Tuesday Afternoon Poster Sessions

Surface Science

Room: 4C - Session SS-TuP

Surface Science Poster Session

SS-TuP1 Size-Selected Deposition of $Mo_6S_8^+$ on Au(111), *M.J. Patterson*, Stony Brook University, *M.G. White*, Brookhaven National Laboratory

Nanoscale MoS_2 has a layered assembly that shows a high propensity towards folding, forming hollow nanotube and fullerene structures which display a wide range of catalytic, photovoltaic, and lubricant properties.[1-3] Supported MoS_2 nanoparticles are known for their ability to catalyze a wide array of heterogenous reactions, in particular hydrodesulfurization (HDS).[4-5] However, understanding the role of size, structure, and overall composition of the MoS_2 particles in HDS has not yet been resolved due to the inhomogeneity of these commercial catalysts. Work done in our laboratory is geared towards preparing homogenous samples in ultra high vacuum (UHV) that can serve as model systems for these types of catalytic reactions. We are currently investigating the reactivity of size-selected transition metal clusters generated in the gas-phase and deposited on a Au(111) surface. Using a magnetron cluster source, we are able to produce a wide range of nanoparticle stoichiometries including the metal sulfide core of the superconducting Chevrel phase[6], $Mo_6S_8^+$. The work presented here focuses on characterization of the $Mo_6S_8^+$ cluster deposited on a Au(111) single crystal using surface science techniques such as TPD, AES, XPS, and UPS.

[1] Rapoport, L.; Bilik, Y.; Feldman, Y.; Homyonfer, M.; Cohen, S. R.; Tenne, R. Nature 1997, 387, 791.

[2] Thurston, T. R.; Wilcoxon, J. P. Journal of Physical Chemistry B 1998, 103, 11.

[3] Chhowalla, M.; Amaratunga, G. A. J. Nature 2000, 407, 164.

[4] Topsoe, H.; Clausen, B. S.; Massoth, F. E. Hydrotreating Catalysis; Springer: New York, 1996.

[5] Delmon, B.; Froment, G. F. Catal. Rev. -Sci. Eng. 1996, 38, 69.

[6] Umarji, A. M.; Rao, G. V. S.; Janawadkar, M. P.; Radhakrishnan, T. S. J. Phys. Chem. Solids 1980, 41, 421.

SS-TuP2 Preparation and Characterization of Au Nanoparticle, *G. Kutluk*, Hiroshima University, Japan, *S. Yagi*, Nagoya University, Japan, *H. Sumida*, Mazda Motor Co., Japan, *H. Namatame, M. Taniguchi*, Hiroshima University, Japan

Gold highly dispersed on metal oxide supports has unexpectedly been found to be highly active for a number of catalytic reactions. However, the electronic nature of the gold species in active catalysts has not been fully elucidated. We have applied a modified version of the gas phase condensation combined with Arc plasma method for the metal nanoparticle synthesis. Which is not only convenient in synthesizing highly dispersive metal nanoparticle with cleaner surface but also is suitable for the size controlling. In addition, this method also shows advantage in synthesizing metal nanoparticle with simple shape on a supporting material (Si Ta, TaN). The performance of the gas phase condensation and Arc plasma method for the size control has been confirmed in the earlier work.[1] In this study, we report the investigations of the thermal stabilities, crystallographic structure and the size dependence of electronic structures of Au nanoparticle in range of 1.5 ~ 5nm in diameter. The Au nanoparticle were characterized by the TEM, AFM, XPS and UPS. Drastic change have observed in the 4f level photoemission spectrum when the size of Au particle down to 1.5nm. The spectrum is characterized by component of an oxidized doublet states of Au_2O_3 coexisting with the doublet states of pure Au. The vanishing of component of Au_2O_3 doublets has been observed with increasing the annealing temperature of the sample in the reduction atmosphere.

[1] G. Kutluk, S. Yagi, H. Sumida, H. Namatame, M. Taniguchi, Mater. Res. Soc. Symp. Proc. Vol. 915 R06-18 2006

SS-TuP3 Surface Reaction of $(CH_3S)_2$ /Rh(100) Depending on Adsorption Coverage Studied by XPS and NEXAFS, *O. Sumi*, *T. Nomoto, S. Yagi, K. Soda*, Nagoya University, Japan, *H. Namatame, M. Taniguchi*, Hiroshima University, Japan

The automobile exhaust catalysts oxidize and/or reduce the exhaust gases, such as CO, C_xH_y and NO_x. As know as Sulfur Poisoning, the sulfur-containing molecules that originate from fuels affect the reactivity of noble metals (Rh, Pt and Pd), which are capital components of the catalysts. There are some reports that Rh has the highest resistance to the Sulfur Poisoning among those noble metals. However there are a few reports that have an interest in adsorption reaction of sulfur-containing molecules at low temperature. Therefore it is important to investigate the reaction mechanism. In this report, we reveal the surface reaction of dimethyl disulfide (DMDS) on the Rh(100) surface using XPS and NEXAFS techniques. The clean Rh(100) single crystal was cooled down to 90 K and subsequently exposed to DMDS. DMDS coverage was controlled to 0.44 ML, 0.32 ML and multilayer. As a result of the XPS spectra at 0.44 ML, DMDS molecules are decomposed into methanethiolate and atomic S at 90 K. Methanethiolate is generated by the dissociation of S-S bond and partial methanthiolate dissociates into atomic S and methyl. After heating up to 170 K, XPS results indicate that some of methanethiolate desorbs. At 0.32 ML, DMDS molecules are also decomposed into methanethiolate and atomic S at 90 K. However the ratio of atomic S has increased and methanethiolate does not desorb but dissociates into atomic S at 170 K. These results indicate that the surface reaction depends on initial DMDS coverage. Polarization dependent S K-edge NEXAFS spectra for submonolayer at 90 K show that the peak intensity of σ*(S-C) at 90° is larger than that of 20°. This results indicates that the coordination angle of σ*(S-C) should be almost lying on Rh(100) surface.

SS-TuP4 XPS and NEXAFS Studies for Co-Adsorption Reaction of Dimethyl-Disulfide and Water on Rh(100), *S. Yagi*, *O. Sumi, T. Nomoto, K. Soda*, Nagoya University, Japan, *H. Namatame, M. Taniguchi*, Hiroshima University, Japan

It is an important reaction that water molecule plays some interaction in the bio-body. There are many sulfur-including molecules in the bio-body, such as L-cysteine amino acid. Is there any interaction between the sulfur-including molecule and water? We have pay attention to the interaction of the co-adsorption system, the sulfur-including molecule and water, on the transition metal surface. For the bio amino molecule of L-cysteine, it is reported that the L-cysteine molecule has an interaction with water molecule on transition metal surface.[1] For the adsorbate of L-cysteine on NI and Cu surfaces, the S-H bond dissociates and becomes thiolate form. It is found that the oo-adsorbed water molecule has a new bonding with the sulfur of the thiolate. Because the Sulfur K-edge Near-edge X-ray Absorption Fine Structure (NEXAFS) shows sigma*(S-O) peak at 2482 eV. It seems that there are bondings of three or four water molecules at the sulfur part of the thiolate. The adsorption systems of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) on Rh(100) surface have been investigated by T. Nomoto[2,3] and O. Sumi[4] by XPS and NEXAFS. For both adsorption systems, the adsorption molecules partly dissociates and becomes thiolate and atomic sulfur on the surface at 90 K. In this paper, the aim is to reveal the co-adsorption reaction of DMDS and water molecules on Rh(100) at 90 K by means of XPS and Sulfur K-edge NEXAFS techniques. Judging from the spectral results of XPS and NEXAFS, it is found that DMDS molecules partly dissociate and the adsorbates are the thiolate and atomic sulfur. In case of the co-adsorption with water, it is cleared that water molecule does not have an interaction with the atomic sulfur, but has a bonding with the thiolate.

[1] S. Yagi et al., Surf. Interface Anal., 36 (2004) 1064.

[2] T.Nomoto et al., e-J. Surf. Sci. Nanotech., 4 (2006) 39.

