

Tuesday Afternoon Poster Sessions

Surface Science

Room: Southwest Exhibit Hall - Session SS-TuP

Surface Science Poster Session

SS-TuP1 MORTON S. TRAUM AWARD FINALIST: Uptake of Copper Acetamidinate ALD Precursor on Metal Surfaces and the Effect of Coadsorption of Hydrogen. *Q. Ma**, *F. Zaera*, University of California, Riverside

Acetamidinate precursors have shown great promise for atomic layer deposition (ALD) applications, but potentially deposit impurities that may degrade the quality of the films and hinder their practical applications. To help solve this problem, the uptake and thermal activation of bis[*N,N'*-di-sec-butylacetamidinate]*Cu*] and *N,N'*-di-sec-butylacetamidine on metals were characterized under ultrahigh vacuum (UHV) conditions by using a combination of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), and temperature programmed desorption (TPD).

In initial studies on a Ni(110) single crystal, a temperature window between approximately 350 and 450 K was identified for the ALD of the Cu acetamidinate on Ni surface: lower temperatures are insufficient for activation of the dissociative adsorption, and higher temperatures lead to continuous decomposition beyond Cu monolayer saturation. Approximately three dosing cycles are required to reach full Cu monolayer saturation, the equivalent of a film growth rate of $\sim 0.75 \text{ \AA/cycle}$ in ALD. Preadsorption of hydrogen on the surface does not modify any of this behavior because of its rapid desorption at temperatures below 350 K once the gas-phase H_2 is removed.

The surface chemistry of the Cu precursor is complex, leading to the desorption of not only hydrogen but also butene and *N*-sec-butylacetamidine ($\text{H}_2\text{N}-\text{C}(\text{CH}_3)=\text{N}-\text{CH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$), it seems that the amidine ligands decompose via beta-hydride elimination from one of their terminal sec-butyl moieties. Copper precursors leading to relatively stable organic surface intermediates are required in ALD because their clean removal can only happen in the second half-cycle of processes that rely on hydrogenation reactions. The ligand of the copper acetamidinate precursors further decomposed on Ni(110) surfaces. The free hydrogenated amidine ligand is less reactive and no *N*-sec-butylacetamidine is produced by its thermal activation, but the remaining chemistry is seen with similar temperature transitions.

SS-TuP2 MORTON S. TRAUM AWARD FINALIST: Understanding and Controlling Rotation at the Single-Molecule Level: Turning Rotors into Motors. *H.L. Tierney**, *A.D. Jewell*, *A.E. Baber*, *E.V. Iski*, *E.C.H. Sykes*, Tufts University

While molecular machines driven by chemical, light or thermal energies can be found throughout nature, little progress has been made toward creating synthetic counterparts. The gap between nature and nanotechnology remains due to the limited fundamental understanding of the transfer of energy to mechanical motion at the nanoscale. Understanding and actuating the rotation of individual molecules on surfaces is a crucial step towards the development of nanoscale devices such as fluid pumps, sensors, delay lines, and microwave signaling applications. Towards this end we have used a group of small molecules in order to understand the fundamental aspects of molecular rotation. Thioethers constitute a simple, robust system with which molecular rotation can be actuated thermally, mechanically and electrically, and can be studied using scanning tunneling microscopy (STM) as a function of molecular chemistry and proximity of neighboring molecules. Interestingly, the thermal onset to rotation was found to be nearly identical for studied thioether molecules with alkyl tails of two carbons or more. It is proposed that this plateau in thermal onset was due to an interplay between degrees of freedom in the alkyl tail vs. the S-metal bond length. While small amounts of thermal energy are capable of inducing rotation, thermodynamics dictates that thermal energy alone cannot be used to perform useful work in the absence of a temperature gradient. Therefore, for molecules to meet their full potential as components in molecular machines, methods for coupling them to external sources of energy that selectively excite the desired motions must be devised. To this end, we have studied using an electrical current to rotate individual dibutyl sulfide molecules on command. For these studies the source of energy is supplied via high energy electrons from the STM tip. By monitoring the rate of rotation as a function of tunneling electron energy (action spectroscopy) we have demonstrated that the rotors can be driven electrically via a

mechanism that involves excitation of a C-H stretch. Finally, using theoretical methods the minimum energy adsorption site was determined and the mechanism of rotation was elucidated for the simplest thioether, dimethyl sulfide. These theoretical results indicate that the rotation of a small, simple molecule is actually rather complex; as the CH_3 groups of dimethyl sulfide rotate around the Au-S bond, the central S atom precesses around a surface Au atom.

