temperature dependence of the O-1s XPS spectra and LEED pattern.

SS-MoP26 Computational Study of the Deposition of Metal-Oxide Thin Films, J.M. McKillip, S.R. Phillpot, S.B. Sinnott, University of Florida

Thin film deposition of SrTiO@sub 3@ is currently a popular area of research due to its widespread use in electronic applications and the motivation to shrink electronic components. Pulsed laser deposition (PLD) is an effective deposition process yielding dense, homogeneous thin films. Here, classical molecular dynamics simulations are used to determine the mechanisms involved in PLD. The simulations show that collisions that occur between the incident particles and the substrate can induce chemical reactions. The simulations consider the deposition of SrO and TiO@sub 2@ molecules with a kinetic energy between .1 and 1 eV/atom on a (001) surface of SrTiO@sub 3@. The effects of impact energy, orientation of incident particles, and surface termination layer (SrO vs. TiO@sub 2@) are examined. The main surface phenomenon of interest is chemical changes that occur at the oxide surface due to the ablating particles. The simulation results are compared to experimental data, where available. This work is supported by the National Science Foundation (DMR-0426870).

SS-MoP29 Chain Structure of Surface Hydroxyl Groups on TiO@sub 2@(110) with Line Oxygen Vacancy Studied by in-situ Noncontact Atomic Force Microscopy (NC-AFM), Y. Namai, O. Matsuoka, Mitsui Chemicals, Inc., Japan

Surface hydroxyl groups are essential species in many catalytic reactions. Especially, in oxide surfaces, they play a crucial role in reforming of the surface reactivity due to the adsorption of hydrogen adatoms at oxygen ion (anion) sites. Therefore controlling of the surface hydroxyl on catalysis surfaces is important in the reactivity and the selectivity. As a model surface to control hydroxyl groups, a slightly reduced TiO@sub 2@(110) surface was utilized. By repeating many cleaning cycles, surface oxygen atoms on bridge oxygen rows of the TiO@sub 2@(110) linearly desorbed, and the line vacancy structures were obtained. The line vacancy was formed by increasing of the density of oxygen vacancies on the TiO@sub

2@(110) surface. After exposing H@sub 2@O (1.0 x 10@super -4@ Pa for 120 s), hydroxyl chain structure, which is linearly arranged hydroxyl groups into two rows on bridge oxygen rows, were formed on the TiO@sub 2@(110) surface with the line oxygen vacancy. In-situ NC-AFM measurements at RT to 1.0 x 10@super -7@ Pa H2O revealed that the hydroxyl chain structure was formed at the line vacancy site. After H@sub 2@O exposure, annealing at above 500 K was sufficient to remove the hydroxyl chains on the TiO@sub 2@(110) surface, and then line vacancy structures reappeared on the surface. Before published STM and other experimental results supported that dissociative adsorption of water occurs on oxygen vacancy sites of the TiO@sub 2@(110). Therefore these results concluded that the hydroxyl chain structure was formed at the line vacancy site. Thus the formation of the hydroxyl chain structure suggests that controlling of surface hydroxyl groups on catalysis surfaces is possible.

SS-MoP30 Local Nanodeposition of Oxides with Focused Beams - Improving Material and Interface Quality, H.D. Wanzenboeck, M. Fischer, S. Mueller, J. Gottsbacher, W. Brezna, M. Schramboeck, A. Tomastik, H. Stoerti, H. Hutter, E. Bertagnolli, Vienna University of Technology, Austria

The fabrication of silicon oxide by direct-write deposition with a focused beam is an advanced nano-engineering technique. This locally confined chemical vapour deposition is a versatile tool for tailored surface modification. Two alternative methods - deposition with a focused ion beam (FIB) and a focused electron beam (FEB) - are compared. A silicon precursor such as siloxane is adsorbed on the surface and decomposed by the energy of the focused electron or ion beam. The chemical and physical phenomena at the oxide surface were investigated experimentally and by simulation of the energy dissipation of the incident beam. The process stage adsorption, surface diffusion, surface reactions, and layer growth are discussed. This work demonstrates the capability of this maskless method to fabricate arbitrary geometries of oxide and to create real 3-dimensional nanostructures. The material qualities of silicon oxide surfaces obtained with both methods are compared by chemical analysis, vibrational spectroscopy, optical and electrical characterisation. The beneficial addition of oxygen is reported and the optimum process window is identified. The chemical composition and the topography of the oxide surface are investigated by Auger electron spectroscopy (AES) and atomic force microscopy (AFM). A correlation between process parameters and the surface properties was found. The interface between the deposited microstructures is investigated by secondary ion mass spectroscopy (SIMS) and by electrical characterisation of capacitor devices with the deposited silicon oxide. Results indicate significant atomic mixing at the interface with FIB induced deposition, while a sharp interface can be obtained with the electron beam. This work contributes to a fundamental understanding of oxide formation on the nanoscale by beam induced deposition. This emerging maskless nanotechnology promises applications in MEMS, optical microstructures and dielectrics for semiconductor devices.