[3] T. Nomoto et al., J. Surf. Anal., 12 (2005) 238

[4] O. Sumi et al., submitted to the conference of AVS-54, Seattle (2007).

SS-TuP5 Illuminating Analysis of Observed Low-Dimensional Plasmons in an Array of Metallic Quantum Wires, *T. Inaoka*, Iwate University, Japan, *T. Nagao*, National Inst. for Materials Sci., Japan

Using self-assembly of adsorbed Au atoms on vicinal surfaces of Si(111) with regular step rows, one can form a regular array of Au atom chains at interval of 1.91 nm on a Si(557) surface. Each atom chain of alternating Au and Si atoms embedded in the topmost Si layer of the terrace creates a one-dimensional (1D) surface-state band of metallic character. Conduction electrons in this band are confined in a narrow region one-atom wide. This array of metallic quantum wires sustains low-dimensional plasmons (PL's), namely, 1D PL's interacting with one another, and strong 1D confinement enhances the exchange-correlation (XC) effect on the PL's. In our previous work, by means of electron energy-loss spectroscopy (EELS) with a high wave-number resolution, we measured the low-dimensional PL's in the quantum-wire array.[1] In the present work, taking account of the interwire interaction and the XC effect, we investigate the dynamical response of the wire array to a probe electron in EELS. To consider the XC effect, we apply a self-consistent local-field-correction (LFC) theory to the wire array.[2] Although the interwire interaction is so significant as to produce a considerable distribution of the PL-mode energy, the calculated PL energy dispersion in EELS agrees with the dispersion of a single isolated wire. This paradox can be ascribed to the fact that the external potential generated by the probe electron is localized so sharply as to act and to produce substantial induced charges only on one or two wires. The calculated dispersion gives a complete explanation of the observed sound-wave character. By comparing the results of the LFC calculation with those of the Random-phase-approximation calculation, we evaluate the XC effect. This effect is found to operate to lower the PL energy and to heighten the energy-loss intensity in EELS. Our analysis can reproduce quantitatively the observed energy dispersion and energy-loss intensity.

[1] T. Nagao, S. Yaginuma, T. Inaoka, and T. Sakurai, Phys. Rev. Lett. 97, 116802 (2006).

[2] T. Inaoka and T. Nagao, Mater. Trans., JIM, 48, 718 (2007).

SS-TuP6 STM Study of Temperature Effect on Electron Induced Hopping Motion of CO/Cu(110)

T. Okada, The University of Tokyo, Japan, *S. Katano*, Tohoku University, Japan, *Y. Kim*, RIKEN, Japan, *M. Kawai*, The University of Tokyo, Japan

Scanning tunneling microscope (STM) enabled the observation and manipulation of the single isolated molecule, and we can follow the molecular motion precisely with its high spatial resolution (~ 0.1 nm).[1] In this study, we investigated hopping motion of carbon monoxide (CO) on metal surface, which is one of the most simple and fundamental molecular motions at surfaces. Same as thermal diffusion, vibrations of the adsorbates are important because some vibrations couple with surface motions strongly. For example, a study using STM has revealed that internal stretching vibration of CO on Pd(110) (~ 250 meV) plays an important role.[2] We can control the energy of innelasticaly tunneled electrons from the tip of STM precisely, and those electrons can excite the vibration of aimed molecule. And recently, time resolved SFG study on Pt(553) has revealed that hindered rotation mode of CO (~ 51 meV) also contributes to hopping motion.[3] They performed the experiment at 100 K where hindered translation mode (~ 4 meV) is thermally excited enough. We took notice of this temperature effect. We performed the experiments at 4.8 ~ 45 K using STM (LT-STM, Omicron GmbH) equipped in an ultrahigh-vacuum chamber ($< 3\times10^{-9}$ Pa). The Cu(110) surface was cleaned by cycles of Ar ion sputtering and annealing cycles, and exposed to CO molecules below 50 K. First, by Inelastic Electron Tunneling Spectroscopy (STM-IETS) on CO/Cu(110) obtained at 4.8 K, the vibrational peaks of two surface parallel vibrations (hindered translation and hindered rotation) are clearly observed. Then, I tried Action spectroscopy on single CO molecule at various temperatures. In that spectra, the sudden change of the yields of hopping motion which corresponds to the internal stretching vibration of CO was observed. It means that anharmonic coupling between vibrations enables hopping motion of CO on Cu(110) surface easily. And temperature dependence of the yields of hopping motion does not obey the simple Arrhenius law. In the presentation, I will discuss the coupling between vibrations and molecular motions from these results.

[1] B. G. Briner, M. Doering, H.-P. Rust, and A. M. Bradshaw, Science 278, 257 (1997).

[2] T. Komeda, Y. Kim, Maki Kawai, B. N.J. Persson, and H. Ueba, Science 295, 2055 (2002).

[3] E. H. G. Backus, A. Eichler, A. W. Kleyn, M. Bonn, Science 310, 1790 (2005).

SS-TuP7 Effects of Interadsorbate Interactions on Surface Resistivity: Oxygen on Sulfur-Predosed Epitaxial Cu(100)

C. Liu, *R.G. Tobin*, Tufts University

Measurements of surface resistivity for oxygen absorbed on sulfur-predosed epitaxial Cu(100) reveal the existence and properties of two types of interadsorbate interactions between sulfur and oxygen: S-O repulsion and scattering suppression. The repulsive interaction causes oxygen atoms to first occupy adsorption sites far from the sulfur atoms. As a result the low-coverage variation of surface resistivity with oxygen coverage is unaffected by predosed sulfur, showing the linear dependence previously observed for oxygen on clean Cu(100).[1] As the oxygen coverage increases, oxygen begins to occupy sites near the sulfur atoms. At these sites the resistivity effect of the oxygen atoms is strongly suppressed, so that the sample resistance levels off, remaining unchanged even as oxygen continues to adsorb on the surface. With increasing sulfur precoverage both the maximum resistivity change and the oxygen coverage at which the leveling occurs decrease, because the number of sites unaffected by sulfur is reduced. Both the S-O repulsion and the scattering suppression have an effective range on the order of about 1.4 lattice spacings, with a rather sharp boundary. Both interactions presumably arise from a through-metal coupling involving the metal's local density of states.

[1] R.G. Tobin, Surf. Sci. 524, 183 (2003).

SS-TuP8 Wettability and Chemical Bonding of Water and Hydroxyl at Metal Surfaces

T. Schiros, Stanford Synchrotron Radiation Laboratory, *O. Takahashi*, Hiroshima University, Japan, *K. Andersson*, DTU/Center for Individual Nanoparticle Functions, Denmark, *H. Öström*, Stockholm University, Sweden, *S. Yamamoto, L.-Å Näslund*, Stanford Synchrotron Radiation Laboratory, *L.G.M. Pettersson*, Stockholm University, Sweden, *A. Nilsson, H. Ogasawara*, Stanford Synchrotron Radiation Laboratory

The nature of the chemical bonding and structure of water and water co-adsorbed with hydroxyl at metal surfaces is of immense relevance to a number of important reactions in heterogeneous catalysis, including the water gas shift reaction over Cu and the fuel cell reaction over Pt and related alloys. We have combined core level x-ray spectroscopy, in both UHV and near-ambient conditions, with density functional theory to derive a detailed picture and comparison of the interaction of water and water plus hydroxyl with different metal surfaces, including Cu(110), Cu(111) and Pt(111). We demonstrate that the ability to form water-metal bonds, or wettability, is controlled by the degree of Pauli repulsion, which is influenced by both the electronic and geometric structure of substrates. At near ambient conditions, formation of OH groups by pre-adsorbed oxygen significantly modifies the ability to form water-metal bonds and plays a decisive role in the wetting of metal surfaces.