SS-TuP3 MORTON S. TRAUM AWARD FINALIST: Growth of Ag on Ge(110) and Ge(111) Studied by LEEM. *C. Muller**, University of California, Davis, *S. Chiang*, University of California at Davis

We studied Ag island growth on reconstructed Ge(110) and Ge(111) surfaces with low energy electron microscopy (LEEM). At 480 C, one-dimensional (1D) island growth was observed on Ge(110). Island nucleation proceeds from defects in the Ge substrate, with island thickness corresponding to the size of the substrate defect where the island nucleation occurred. As Ag is deposited, islands lengthen but do not thicken. At 9 ML, Ag coverage islands were up to 10 μm long, and thicknesses varied from 100 nm to 250 nm. One-dimensional islands were also produced by Ag deposition at room temperature followed by sample heating. Round Ag islands resolvable in LEEM were observed and coalesced into many long 1D islands as temperature was increased. Islands formed by deposition at room temperature followed by heating to a particular temperature were shorter and thicker than islands grown by deposition on a substrate held at that same temperature. Ag growth on Ge(111) is Stranski-Krastanov. Multilayer Ag island formation begins after the Ag ($\sqrt{3}\times\sqrt{3}$)R30° phase completes at one monolayer. Ag islands exhibit hexagonal faceting. For both the Ge(111) and Ge(110) surfaces, Ag islands induce changes in the Ge substrate that leave a "footprint" observable in LEEM after all Ag has been desorbed from the surface.

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SS-TuP4 Kinetics and Mechanism of NO Reduction with CO on Ir Surfaces. *T. Fujitani*, *A. Takahashi*, *I. Nakamura*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reaction of NO and CO has been studied over various transition- and noble-metal catalysts because of its importance for three-way catalytic converters. Recently, Ir-based catalysts were found to be effective for the selective reduction of NO with CO in the presence of O_2 . However, the reaction mechanism, kinetics, and adsorption behavior for the NO + CO reaction on Ir-based catalyst surfaces are not fully understood.

In this study, we investigated the adsorption and thermal reactivity of NO and CO over Ir single crystals to clarify the influence of the Ir surface structure. Furthermore, we examined the kinetics and mechanism of the NO + CO reaction over Ir single crystals at high-pressure and compared the results with results for a conventional Ir/SiO₂ powder catalyst.

The kinetics of the NO reduction with CO over the Ir single crystal and the powder Ir/SiO₂ catalyst were investigated under real reaction conditions. N₂ and CO₂ were formed by the reaction of NO + CO. The Ir(111) plane showed low activity for N₂ and CO₂ production compared with the Ir(100) and Ir(211) planes. The TOFs for N₂ and CO₂ formation for the Ir planes decreased in the order (100) > (211) >> (111). The apparent activation energies for N₂ and CO₂ formation were estimated to be 107–115 kJ/mol and 110–120 kJ/mol, respectively; and these values were almost the same, regardless of the changes of the Ir surface structure. Furthermore, the order of the pre-exponential factors for the various surface structures was in good agreement with the order of the planes with respect to NO dissociation activity, indicating that the catalytic activity for NO reduction over Ir surfaces was strongly dependent on the NO dissociation activity.

The activation energies for N₂ and CO₂ formation over an Ir/SiO₂ catalyst were estimated to be 117.2 kJ/mol and 123.1 kJ/mol, respectively, and these values were similar to those of the Ir single crystal. The TOFs for N₂ and CO₂ formation over Ir/SiO₂ were almost same for those for Ir(211), which indicates that the Ir surface structure of Ir/SiO₂ was close to that of Ir(211). That is, the Ir(211) surface can be regarded as an appropriate model catalyst for the NO + CO reaction over an Ir/SiO₂ catalyst because the apparent activation energies and the TOFs for N₂ and CO₂ formation over Ir(211) were in good agreement with those over the Ir/SiO₂ catalyst.