SS-MoP31 Structure and Growth of Small Au Particles on TiO@sub 2@(110), D. Pillay, G. Hwang, The University of Texas at Austin

*****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY PRESENT ONLY ONE (1) PAPER AT THE CONFERENCE*****While Au is known to be chemically inert in its bulk form, nanometer size Au particles dispersed on TiO@sub 2@ have been found to exhibit high activities for a variety of catalytic oxidation processes at or below room temperature. Au atoms weakly interact with the TiO@sub 2@ surface and become unstable toward sintering in response to changes in the gaseous environment even at moderate temperatures. Given the weak Au-TiO@sub 2@ interfacial interaction, Au particle nucleation is thought to predominantly occur at the sites of surface defects, such as (bridging) oxygen vacancies. Similarly, during oxidation processes, a reactant O@sub 2@ molecule may adsorb on the vacancy site molecularly or completely heal the defect (while ejecting an oxygen atom). Oxygen species may also interact with Au particles directly or indirectly. Thus, oxygen adspecies can greatly alter TiO@sub 2@ surface properties and Au-TiO@sub 2@ interfacial interactions, which may in turn influence the nucleation, growth, and sintering of Au particles. In this poster, we will present the results of our recent density functional theory calculations on the interactions between oxygen species and small Au particles on TiO@sub 2@ (110), with a focus on understanding i) the dynamics of oxygen species on Au/TiO@sub 2@ and ii) the effect of oxygen species on Au particle nucleation, growth, and sintering.

Monday Afternoon Poster Sessions, October 31, 2005

SS-MoP32 Gas-Phase Catalytic Processes on Metal-Oxide Supported Gold Nanoparticles, B. Roldan Cuenya, University of Central Florida

Our experimental work aims to improve the understanding of the processes taking place in nanocluster-catalyzed reactions by systematically studying how the nanoparticle size and shape affects its chemical reactivity. For this purpose, the low temperature carbon monoxide oxidation reaction on metal-oxide-supported gold nanoparticles will be used as a model system. Different ex-situ wet chemistry methods such as nanosphere lithography or the self-assembly of metal loaded block-copolymer micelles are being used to create ordered arrays of size- and shape-selected nanospheres, nanorods and triangular nanoprism catalysts. In addition, in-situ (UHV) nanoparticle size and shape modifications by high temperature annealing, Ar⁺ sputtering and O₂-/H₂ plasma treatment are being conducted. Interconnections between directly measurable electronic phenomena and surface chemistry will be established and used to provide insight into catalytic reactions. Temperature-Programmed Desorption (TPD), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), and X-ray Photoelectron Spectroscopy (XPS) are being employed to characterize the changes induced in the metal nanoclusters and their supports upon gas exposure. Our approach relies on the combination of ex-situ size- and shape-selected nanoparticle preparation methods and in-situ reactivity characterization measurements at different stages of well-controlled thermally and chemically induced size and shape transformations.

SS-MoP33 The Preparation and Chemical Reaction Kinetics of Microcrystalline Tungsten Bronze Thin Films with Peroxide and Nitrobenzene Solutions, N.F. Materer, A. Apblett, E.B. Kadossov, K. Khan, E.F. Shams, Oklahoma State University

Microcrystalline tungsten bronze (H_xWO₃) thin films are prepared using wet chemical techniques or atomic hydrogen to reduce a tungsten oxide thin film. The oxide film is prepared by thermal oxidation of sputter deposited tungsten metal film on a quartz substrate. The crystallinity of these films is determined by X-ray diffraction. X-ray and ultra-violet photoelectron spectroscopy show that these films are indistinguishable from conventionally prepared tungsten bronze powders. In addition, platinum or silver metal is deposited on these films. The quartz support allows the total amount of incorporated hydrogen in the film to be quantified by monitoring the absorbance at 900 nm. This technique is utilized to study the oxidation kinetics of these films by either organic nitrides or peroxides. A satisfactory fit to a kinetic model that involves two simultaneous processes is obtained. The first one is the proton diffusion from the bulk of the film to its surface, and the second is a reaction of the surface proton with the oxidant. In the latter process it is assumed that the surface concentration of the oxidant is effectively constant. The proton diffusion coefficient and the activation energy for the reaction of tungsten bronze films with oxygen gas are also estimated. The addition of catalytic amounts of platinum or silver on the rate is also discussed.

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