SS-TuP9 Low Temperature Microcalorimetry to Measure the Heat of Adsorption of Cyclohexene, Cis and Trans 2-Butene on Pt(111)

O. Lytken, ***W. Lew***, *J.W. Harris, E.K. Vestergaard, C.T. Campbell*, University of Washington

The hydrogenation and dehydrogenation of cyclic hydrocarbons and short chain alkenes on platinum catalysts are important petrochemical reactions. We have used low temperature microcalorimetry measurements to determine their enthalpy of adsorption and sticking probability on Pt(111) at 100 K. Cyclohexene adsorbs intact at surface temperatures below 180 K, but decomposes at higher temperatures via several intermediates, including benzene and hydrogen starting at ~300 K. Trans-butene adsorbs intact below 200 K and cis butane adsorbs intact below 230 K. The difference between the heat of adsorption energy of the two isomers is compared with results from Zaera et al.[1] Since cyclohexene and butene both adsorb irreversibly on platinum, the traditional method to measure adsorption enthalpies, Temperature Programmed Desorption (TPD), cannot be used. Low temperature microcalorimetry makes it possible to measure the heats of formation of important reaction intermediates that are frequently unstable at room temperature. One of the major challenges of conducting low temperature calorimetric studies for small heats of adsorption is getting the microcalorimeter to detect small temperature changes on the order of 10 milliKelvins with minimal noise. This study explores modifications to the microcalorimetry apparatus to detect small adsorption energies.

1. Ilkeun Lee, I., Zaera, F. J. Amer. Chem. Soc. 2005, 127, 12174.

SS-TuP10 Electron Correlation Effects in Co Nano-Islands on a Nitrogen Covered Cu(001) Surface

Y. Takagi, RIKEN, SPring-8 Center, Japan, *K. Nakatsuji, Y. Yoshimoto, D. Sekiba*, University of Tokyo, Japan, *Y. Harada*, RIKEN, SPring-8 Center, Japan, *K. Amemiya*, University of Tokyo, Japan, *Y. Takata*, RIKEN, SPring-8 Center, Japan, *T. Ohta*, University of Tokyo, Japan, *S. Shin*, RIKEN, SPring-8 Center and University of Tokyo, Japan, *F. Komori*, University of Tokyo, Japan

Recently, the atomic and electronic structures of magnetic nano-structure on surfaces have been intensively studied. We have investigated the initial growth of Co nano-islands on a nitrogen saturated Cu(001) c(2x2)-N surface by scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy and found that the nitrogen segregates on top of the Co islands and form Co-c(2x2)N structure.[1] In the present study, we discuss the electronic structure of this system in terms of electron correlation effect investigated by x-ray absorption spectroscopy (XAS) at both Co 2p and N 1s absorption edges comparing with the growth process studied by STM. N 1s XAS spectrum shows gradual increase of the absorption intensity just above the Fermi level with the increase of Co coverage. This indicates that the bonding of N 2p with Cu 3d changed into that with Co 3d which has smaller number of d electrons than Cu. The result strongly supports the segregation of N atoms. In the Co 2p XAS spectrum, a shoulder-like structure was found at 3 eV higher energy side of the main peak both at L_3 and L_2 absorption edges. Its relative intensity of this "3 eV satellite" to the main peak gradually decreases with Co coverage below 2 ML on average. In the case of Ni thin film, the origin of 3 eV and 6 eV satellites in the Ni 2p XAS spectrum are attributed to the configuration interaction of correlated electrons (CI) and multiple scattering in absorption process (MS), respectively.[2] We simulated XAS spectrum including the MS effect by FEFF code with the optimized atomic structure parameters obtained from first-principles calculation. However, the experimental results were not reproduced. Therefore, the origin of 3 eV satellites in our case is considered to be CI, indicating the presence of d^7 configuration as well as d^8. Comparing with the STM observation, the satellite is attributed to the mono-atomic height isolated Co-N islands. In such small islands, the charge transfer between Co and N would be different from that in the larger islands possibly by lattice compression.

[1] D. Sekiba et al., Surf. Sci. 590 (2005) 138.

[2] K. Amemiya et al., Phys. Rev. B72 (2005) 201404R.

SS-TuP11 LEED and XPS Investigations of Surface Alloying of Ir on Cu(110)

P.F. Lyman, ***S.S. Parihar***, University of Wisconsin-Milwaukee

Subsurface alloying is an interesting phenomenon that has been observed for several transition metals deposited on noble-metal surfaces, even where there is no bulk solubility of the two metals. In particular, while the bulk phase diagram of Ir-Cu has a large miscibility gap, subsurface alloying has been observed for Ir/Cu(100).[1,2] The Ir atoms appear to occupy ordered subsurface sites, forming a (2x1) reconstruction, with the required atomic place exchange taking place even for deposition at 200 K.[1] In the second layer, Ir and Cu atoms form Ir-Ir and Cu-Cu chains along every other close-packed direction. We evaporated submonolayer to monolayer Ir films on clean Cu(110) surfaces, and investigated the Ir-induced reconstruction using low energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS). The (1x1) LEED pattern changes into a (2x1) pattern for Ir coverages of close to half a monolayer. We expect that the Ir will still be confined to the near-surface region by the lack of bulk solubility, and we hypothesize that the Ir atoms will occupy subsurface sites based on their behavior on Cu(100). Based on LEED and XPS results, we propose that Cu and Ir form Ir-Cu-Ir-Cu chains along the close-packed direction for Ir/Cu(110)-(2x1), in contrast to the finding for Ir/Cu(100)-(2x1).

[1] S. Heinze, R. Abt, S. Blügel, G. Gilarowski, and H. Niehus, Phys. Rev. Lett. 83, 4808-4811 (1999).
[2] G. Gilarowski and H. Niehus, Surf. Sci. 436, 107-120 (1999).

SS-TuP12 Surface Diffusion of Hydrogen Atoms on Cu(111) Studied by Optical Diffraction from Hydrogen Density Patterns formed on Removable Templates of Xenon Monolayers*, **Y.Y. Fei**, X.D. Zhu*, University of California at Davis

We formed grating-like patterns of hydrogen adatom density on Cu(111) by using complementary patterns of xenon adatom density as the template. The template was pre-formed by laser-induced thermal desorption of a Xe monolayer on Cu(111) using the interference pattern of two coherent laser pulses. By following the evolution of hydrogen density gratings on Cu(111) from 153 to 183 K with linear optical diffraction, we found that the diffusion of hydrogen atoms on Cu(111) in this temperature range is the classical over-barrier hopping characterized by an activation energy barrier E_{diff} = 6.4 kcal/mol (or 279 meV) and a pre-exponential factor $D_0 = 2.0 \times 10^{-3}$ cm^2/sec. Based on the potential model proposed by Basdescu and coworkers for hydrogen on Ni(111), the WKB tunneling coefficient between the first vibrational excited states of a hydrogen adatom on Cu(111) is expected to be at least one order of magnitude smaller than that on Ni(111), indicating that the classical over-barrier hopping of hydrogen atoms could directly cross-over to under-barrier tunneling between ground-states on Cu(111).

SS-TuP13 Surface Temperature Dependence of Methane Dissociation on Ni*, **V.L. Campbell**, A.L. Utz*, Tufts University

The past decade has seen major groundbreaking work in the understanding of the role vibrational energy plays in the dissociation of methane on nickel surfaces. Yet, little work has been done on developing an understanding of the effect of surface temperature on this reaction. Two questions remain regarding the energy contained in the surface: First, how does the thermal bath of the surface atoms couple to the reaction coordinate? Second, does dislocation of the surface atoms alter the distribution of barriers to dissociation? Recent theoretical work suggests that the system is able to access lower barriers when the surface atoms are displaced above the plane of the surface. A change in the location of the Ni surface atom below the incident methane molecule could result in a lower energetic barrier making the reaction much more probable. As the surface temperature is increased, the probability of the incident methane molecule impacting on a displaced Ni atom increases. Experimentally, the biggest hurdle in understanding the dynamics that surface temperature plays in reactivity is deconvolting the gas-phase dynamics from the surface temperature dynamics. In thermal bulb experiments, it is not possible to discern the role of energy in the gas-phase comparatively to that of energy of the surface. Supersonic molecular beam experiments allow independent control of both the surface temperature, the impact energy and the average vibrational energy of the incident gas-phase molecules. Additionally, we use a narrow-bandwidth IR laser to prepare a non-equilibrium distribution of vibrational states, which allows us to determine the reactivity of select rovibrational eigenstates of the methane molecules over a range of incident kinetic energies and surface temperatures. The overall goal of these experiments is to determine the coupling of the vibrationally excited methane molecules to the phonon bath of the surface atoms and see what impact different surface temperatures have on reactivity.