SS-TuP5 Development of Boundary Layer in the Flowing Water on the Solid Surface with Various Wettability. *M. Sakai*, Kanagawa Academy of Science and Technology, Japan, *M. Nishimura*, *T. Furuta*, *A. Nakajima*, Tokyo Institute of Technology, Japan, *A. Fujishima*, Tokyo University of Science, Japan

Recently, the importance of controlling wettability on the solid surface is recognized in various industries. Superhydrophobic surfaces with water

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contact angles exceeding 150° are currently the subject of great interest and intensive study. Superhydrophobic coatings that produce rough surfaces at the micro- and nanoscale level with low surface energies have been prepared by several methods. On the other hands, highly hydrophilic surface is obtainable, when the photocatalyst TiO₂ is irradiated by ultraviolet light. In the current paper, we evaluated friction drag of water on various surfaces including these surfaces. The amount of friction drag was evaluated by the static pressure during flowing in the tubes coated by various materials. Compared to Darcy-Weisbach's equation, a superhydrophobic coating and highly hydrophilic coating decreased the friction drag of the flowing under the condition of small Reynolds number. However, a highly hydrophilic coating contributed significantly to the reduction of friction drag, when Reynolds number is large. Moreover, the velocity gradient of the flowing water in the tube was measured by particle image velocimetry (PIV). The development of boundary layer depended on the wettability in the tubes, when the flowing was the same in the flow rate. The mechanism was discussed from the viewpoints of fluid mechanics and surface materials science.

SS-TuP6 Hydrogen Termination of Si(110) Surface in UHV Conditions, M. Yoshimura, A. Visikovskiy, Toyota Technological Institute, Japan

Hydrogen termination on silicon surfaces is very important in science and technology. Hydrogen (H) is used for surface passivation, and may play role of surfactant for epitaxial growth and also present in many technological processes including chemical vapor deposition. The behavior of H on Si(100) and Si(111) surfaces is extensively studied. However, the information on interaction of H with Si(110) is very limited. The (1x1) bulk-terminated structure was reported for chemically hydrogenated Si(110) in solution [1,2]. The surface structure and processes occur on Si(110) hydrogenated in ultra-high vacuum (UHV) may be very different from chemically treated samples. There are very few reports on *in situ* hydrogenation of Si(110) surface. Here, we report scanning tunneling microscopy (STM) study of atomic H adsorption on Si(110) in UHV.

The high efficiency hot capillary source was used to produce atomic H flux. The large concentration of highly reactive H atoms in the flux allows us to reach surface saturation for hydrogenation at ~2 L exposure. Chemically etched tungsten tips have been used for STM (Omiron VT-system).

The initial adsorption process of hydrogen reveals itself as suppression of individual protrusions of pentagon pairs on STM image. The number of these "missing" protrusions increases with H coverage, although the overall "16x2" structure of clean Si(110) preserves. More drastic changes were observed on unreconstructed areas exposed to small amount of H at elevated temperatures. Si pentagon pairs, usually randomly distributed on these areas, were arranged in patches with local "5x4" periodicity. Further exposure at room temperature (RT) led to loosing of atomic resolution on STM images. At higher temperatures (400~500°C) the surface have reconstructed to the zigzag row structures. Depending on relative shift of neighboring zigzag rows the local periodicity was either (2x3) or (2,1)x(0,3). The up-and-down terrace structure of "16x2" reconstruction could still be observed, probably, due to insufficient temperature to initiate massive Si transport to smooth out the surface. At temperatures more than ~550°C the H atoms start to desorb from Si(110). These kinds of structure have not been observed before for H/Si(110) surface. No (1x1) reconstruction reported for chemically hydrogenated Si(110) was confirmed. Only small patches of (1x1) were observed in very narrow temperature window at ~350°C.

References

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SS-TuP7 Spectroscopic Investigation on Water Behavior in Mesoporous Silica, Y. Aoki, J. Hieda, O. Takai, N. Saito, Nagoya University, Japan

Mesoporous materials are widely used in industrial fields such as biotechnology and chemical engineering; catching and filtering a specific molecule, supplying novel reaction field for nanocatalysis. In particular, mesoporous silica is defined as a material with size-regulated mesopores (2-50 nm). Generally, highly-ordered arrangement of pores is attractive for chemists because the most of properties are controlled by the arrangement.

Recently some researchers reported that the internal water trapped by mesopores extraordinary behaved compared with bulk water. For examples, the water showed the lower melting point and increasing effect of non-freezing water. These phenomena were originated from the increasing ratio of interactions to water molecules from surface.

In this research, we aimed to reveal water behaviors in mesoporous silica from IR spectroscopy, Raman spectroscopy, and DSC. Mesoporous silica

was synthesized conventional thermal calcinations with several organic templates because it control the pore diameters. The synthesized mesoporous silica was characterized by XRD, TEM and N₂ adsorption-desorption isotherm curve.

The complete removal of organic template and the OH-termination in inside wall resulted in the presence of water in the mesopores. As the water features, we observed the both types of non-freezing and freezing water. Finally, the types of water were separated in the properties by both spectroscopy and DSC.

SS-TuP8 Mechanism of Laser Assisted Field Evaporation from Oxides, M. Tsukada, H. Tamura, Tohoku University, Japan, K. Mckenna, University College London, UK

Recently, experimental methods for 3D-atom probe microscopy for a wide class of oxides and semiconductor materials have been developed by Hono et al using laser assisted field evaporation. Though this method is really epoch-making, the mechanism of laser assisted field evaporation has not been clarified so far and the best operation condition is still unexplored. Therefore we studied theory on the mechanism of laser assisted field evaporation from MgO crystal, as a prototype of oxides. As a result, we found the mechanism is explained by electronic excitation model, which is remarkably different from the usual field induced evaporation from metal tips.

An important fact we clarified is that a certain amount of holes at the evaporation region exert a driving force of the evaporation by reducing the potential barrier of the ion desorption. The holes are generated by a strong positive electric field on the tip, as well as by the laser irradiation.

Using MRMP2 ab initio calculations, we obtained the potential energy surfaces of the ground states and photo-excited states of somewhat larger MgO clusters leading to the photo-induced desorption of corner ions. We found when two holes are captured in the MgO clusters, the activation barrier height of the excited diabatic potential energy surface is remarkably reduced, indicating such an excited potential energy surface provides an effective evaporation pathway. Using ab initio embedded cluster method with 6-311G*/B3LYP for much larger MgO cluster models including more than 1000ions, we calculated the effect of positive charging on the sublimation energy of the corner ions and found only two holes captured by the cluster remarkably reduce the sublimation energy. We also obtained analytic expressions of the potential energy surfaces from phenomenological analyses, from which evaporation rates are estimated as the function of the applied voltage. The holes generated and accumulated near the evaporation region play an important role for triggering the ion desorption. We also discuss how such surface hole accumulation can be detected by the FIM images.

Based on theoretical analyses as above, we establish a systematic scenario leading to the laser assisted field evaporation from oxides and semiconductors. Moreover, theoretical clue will be provided towards finding a condition for the best resolution of the 3D-atom probe method using the laser assisted field evaporation.

SS-TuP9 Surface Roughness of Anodized Titanium Coatings, D.A. Chinn, M.T. Dugger, Sandia National Laboratories

Samples of grade five 6Al4V titanium alloy were coated with two commercial fluoropolymer anodizations (Tiodize and Canadize) and compared. Neither coating demonstrates significant outgassing. The coatings show very similar elemental analysis, except for the presence of lead in the Canadize coating, which may account for its lower surface friction in humid environments. Surface roughness has been compared by SEM, contact profilometry, optical profilometry, power spectral density and bidirectional scattering distribution function (BSDF). The Tiodize film is slightly smoother by all measurement methods, but the Canadize film shows slightly less scatter at all angles of incidence. Both films exhibited initial friction coefficients of 0.2 to 0.4, increasing to 0.4 to 0.8 after 1000 cycles of sliding due to wear of the coating and ball. The coatings are very similar and should behave identically in most applications.