SS-TuP14 Vibrational Effects on Precursor Mediated Surface Reactions*, **D.F. Del Sesto**, C.R. Thomas, N. Chen, A.L. Utz*, Tufts University

At high translational energies, methane dissociation on metal surfaces is generally shown to be dominated by a direct mechanism. The majority of methane molecules in a steam-reforming reactor have little translational energy, but are vibrationally excited. The vibrational energy content of these molecules is significant relative to the barrier to dissociation. In contrast, low translational energy molecules in conventional beam surface experiments are predominantly in the vibrational ground state. We propose experiments to explore the possibility that a precursor mechanism involving vibrationally excited molecules may be an important contributor to methane activation on metal surfaces at the high temperatures characteristic of industrial steam reforming reactors.

SS-TuP15 XPS Study of the Early-stage Oxidation Behavior of (Pt, Ni)$_3$Al(111) Surfaces in Air*, **F. Qin**,* Iowa State University and Ames Laboratory, *J.W. Anderegg, C.J. Jenks,* Ames Laboratory, *B. Glesson,* Iowa State University, *D.J. Sordelet,* Ames Laboratory, *P.A. Thiel*, Iowa State University and Ames Laboratory

We have studied the early stage of oxide formation on (111) oriented (Pt, Ni)$_3$Al single crystals in air. From X-ray photoelectron spectroscopy (XPS), the predominant surface oxide changed from NiO to Al_2O_3, as oxidation temperature increased from 900 to 1300 K. Some $NiAl_2O_4$(spinel) also formed at the higher temperatures. Under conditions where NiO and/or $NiAl_2O_4$ was present, it resided atop a layer of aluminum oxide, mixed in some cases with metallic Ni. By comparing samples that contained 0, 10 and 20 at. % Pt in the bulk, we found that the effects of Pt were to (1) promote the preferential formation of aluminum oxide over nickel oxide(s) in the top layer at all temperatures studied, (2) suppress the amount of metallic Ni mixed with Al_2O_3 in the underlying oxide region, (3) reduce the total oxide layer thickness, and (4) sharpen the interface between the oxide and the metallic alloy. The effects of Pt probably arise from a combination of sources: The non-oxidizing nature of Pt relative to Ni or Al; the substitution of Pt for Ni that occurs in the Ni_3Al lattice structure; and the increase in Al activity that is induced by Pt.

SS-TuP16 Ion Beam-Induced Formation and Interrogation of Metal Nanoclusters*, **J.A. Yarmoff**, A.B. Arjad, P. Karmakar, G.F. Liu,* University of California, Riverside*, Z. Sroubek*, Czech Academy of Sciences

Metal nanoclusters are important systems that display quantum size effects and have remarkable catalytic activity. We utilize low energy (0.5-5 keV) ion beams as a simple, but efficient means for both the controlled production and the characterization of nanoclusters. Low energy Ar^+ beams enable control of the size and shape of nanoclusters because of the curvature dependence of ion sputtering. The neutralization of scattered low energy alkali ions provides a sensitive measure of the localized electronic states. It was previously shown that scattered alkalis couple to atomic-like states specific to Au nanoclusters grown by deposition, and the neutralization probability is a function of the cluster size.[1] We further showed that sputtering a thin Au film on TiO_2(110) with Ar^+ forms self-organized nanoclusters that display quantum size effects.[2] The scattered alkali neutral fractions increase as the cluster dimensions decrease, indicative of the quantum size effects, and the data shows that the electronic structure of clusters grown by deposition and by sputtering are similar. In this work, Li^+, Na^+ and K^+ ions are employed to probe metal nanoclusters formed by both deposition and sputtering, and the dependence of neutralization on cluster size is compared. Au or Ag is first deposited on an insulating or semiconducting substrate, and self-organized clusters are produced either during the deposition, or by Ar^+ sputtering a thin film. The ion scattering NF's have different dependences with respect to cluster size for each alkali projectile. The microscopic mechanisms responsible for the formation of the nanoclusters, and for the charge exchange between scattered alkali ions and the nanoclusters, will be discussed.

[1] G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. 92, 216801 (2004).
[2] P. Karmakar, G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. 98, 215502 (2007).

SS-TuP17 The Formation of Iron Oxide Nanoparticles and Thin Films on Au(111)*, **N.A. Khan**, C. Matranga*, National Energy Technology Laboratory (NETL)

Iron-based catalysts, including iron oxides, are an important class of materials with relevance to Fischer-Tropsch catalysis and gas-sensing applications. The controlled growth of nanoparticles and atomically thin films on single crystal surfaces allows for systematic studies of how size, shape, and atomic structure affect the chemical reactivity of these materials. We have studied the formation of monolayer thick iron oxide nanoparticles and thin films on the reconstructed Au(111) surface. STM, XPS, ISS, and LEED were used to evaluate the structure and composition of the iron oxide nanoparticles and films as a function of growth conditions. Iron oxide growth was achieved by first depositing iron nanoparticles on Au(111) at room temperature. At coverages of 0.2-0.5 monolayer (ML), Fe forms triangular islands at the elbows of the Au(111) herringbone reconstruction. At higher coverages, the particles begin to coalesce and the second and third layers of Fe start to form before the first layer is complete. The oxidation of Fe was performed by exposing the nanoparticles to molecular oxygen at 323 K and 423 K, followed by annealing to 500-700 K. XPS results indicate that the Fe is oxidized, with a shift of the Fe 2p peak to a higher binding energy. Atomically-resolved STM images show the formation of iron oxide particles that are hexagonal in shape and one monolayer high with a diameter of 10-20 nm. STM images at higher iron oxide coverages also show evidence of a non-coincidence overlayer lattice with a short periodicity of 0.25-0.3 nm modulated by a larger periodicity of approximately 3.5 nm. The larger periodicity results from a moiré pattern formed between the iron oxide overlayer and the underlying Au(111) surface.

SS-TuP18 Binding Character for a Xe Adatom on Nb (110)

C.Y. Fong*, M.C. Qian, X.D. Zhu,* University of California at Davis*, L.H. Yang*, Lawrence Livermore National Laboratory*, S. Dag*, Oak Ridge National Laboratory

We determined the binding characteristics of a Xe adatom on Nb (110) using density functional theory within the local density approximation. The on-top site is the most favorable for adsorption with a binding energy of 271 meV. Although the preference for the on-top site is the same as on the (111) surface of Pt and a number of other fcc metals, there is a discernable charge accumulation showing a weak covalency between Xe and its nearest-neighboring Nb atom. Compared to the Xe on Pt case, the differences are manifested by (i) the hybridization of Xe p-state with nearly half-filled Nb d-states causes the energy levels of Xe p-states to shift downward by 1.2 eV with the p_z-state splitting off from the p_x- and p_y-states, and (ii) the shifted Xe p-states have relatively narrow bandwidths due to the off-resonant condition between the p-states of an isolated Xe and the Nb d-states. They can be attributed to the less than half filled d shell of the Nb atom inducing stronger hybridization with the p-states of the Xe atom. †Work done at Lawrence Livermore National Laboratory under the auspices of the US Department of Energy under Contract No. W-7405-Eng-48.