SS-TuP10 Measurement of the Dielectric Properties of SiO₂ Wafers using Optical Spectroscopy, D. Popovic, A. Zekic, University of Belgrade, Serbia, V. Milosavljevic, Dublin City University, Ireland & University of Belgrade, Serbia

Low dielectric constant materials (low-k) are used as interlevel dielectrics in integrated circuits. As components have scaled and transistors have gotten closer and closer together, the insulating dielectrics have thinned to the point where charge builds up and crosstalk adversely affects the performance of the device. It is this reduction in scale which drives the need for insulating materials with lower dielectric constant. A 'low-k' material is one with a small value for dielectric constant relative to silicon dioxide (SiO₂) a former dielectric of choice. There are many materials with lower

dielectric constants, but few of them can be suitably integrated into a semiconductor manufacturing process.

The SiO₂ is frequently used in a plasma chamber as a wafer for etching. The interaction of the plasma and the SiO₂ surface leads to incorporations/removing material for structure of SiO₂ and also to increasing of the dielectric constant. So the optimization problem in materials development for semiconductors is to lower the permittivity of the dielectric material as far as possible without compromising mechanical integrity.

The dielectric function spectra of low dielectric constant (low-k) materials have been determined using spectroscopic ellipsometry, near-normal incidence spectroscopic reflectometry, and Fourier transform infrared transmission spectrometry over a wide spectral range from 0.03 to 5.4 eV (230nm to 40.5µm wavelength region). The electronic and ionic contributions to the overall static dielectric constant were determined for representative materials used in the semiconductor industry for interlayer dielectrics. The main contributions to the static dielectric constant of the low-k materials studied were found to be the electronic and ionic absorptions.

To perform the study, square shape wafers (15x15mm) are placed in the discharge tube. The angle between wafers plane and a constructed channel is 45°. The DC discharge is produced in a Pyrex tube of 5mm inner diameter and an effective plasma length of 72mm. The discharge tube is evacuated using a vacuum pump that gives a base pressure of 2Pa. The working pressures from 50 to 266 Pa are achieved using a gate valve positioned above the rotary pump. Gas flow into the chamber is controlled via mass flow controllers that precisely determine gas content in the discharge tube. The working gas is a sulphur-hexafluoride (SF₆) with flow rate up to 40 sccm. The power supply used was a Keithley Model 248 high voltage supply with a maximum voltage of 5kV and discharge current of 5 mA. In this experimental campaign the maximum voltage is 2.2kV. The wafer processing time is 30 min.

SS-TuP11 Stereoselective Adsorption Configurations of S-Proline Molecules via N Dative Bonding on Ge(100). *Y.-S. Youn*, Korea Advanced Institute of Science and Technology (KAIST), Korea, *K.-J. Kim*, B. Kim, Pohang Accelerator Laboratory, Korea, *D.H. Kim*, Daegu University, Korea, *H. Lee*, Sookmyung Women's University, Korea, *S. Kim*, Korea Advanced Institute of Science and Technology (KAIST), Korea. The adsorption configurations of S-proline on Ge(100) were studied using scanning tunneling microscopy (STM), density functional theory (DFT) calculations, and high-resolution core-level photoemission spectroscopy (HRCLPES). We identified three adsorption structures of S-proline on Ge(100) through analysis of the STM images, DFT calculations, and HRCLPES results: (i) an 'intrarow O-H dissociated and N dative bonded structure', (ii) an 'O-H dissociation structure', and (iii) an 'N dative bonded structure'. Moreover, because adsorption through the N atom of S-proline produces a new chiral center due to symmetry reduction by N dative bonding, we found that the adsorption configurations have either (R,S) and (S,S) chirality with a preference for reaction at the Re face.

SS-TuP12 Islands and Holes as Measures of Mass Balance in Growth of the (√3x√3)R30° Phase of Ag on Si(111). *A. Belianinov*, Iowa State University & Ames Laboratory U.S. D.O.E.

It is well-known that conversion of Si(111)-(7x7) into the (√3x√3)R30° phase of adsorbed Ag requires a change in the Si density, and causes formation of islands and holes at the surface. By mass balance, the ratio of areas of islands and holes (R_{IH}) should be approximately 1. However, we find that the ratio is significantly higher, depending on preparation conditions. A possible explanation would be that there are different types of (√3x√3)R30° structures. However, neither scanning tunneling microscopy nor density functional theory (implemented as a genetic algorithm search) supports this explanation. The reason for the unexpectedly high values of R_{IH} is unknown.

P.A.C.S. Numbers 68.37.Ef, 68.55.-a, 81.15.Aa, 68.47

SS-TuP13 Secondary Electron Yield for As-Received, Electrodeposited, and Crystalline Silver Surfaces. *T.P. Graves*, *P.D. Fuqua*, *P.M. Adams*, *R. Spektor*, *J.R. Lince*, *D.B. Witkin*, The Aerospace Corporation

Silver electroplating is commonly used to provide low electrical loss characteristics for RF and microwave devices. These RF devices can also be susceptible to multipactor discharge, a resonant electron phenomenon that relies on electron density growth by secondary electron emission. The secondary electron yield (SEY) can determine whether a multipactor discharge can form; therefore, understanding SEY variations in silver surfaces is necessary for accurate multipactor breakdown prediction. In this work, SEY is measured for a variety of silver surfaces using a retarding

potential method. Starting with as-received silver with no specific surface preparation, SEY values are shown to be considerably increased due to adsorbed gases on both bulk and electrodeposited silver substrates. Auger analysis was performed to determine the contaminant layers, as it is these technical silver surfaces that are realistic for space hardware where in-situ surface conditioning is not possible. Additional SEY measurements were performed on both polycrystalline and single crystal silver surfaces to determine the effect of the crystalline orientation on the SEY. Different crystallographic orientations at the surface of the electrodeposit may arise due to differences in plating variables such as bath chemistry, electrode geometry and localized current density. These measurements serve to better understand possible improvements in plating processes to minimize secondary electron emission and multipactor risk. Lastly, the effect of baking and multipactor conditioning on silver SEY is presented. Formation of thin carbon films are observed as a result of multipactor exposure, and x-ray photoelectron and Raman spectroscopy film analysis results are presented.

SS-TuP14 Characterization and Chemical Activity of Supported Ni-Au and Pt-Au Bimetallic Clusters: Reactions of Methanol. *S.A. Tenney*, *B.A. Cagg*, *W. He*, *D.A. Chen*, University of South Carolina

The activity of methanol on Ni-Au and Pt-Au clusters deposited at 300 K on TiO₂ (110) was investigated using temperature programmed desorption (TPD), scanning tunneling microscopy (STM), and low energy ion scattering (LEIS). Bimetallic clusters were grown by first depositing the metal with stronger metal-support interactions (Ni or Pt) onto the surface in order to seed the more mobile Au at existing Ni or Pt clusters. The preexisting Ni or Pt clusters also inhibited the sintering of Au at higher temperatures. The composition at the surface of the clusters was established by the major products observed in TPD experiments. Methyl (~717 K) was produced on the TiO₂ support, CO (~429 and ~775 K) and H₂ (~357 K) were produced at Ni sites, and formaldehyde (~580 K) production was attributed to the Au-titania interface. CO (~503 K) and H₂ (~503 K) were also characteristic of Pt at the surface. LEIS data for 0.25 ML of total coverage shows that for clusters with > 50% bulk Au composition, the surface of the cluster is almost entirely pure Au. TPD of methanol on clusters with > 50% bulk Au composition still show activity characteristic of Ni or Pt at the surface, suggesting that methanol is able to induce the migration of Ni and Pt to the surface of the clusters. Increasing the amount of Au on the surface for pure Au clusters beyond 1 ML resulted in a decrease of the formaldehyde signal, which is attributed to a subsequent decrease in the Au-TiO₂ interface as more Au is deposited onto the surface. Formaldehyde production on 0.25 ML of pure Au and 25% Ni / 75% Au clusters showed no decrease in activity even after 6 consecutive TPD cycles to 800 K.

SS-TuP15 Growth of Nanoparticles and Reactivity of a Copper Metal-Organic Precursor on Functionalized Silicon Surfaces. *K.A. Perrine*, *J. Lin*, *A.V. Teplyakov*, University of Delaware

As the sizes of the devices are quickly approaching the nanometer scale in the microelectronics industry, the need to control reactions at the molecular level and at the interface becomes very important for developing cleaner deposition techniques. For example, metal contacts grown using atomic layer deposition (ALD) have already made an impact on modern devices.