SS-TuP19 Coverage and Temperature Dependence of LEED Streak Intensity on Li adsorbed on Cu(001) Surface at Lower Coverage

H.M. Mitani, Fukuoka University of Education, Japan

Arced shape streaks, which connect four fold spots are observed in LEED experiment, in Li adsorbed system on Cu (001) surface, where the four fold spots correspond to c(2x2) structure of adsorbed Li atoms. The streaks originate from second neighbor pair (d=2a) of Li atoms in the c(2x2) structure sites. Especially, there are two types of adatoms in terms (y-)component of wave number of the streak ($k_y = \pi /a$). Both types of the sub-lattices give an anti-phase relation on the streak. If Li atoms are fully occupied on the c(2x2) sites at a coverage 0.5, the intensity is vanished. While, if the coverage is less than 0.5, a deviation of the number of atoms in the two types of sub-lattices gives a certain intensity of the streak; it becomes strongest at coverage 0.25 (H.Mitani et al. J.Phys.Soc.Jpn. 2005). In this paper, using Monte Carlo simulation, we obtain arrangements of Li atoms on adsorption sites on Cu (001) surface, as a lattice gas model, in a range of coverage (0-0.5), and a certain temperature width. By Fourier transforming of the arrangement of the atoms, we obtain almost square type streaks, which correspond to the arced shape steaks in the experiment. The reason of change from the line streaks in the square to the arced one, as shown in the experiment has already been clarified (H.Mitani et al. J.Phys. Cond.Matt. 2006). It is not a matter in the present paper. We also obtain coverage and temperature dependence of an intensity of the streak and also the four fold spots. Especially the coverage dependence of the intensity, reproduces a result of experiment; it increase along the coverage (0-0.25), and decrease in coverage (0.25-0.5). We also obtain the coverage-dependence of the intensity of the four fold spots. In terms of temperature-dependence, there is no result in experiment now. We obtain that the intensity of the streaks, broadly speaking, increases as temperature. Especially at coverage 0.5, it shows as Shottkey type behavior. On the other hand, the intensity of the four fold spots, shows second order transition, which has a certain phase transition point.

SS-TuP20 Thickness Dependence of the Interaction of NO_2 with Thin MgO(100) Films Grown on Ag(100) as Studied Photoemission Spectroscopy

D.E. Starr, Ch.D. Weiss, Lawrence Berkeley National Laboratory*, S. Yamamoto, A. Nilsson,* Stanford Synchrotron Radiation Laboratory*, M. Salmeron,* ***H. Bluhm***, Lawrence Berkeley National Laboratory

The adsorption of NOx compounds onto alkaline-earth metal-oxide surfaces has recently received a great deal of attention due to the use of alkaline-earth metal-oxides as NOx storage compounds for controlling emissions during combustion under fuel lean conditions. In this work we have studied the adsorption of NO2 onto MgO(100) thin films grown on Ag(100) ranging from 2 ML to over 8 ML in thickness and NO2 exposures from a few hundred Langmuir up to twenty thousand Langmuir at 300 K. We have used the Ambient Pressure Photoemission Spectroscopy experiment at beamline 11.0.2 of the Advanced Light Source to characterize this system using both core level and valence band photoemission as well as Auger-yield Near Edge X-ray Adsorption Spectroscopy. On thin films (~ 2 ML thick) we observe exclusively the adsorption of NO2 with coverages of ~ 0.5 ML for all exposures. As the film thickness increases the initial amount of NO2 adsorbed onto the surface decreases (~0.05 ML on films with thicknesses greater than ~5 ML) and we observe the formation of NO3 with increasing exposures. The final amount of NO3 on the surface of films thicker than 5 ML is ~ 0.3 ML. This indicates that the adsorption and reaction of NO2 on the surfaces of MgO(100) can, to some extent, be controlled by growing MgO(100) films of specific thicknesses. The mechanism of NO2 stabilization on the surfaces of thin MgO(100) films on Ag(100) will also be presented.

SS-TuP21 Comparative Study of the Electronic Structure of ZrB_2 and ZrB_{12}

L. Huerta*, R. Escamilla, E. Regalado,* Universidad Nacional Autónoma de México*, M. Flores*, Universidad de Guadalajara, México

X-ray photoemission spectroscopy (XPS) and Ultraviolet photoemission spectroscopy (UPS) are used to compare the electronic structures of ZrB_2 and ZrB_{12}. The Zr 3d and B 1s core levels associated with the chemical states of ZrB_2 and ZrB_{12} were identified, the Zr 3d core level shows a spin-orbit split $3d_{5/2}$ and $3d_{3/2}$ while that the B 1s core levels exhibit a single asymmetric peak typical of a metallic boride. Comparing with Zr metallic, boron and ZrO_2 reference materials, for ZrB_2 we observed a positive chemical shift for B 1s and a negative chemical shift for Zr $3d_{3/2}$ while that in ZrB_{12} the chemical shift in B 1s and Zr $3d_{3/2}$ is inverse, suggesting that a some charge transfer occurred from the Zr atoms to the B atoms in the ZrB_2 and from the B atoms to the Zr atoms in ZrB_{12}. The measured valence bands using UPS and XPS are consistent with band-structure calculations indicating a higher density of states (DOS) at E_F for ZrB_{12} compared to ZrB_2. That's suggesting that the T_c in ZrB_{12} is due to B 2p and Zr 4d-derived DOS at E_F.

SS-TuP22 Reactivity of Model Iron and Iron Oxide Surfaces and Nanoparticles with Chlorinated Hydrocarbons

G.S. Parkinson*, Z. Dohnalek, R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

Iron and iron oxide surfaces and nanoparticles have been shown to be catalytically active in the destruction of chlorinated hydrocarbons in environmental remediation applications. We employ a combination of molecular beam and surface analytical techniques to synthesize and characterize model iron and iron oxide thin films grown on Pt(111) and supported nanoparticles deposited on FeO(111)/Pt(111). The chemical activity of these model catalysts is explored using temperature programmed desorption and X-ray photoelectron spectroscopy. The reactivity of a series of chlorinated methanes is explored both anhydrously and in the presence of coadsorbed water. The experimental methods, results, and their mechanistic implications will be presented.

The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

SS-TuP23 High Temperature Scanning Tunneling Microscopy on the Ion Conducting Material YSZ(111)

A.J. Carter, J. Lahiri, ***M. Batzill***, University of South Florida

Most STM studies are performed on samples with good electron conductivity. Here we demonstrate STM measurements on the ion conductor yttrium stabilized zirconia (YSZ) at elevated temperatures. YSZ is the prototypical solid electrolyte that finds applications as an ion conductor for solid fuel cells and in gas sensing applications. In spite of these important technological applications the fundamental surface properties of ZrO2 are not well investigated. The wide band gap (>5eV) of zirconia and its poor electron conductivity hamper surface studies. Here we show that at elevated temperatures of about 600 K the ion conductivity is high enough to enable scanning tunneling microscopy investigations of this material and thus open the door for the investigation of the surface and defect structure at the atomic scale.

SS-TuP24 Nature of Photoactive Species on the TiO_2 Nanotube Thin Films

T.-L. Hsiung, Y.Y. Hsu, ***H.P. Wang***, National Cheng Kung University, Taiwan

The TiO_2 nanotube thin films were synthesized using ZnO nanorods as a template on the silica substances. By scanning electron microscopy (SEM), the TiO_2 nanotube thin films having a pore opening of about 200 nm were observed. Experimentally, the TiO_2 nanotube thin films have a very high activity in photocatalytic degradation of 2-chlorophenl (2CP) (220 mg/gTiO_2 hr) under UV/Uis irradiation. By pre-edge X-ray absorption near edge spectroscopy (XANES), the photoactive species may be distinguished in three titanium structures such as A_1 (TiO_4), A_2 ((TiO_4)=O), and A_3 (TiO_6). Interestingly, the A_2 species with a Ti=O and four Ti-O bonds to form a polyhedron in the TiO_2 nanotube thin films might be the main active sites involved in the photocatalytic degradation of 2CP. The TiO_2 nanotube thin films were also used in photocatalytic degradation of toxic pollutants such spill oils in the harbor or seashores.

SS-TuP25 Reaction Properties of NO over the Rh/Al_2O_3/NiAl(110) Model Catalyst, ***I. Nakamura***, *A. Takahashi*, *T. Fujitani*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of the noble metal content in the three-way automotive catalyst is currently required. In order to reduce noble metal loading, the enhancement of atomic efficiency of noble metal is an important subject. In this study, we investigated the NO reaction properties using Rh supported model catalyst. The model catalyst was prepared by deposition of Rh onto the Al_2O_3 thin film. It was shown that the NO dissociation activity on Rh deposited on Al_2O_3 is higher than that on Rh(111). Furthermore, we found that the NO dissociation activity on the Rh supported model catalyst increased by annealing treatment, where the activity increased with increasing heating temperature up to 500 K, and then decreased above 600 K. These results indicate that the atomic efficiency of Rh for NO dissociation is enhanced by supporting on Al_2O_3. To clarify the effect of Al_2O_3 support on Rh, we examined the NO adsorption state on the Rh supported model catalyst using IRAS. The IRA peak due to NO adsorbed on hollow site was observed at 1615 cm^{-1} for the surface without heating, which agreed with the frequency observed for Rh(111). In contrast, the peak due to NO adsorbed on bridge site was newly observed at 1645 cm^{-1} for the surface annealed to 500 K. Thus, we considered that the Rh surface structure changes from (111) face to (100) face by heating to 500 K. We previously found that the NO dissociation activity on Ir(100) was about twice of that on Ir(111), which was consistent with the relationship between the Rh supported model catalyst annealed to 500 K and Rh(111). Therefore, the enhancement of atomic efficiency of Rh is due to a change of the Rh surface structure to (100) face with a high NO dissociation ability. We concluded that the effect of Al_2O_3 support on NO dissociation is not electronic effect on Rh, but stabilization of (100) Rh surface structure.

SS-TuP26 Quantum-Resolved Photodesorption and Photodissociation Studies of Organic Nitrates and Halides on Ice, ***B. Olanrewaju***, *T.M. Orlando*, Georgia Institute of Technology

Several mechanisms have been proposed for the release of reactive species from organic halides and nitrates on ice during tropospheric ozone depletion episodes at polar sunrise. However, the description of the initial reactions that lead to the formation of precursors for these species remains incomplete because the surface enhanced catalytic effect of ice/snow interfaces is not well understood. Since the photochemical processing of interfaces involving these systems may be an important source of reactive species; we have carried out state resolved studies of photochemical production and release of Br and NO_x from selected organic halides and nitrates adsorbed on ice. Specifically, we utilized resonance enhanced multiphoton ionization to detect the 300 nm photoproduced and desorbed NO and Br (Br^*) from photoexcitation of bromoform and isopropyl nitrate adsorbed on crystalline and amorphous ice. We report cross sections and discuss the potential atmospheric relevance.

SS-TuP27 Antirelaxation Surface Coatings for High-Density Alkali-Metal Magnetometers, ***D.M. Rampulla***, *S.J. Seltzer*, *M. Romalis*, *S.L. Bernasek*, Princeton University

Atomic magnetometers containing spin-polarized alkali-metal atoms are capable of detecting magnetic fields with a sensitivity superior to that found in SQUIDs; however, a current issue with atomic magnetometers are depolarizing collisions between alkali-metal atoms and the cell walls. An inert buffer gas can be used to slow diffusion of spin-polarized alkali-metal atoms to cell walls, but a preferable solution would be a high-quality antirelaxation surface coating that would diminish the depolarization events that lead to the loss of spin-coherence and reduce the need for buffer gas. Although some coatings have been proven effective, paraffin and others presently in use typically can not operate at the relatively high temperatures ($T > 100°C$) for cesium and ($T > 150°C$) for potassium required for high-density magnetometers; therefore, it is desirable to find an effective antirelaxation coating suitable for these temperatures. In previous work, we have found that a coating of octadecyltrichlorosilane (OTS) at $T > 150°C$ can allow a potassium atom to collide more than 2000 times with the walls of a spherical borosilicate glass cell before depolarizing. However, spherical glass cells are not easily studied with surface science techniques (X-ray photoelectron spectroscopy and reflection-absorption infrared spectroscopy), thus we constructed a reusable alkali vapor cell for measuring antirelaxation properties of multiple flat surfaces coated with various monolayers (chlorosilanes and phosphonic acids). In addition to antirelaxation properties, the coatings were tested for reactivity toward alkali metals and temperature stability.

SS-TuP28 Co-deposited $BaTiO_3$ Nanocomposites in Polymer and LiF Host for Embedded Capacitor Applications, ***A. Biswas***, *I.S. Bayer*, *P.C. Karulkar*, University of Alaska, Fairbanks

Embedding capacitors has become a critical system need for high performance miniaturized electronic systems. Fabrication and performance constraints make developing materials, processes, structures, and devices for embedded capacitor technology a great challenge. Nanocomposites comprising metal or ceramic nanoparticles in polymer have recently emerged as promising candidates. They offer potential for attaining high capacitance value, high frequency performance, process compatibility, and reliability, while being lightweight, volume-efficient, flexible and low-cost. Among other materials, barium titanate is considered one of the most promising dielectric materials due to its high dielectric constant to blend with polymers to develop high-value capacitors. However, the existing techniques that are mostly based on chemical synthesis and high temperature (>1000°C) sintering followed by blending with the polymers. This makes implementation difficult. In this paper, we present a single-step method based on electron-beam assisted vapor-phase codeposition in vacuum that allows ambient temperature fabrication of nanocomposites (~0.5 μm thick) comprising ferroelectric barium titanate nanoparticles in polymer (polymethyl methacrylate and polyurethane/polyaniline block copolymer) as well as inorganic matrices (LiF). Ferroelectric properties of barium titanate can be achieved without post deposition annealing. Preliminary capacitance-frequency results exhibit flat capacitance densities around 12-15 nF/cm^2 in most of the devices with a low tangent loss (~ 0.03) and leakage current of about 70 nA/cm^2 in the -20 V to +20 V bias region over a frequency region of 10-100 MHz. Exposing the capacitors to prolonged heating at 125°C for several days to investigate the effects of thermal stress on the device capacitance resulted in a slight reduction in the capacitance density which may be due to the possible transition from ferroelectric to paraelectric phase in barium titanate. However, overall high-frequency response improved significantly due to minimized ferroelectric loss that resulted in self-resonance frequencies occurring beyond 250 MHz. The paper will describe the novel application of vacuum codeposition technique, very encouraging physical and electrical characterization results, and their potential for embedded technology.[1]

[1] Financial support of the Defense Microelectronics Activity is acknowledged.

SS-TuP29 Heats of Adsorption and Growth Mode of Lithium on MgO(100), ***N. Ruzycki***, *J. Farmer*, *J.H. Baricuatro*, *C.T. Campbell*, University of Washington

MgO(100) is a very well studied model oxide surface in model oxide-supported metal catalysis. Lithium-promoted MgO is an active catalyst for the partial oxidation of methane. Inherent surface defects change the surface reactivity and act as anchors for catalytically active metal nanoparticles. This study explored the adsorption energetics and growth mode of lithium atoms on stochiometric and defected MgO(100) surfaces, in a unique UHV chamber designed for sensitive adsorption calorimetry measurements, electron and ion spectroscopies and LEED. The MgO(100) thin films (4 nm thick) were grown on a Mo(100) single crystal. The lithium was vapor deposited onto the MgO(100) film under UHV conditions using a pulsed metal atom source. The sticking probability of lithium was near unity. The heat of adsorption for lithium on MgO(100) was 260 kJ/mol initially, dropping with coverage to reach the heat of sublimation of pure lithium metal (159 kJ/mol) above 0.5 ML. Low energy He+ ion scattering (LEIS) revealed the growth mode for Li adsorption: Li initially wets the surface as adatoms up to ~0.5 ML, after which 3D islands of Li grow. Work function measurements yielded a change with coverage typical for alkali metal adsorption on late transition metals, with a 2.2 eV initial decrease associated with cationic Li adatoms, followed by an increase back to the value for bulk Li metal as the Li depolarizes at higher coverages due to dipole-dipole repulsions in the Li adlayer. Argon ion beam damage created defects which adsorb Li more strongly than MgO(100) terraces (up to 370 kJ/mol or more).

SS-TuP30 Strong Interaction between BaO and Al_2O_3 in NO_x Storage Materials: Correlation between Model and High Surface Area Catalysts, ***C.-W. Yi***, *J.H. Kwak*, *C.H.F. Peden*, *C.M. Wang*, *J. Szanyi*, Pacific Northwest National Laboratory

A series of Ba-containing NO_x storage reduction (NSR) model catalysts were prepared by reactive layer-assisted deposition (RLAD) of Ba onto Al_2O_3/NiAl(110) and investigated with surface science techniques. Upon NO_2 exposure the model catalysts demonstrated corresponding properties to the high surface area ones. Initially nitrite species form, and then Ba ions are pulled out from the surface at higher NO_2 exposures, resulting in the formation of ionic barium nitrates. The formation and agglomeration of $Ba(NO_3)_2$ clusters were observed by infrared reflection absorption (IRA) and x-ray photoelectron spectroscopies (XPS) for the model systems, and by Fourier transform infrared (FT-IR), time-resolved synchrotron x-ray diffraction (TR-XRD), and high resolution scanning transmission electron microscopy (HR-STEM) for the high surface area catalysts. The correlation between the model and real catalysts shown here for NO_2 adsorption and reaction strongly emphasizes the value of well-designed surface science studies aimed at understanding practical catalytic systems, and this approach ultimately can allow us to develop NSR catalysts with better performances.

SS-TuP31 Substitution of Carbon for Oxygen in TiO_2 for Photocatalysis Applications, ***P. Nachimuthu***, *S. Andrews, V. Shutthanandan, M.H. Engelhard,* Pacific Northwest National Laboratory, *T. Tyliszczak, D.K. Shuh,* Lawrence Berkeley National Laboratory, *S. Thevuthasan, M.A. Henderson*, Pacific Northwest National Laboratory

In semiconductor photochemistry, the redox potential of a photocatalyst is strongly modified by its band gap, which in turn dictates the energy separation of the electron-hole (e^-/h^+) pairs. The position of the bands relative to the band gap with respect to the electron donor and acceptor orbitals in the reactants determines the degree of overlap between adsorbate molecular orbitals and the electronic states associated with the e^-/h^+ pairs. TiO_2 is one of a few candidate materials with promising photocatalytic properties although the optical absorption spectrum of pure TiO_2 has poor overlap with the solar spectrum and high e^-/h^+ pair recombination rates. However, anion doping of TiO_2 is known to red-shift its optical absorption spectrum into the visible region and as a result, visible light phtotoactivity has been observed for N-doped TiO_2. Recently, we have investigated C-doped TiO_2(110) rutile using ion beam implantation as a function of temperature and dopant concentrations. Subsequent high temperature annealing was carried out on selected samples to heal the implantation damage as well as to understand the location and mobility of the dopants in the rutile lattice. Following implantation and annealing, the samples were characterized using several surface and bulk sensitive techniques such as x-ray photoelectron spectroscopy (XPS), near-edge x-ray absorption fine structure (NEXAFS), Rutherford backscattering spectrometry (RBS) (both random and channeling), and nuclear reaction analysis (NRA). NRA measurements along the channeling and random geometries clearly indicate the substitution of carbon for oxygen in the TiO_2 lattice under certain conditions. XPS data on sputter cleaned samples show the presence of carbon in two different environments with binding energies of 282.4 eV (carbide; Ti-C interaction) and 284 eV (C-C and/or C-O interactions). However, sputter cleaning followed by annealing in oxygen, eliminates the higher binding energy features suggesting that sputtering effects play a role in modifying the carbon environment in the rutile lattice. Carbon K-edge NEXAFS data are consistent with the XPS findings. Both XPS and NEXAFS show that non-carbidic interactions were significantly developed following annealing at high temperatures, although no evidence of carbon release was found from these C-doped samples.

SS-TuP32 Formation and Surface Chemistry of TiO_2 Nanoparticles on Au(111), ***Y.Z. Le***, *N. Stojilovic, R.M. Osgood,* Columbia University, *J. Hrbek*, Brookhaven National Laboratory

Titania (TiO_2) nanoparticles are formed on Au(111) surfaces under ultrahigh vacuum conditions using the method of reactive-layer-assisted deposition (RLAD). In this method, physical-vapor deposited Ti on H_2O/Au(111) reacts with oxygen from water to produce TiO_2 nanoparticles. During heating of the substrate unreacted water molecules and its fragments desorb leaving the TiO_2 nanoparticles on Au(111) surfaces. Characterization of the nanoparticles is performed using Auger electron spectroscopy (AES) whereas temperature programmed desorption (TPD) experiments are used to probe the surface chemistry of water and halogenated alkanes on these nanoparticles. Effect of titania coverage and particle size on subsequent desorption kinetics and surface chemistry is investigated. In particular, we have probed the reactive formation of these particles as a function of surface annealing temperature and observed changes in desorbed species. This formation chemistry is aided by a separate scanning tunneling microscopy (STM) study of the particle morphology, which reveals nanoparticles of 1-5 nm in size.

SS-TuP33 Characterization of Ceria-Titania Nanostructures: Insights into the Catalytic Performance, ***A.S. Karaoti***, *S.V.N.T. Kuchibhatla, T. Spalding, K. Suresh babu, S. Seal*, University of Central Florida

Oxide based semiconductors such as ceria and titania are used prolifically for a host of catalytic applications. Recently there has been an upsurge in the research, marrying the two materials for enhanced catalytic applications. A marked increase in the catalytic performance of the mixed ceria-titania oxides have been reported by various groups. However, a clear understanding of the underlying mechanisms is still at large. The present work focuses on the characterization of ceria mixed titania using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC) and Photoluminescence (PL) experiments. The retention of more catalytic anatase phase at higher temperature upon mixing with ceria and the electronic properties which result in enhancing the catalytic behavior are critically analyzed. Influence of increasing ceria concentration on phase stability, particle size and electronic properties of titania will also be discussed.

SS-TuP34 Surface Structure of $BaTiO_3$ (001), ***D.B. Li***, *R. Shao, A. Kolpak, A. Rappe, D.A. Bonnell*, University of Pennsylvania

Although oxide surfaces have been extensively studied over the last 2 decades, the atomic structure of $BaTiO_3$ (001) has received relatively little attention as a consequence of a variety of experimental challenges. The fundamental aspects of reactions on ferroelectric surfaces are critical to a range of device applications and $BaTiO_3$ (001) is the prototypical model surface. On overcoming these challenges we have used STM, nc-AFM, LEED and AES, to show that this surface adopts a family of reconstructions depending on thermo-chemical history. Most of these structures have not been observed previously. Some of the reconstructions are reminiscent of those that occur on $SrTiO_3$ (001) but the details differ significantly. Using a combination of density functional theory and ab initio thermodynamics, we compute the surface phase diagrams with oxygen potential as a dependent variable, since this is a critical variable in the experiment. The stabilities of reconstructions with Ba-adatoms, O-vacancies and Ti-O clusters are compared for different thermo-chemical conditions. Comparisons of the results of the calculations with the STM and nc-AFM results are used to construct atomic models for the reconstructed surfaces.

SS-TuP35 Water Dissociation on TiO_2(110) Supported Au Catalyst: A DFT Study, ***G. Wang***, *J. Jiao*, Nankai University, China

The present DFT calculations have clearly reproduced the experimental phenomena for H2O dissociation on TiO2(110) supported Au catalyst (including both Au cluster and scattered Au-atoms). Our results indicate that the Au-atom scattered on TiO2 strongly interacted with the supported TiO2, and compared with the supported metallic Au particle, is the most active site for the H2O dissociation reaction to occur due to the low activation energy (0.80eV). Second, the neighboring supported metallic Au particles have no effect on the catalysis activity of scattered Au-atoms for adsorbed H2O dissociation; Third, the supporting TiO2(110) has positive effect as regard to the scattered Au-atom-catalyzed H2O dissociation reaction, because it could reduce the reaction activation energy by about 0.37eV; on contrast, it has little effect on the activity of metallic Au particles; Fourth, the calculations also indicated that the active site for molecular decomposition reaction is just opposite to that of its reverse reaction, that is, as the reverse reaction of H2O dissociation, H(a)+OH(a)=H2O(a), has a less activation energy on supported metallic Au particles than on scattered Au-atoms.

SS-TuP36 Preparation and Chemical Modification of Nanoparticle Layers by Plasma Treatments, *B. Gehl*, University Bremen, Germany, *A. Frömsdorf, V. Aleksandrovic,* University Hamburg, Germany, *T. Schmidt, J. Falta*, University Bremen, Germany, *H. Weller,* University Hamburg, Germany, ***M. Baeumer***, University Bremen, Germany

Nanoparticles deposited as thin films on oxidic substrates represent a highly interesting class of materials systems not only for physical (e.g. magnetic) but also chemical applications, such as heterogeneous catalysis for example. A flexible and relatively simple way to prepare such layers is to wet-chemically synthesize nanoparticles in colloidal solution and deposit them onto a flat substrate by spincoating or a comparable method. In most cases the as-prepared particles are surrounded by a shell of organic molecules stabilizing the colloidal suspended state. To freely access the properties of the metallic particle surface for measurement or application, it is necessary to remove this shell of physically obstructing and chemically passivating ligands. It is important that the method used to strip the particles of their organic sheath neither disturbs the particle material, the substrate nor the structure of the layer. This can be achieved by exposing the deposited nanoparticles to a mild plasma removing the ligand shell through a combination of sputtering and etching processes with free radicals. It will be demonstrated that both reducing and oxidizing plasmas can be used for this purpose. Moreover, by varying plasma gasses and parameters, it is also possible to modify the chemical state of the particles selectively but leaving the lateral arrangement on the surface undisturbed. The contribution will shed light on the possibilities and limits of the approach also comparing the results to experiments where the ligand shell was removed by thermal treatment. Another aspect that will be addressed is the risk of chemical interactions with the support material induced by the plasma treatment.

SS-TuP37 Behavior of Deuterated Ethanol on Zircaloy-4 Surfaces, *Y.C. Kang*, ***J.Y. Park***, Pukyong National University, S. Korea

The surface chemistry of deuterated ethanol on the zircaloy-4 surfaces was investigated by means of temperature programmed desorption(TPD) and Auger electron spectroscopy (AES) techinques. The cleanliness of the zircaloy-4 was checked by AES and the purity of deuterated ethanol was checked by quadruple mass spectrometer (QMS) after several cycles of freeze-pump-thaw method. Depending on the adsorption temperatue, water evolution was changed as peak maximum position and absolute peak intensity. Even highly pure deuterated ethanol was used, hydrogen exchange was observed in this experiment. As the amount of exposed deuterated ethanol increased, the oxidation state of zirconium was changed from metallic to zirconia form. During linear heating of the deuterated ethanol dosed zircaloy-4 surfaces, hydrogen evolution was observed. This implys that this system has potential of production of hydrogen.

SS-TuP38 Design and Construction of a Batch Microreactor for Investigations of Heterogeneous Catalysts Deposited on Flat Supports, ***M. Sushchikh****, J. Colby, L. Cameron, W. Tang, A. Kleiman-Shwarsctein, J.N. Park, H. Metiu, E. McFarland*, University of California, Santa Barbara

A five microliter volume batch microreactor system has been developed for the investigations of the reaction kinetics over low surface area catalysts deposited on flat supports including submonolayers of metals on single crystals. The main features of the reactor are: micro-probing capability using principle of variable leak valves (minimal altering of the amount of gases in the reactor volume); direct probing of the gases into ultra-high vacuum (UHV) mass-spectrometer volume (high sensitivity); enclosure of the reactor volume in larger tank (leak-proof by design). The reactor is made of UHV compatible components and is ready to be attached to an UHV chamber equipped with linear stage sample transfer. The reactor has been tested at initial total pressure 500 Torr, but both, lower and higher pressures are possible. The temperature is controlled over the range of 20°C to 250°C. The reactor allows monitoring of the reactions over time from tens of minutes to hours. The performance of the reactor has been demonstrated for CO oxidation reaction over Pd foil.

SS-TuP39 Growth and Physical Properties of Epitaxial Metastable $Hf_{1-x}Al_xN$ Alloys Deposited on MgO(001) by Ultrahigh Vacuum Reactive Magnetron Sputtering, ***B.M. Howe****, J. Bareño*, University of Illinois at Urbana-Champaign, *M. Stoehr*, Université de Haute Alsace, France, *M. Sardela, J.G. Wen, J.E. Greene*, University of Illinois at Urbana-Champaign, *L. Hultman*, Linköping University, Sweden, *A.A. Voevodin*, Air Force Research Laboratory, *I. Petrov*, University of Illinois at Urbana-Champaign

Epitaxial metastable $Hf_{1-x}Al_xN$ alloys with 0 = x = 0.50 were grown on MgO(001)substrates at 600°C by ultrahigh vacuum reactive magnetron sputtering from Hf and Al targets in 90 % Ar + 10 % N2 discharges at 7 mTorr. X-Ray diffraction and crosssectional transmission electron microscopy show that $Hf_{1-x}Al_xN$ alloys are single crystals with the B1-NaCl structure. Rutherford backscattering spectroscopy investigations reveal that all films are slightly overstochiometric with N/(Hf+Al) = 1.05 ± 0.05. The relaxed lattice parameter decreased linearly from 0.4519 nm with x = 0 to 0.4438 nm with x = 0.50, compared to 0.4320 nm expected from the linear Vegard's rule. We find a metastable single phase field that is remarkably broad given the large lattice mismatch (~ 9 %) between the two alloy components. Alloying HfN with AlN leads to an increase in hardness (~ 30% to 32.4 ± 0.7 GPa), as well as nanostructured compositional modulations due to the onset of spinodal decomposition.

SS-TuP40 Effect of Water Vapor on Monolayer Features Produced by Pulsed 248-nm Irradiation of Cleaved Alkali Halide Surfaces[1], ***K. Kimura****, S.C. Langford, J.T. Dickinson*, Washington State University

Low doses of energetic electrons can produce monolayer etch pits on alkali halide cleavage surfaces.[2] Similarly, UV laser radiation can roughen steps and produce monolayer islands and pits on NaCl at fluences well below the macroscopic damage threshold.[3] Step edges on NaCl are highly vulnerable to erosion due to high densities of kinks. In NaCl, step erosion is dramatically accelerated in the presence of 10^{-5} Pa water vapor.[4] In this work, we compare atomic force microscopy (AFM) images of NaCl, KCl, and KBr cleavage surfaces exposed to pulsed 248-nm laser radiation in vacuum. Since atmospheric water vapor affects all these surfaces, AFM was performed under dry nitrogen. Prior to laser exposure, the principal features are straight, monatomic cleavage steps. Fifty 248-nm pulses at 100 mJ/cm^2 are sufficient to produce monolayer islands and to roughen cleavage steps in ultrahigh vacuum on all three materials. Island-free zones are observed on both the upper and lower terraces along cleavage steps. The island densities and the width of the island free-zones vary significantly with laser fluence. Islands appear to be formed from material eroded from the steps. Similar laser exposures in the presence of 10^{-5} Pa water vapor produce monolayer etch pits, rather than islands, on KBr and KCl. Higher laser fluences are required to produce pits on NaCl. Calibrated quadrupole mass spectrometry on the products emitted during laser irradiation shows emission intensities consistent with that required to form the etch pits. In the presence of 10^{-5} Pa water vapor, the detected intensities are typically several times higher than in ultrahigh vacuum. Islands and etch pits are also observed on surfaces exposed to low doses of 2 keV electrons; again, these features are dramatically affected by the presence of water vapor. Although mechanism for the effect of water vapor is not clear, the dissociative adsorption of water at surface halogen vacancies is expected to play a role.

[1] This work was supported by the U.S. Department of Energy-under Grant DE-FG02-04ER-15618.

[2] B. Such, P. Czuba, P. Piatkowski, and M. Szymonski, Surf. Sci. 451(1/3), 203-207 (2000)

[3] K. H. Nwe, S. C. Langford, and J. T. Dickinson, J. Appl. Phys. 97, 043501 (2005).

[4] K. H. Nwe, S. C. Langford, and J. T. Dickinson, J. Appl. Phys. 97, 043502 (2005).

Authors Index

Bold page numbers indicate the presenter