A common precursor used to grown copper metal contact, Cu^I (hexafluoroacetylacetonato) vinyltrimethylsilane or Cu(hfac)VTMS, has been previously studied at the molecular level on Si(100)-2x1 and other surfaces using surface sensitive techniques. Here we use this precursor as a reactant on several functionalized silicon surfaces to produce and control the size distribution of metallic nanoparticles.

We compare the reaction of Cu(hfac)VTMS with H-Si, NH₂-Si, NH-Si, and OH-Si surface reactive sites and follow it by *in situ* infrared spectroscopy (FTIR), temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and complement with Density Functional Theory calculations. The growth of the hfac vibrational signatures indicates reaction on these functionalized surfaces and losses in the Si-H stretch spectral region can be used to follow the deposition kinetics. The surface is used here as a reducing agent providing the hydrogen to remove the ligands of the copper deposition precursor and to produce metallic nanostructures.

SS-TuP16 Preparative Mass Spectrometry: A Novel Approach for the Creation of Catalyst Materials. *G. Johnson*, Pacific Northwest National Laboratory, *W.-P. Peng*, National Dong Hwa University, Taiwan, Republic of China, *R.G. Cooks*, Purdue University, *J. Laskin*, Pacific Northwest National Laboratory

Soft- and reactive landing of mass-selected ions onto surfaces is a unique approach for the highly controlled preparation of catalyst materials that are often inaccessible using conventional synthesis techniques. Mass selection

allows polyatomic ions with known charge and chemical identity to be deposited onto surfaces under carefully controlled conditions, thereby avoiding purification steps which are typically necessary with traditional catalyst preparation methods. A new apparatus has been designed and assembled at PNNL that allows in situ reactivity and time of flight secondary ion mass spectrometry analysis of surfaces prepared or modified through soft- and reactive landing. The capabilities of this instrument for the preparation and analysis of catalyst materials are demonstrated for two different systems consisting of monolayer catalysts produced by the deposition of organometallic metal-salen and ruthenium bipyridine cations onto self assembled monolayer surfaces. It is shown that through soft landing of vanadium-salen cations and a proton donor it is possible to achieve proton mediated reactivity in an inert fluorinated monolayer that is normally only observed in highly acidic solutions. In addition, it is demonstrated that gas-phase ligand stripping may be used to generate highly reactive undercoordinated metal complexes which exhibit enhanced activity towards reactive landing in comparison to fully ligated species. The immobilized complexes, which are covalently bound to the surface, are shown to exhibit catalytic activity when exposed to gaseous reagents.

SS-TuP17 Charge Transfer and Shake Satellites in XPS: A Unified View, C.J. Nelin, Maury's Trail, P.S. Bagus, University of North Texas, H.-J. Freund, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The satellites in X-Ray photoemission spectroscopy, XPS, can provide information about the electronic structure, especially for ionic materials. [1,2] We present a new analysis of the XPS satellites that, when applied to CeO₂ which is an important substrate for model studies of catalysis, enables a new understanding of this material. While the origin of intra-atomic effects in terms of atomic near-degeneracies is well understood, [1] there are two different ways of describing the inter-atomic effects that lead to satellites. The first is to ascribe the satellites to charge transfer, CT, from ligands, or other neighboring atoms, into unoccupied or partly occupied shells of the ionized atom. This interpretation is commonly applied to oxides and other ionic crystals. [2] In the CT model, the satellites gain intensity through the mixing of XPS allowed configurations with XPS forbidden configurations. However, changes in the orbitals between the initial and final states are normally neglected in the CT model. On the other hand, the second way of understanding satellites as shake satellites, [3,4] ascribes the driving force for the loss of intensity from the main peak into the satellites to the orbital relaxation, which screens the core-hole. This orbital relaxation allows valence excited, or shake, states to obtain intensity. [3] However, both mechanisms must be taken into account to correctly describe the inter-atomic contributions to XPS satellites and, in the present work, we reconcile these two different points of view. We show that the covalent mixing of metal and ligand orbitals in the wavefunctions, for both initial and final states, is a powerful way to understand the intensities of satellites due to inter-atomic effects. For the XPS of NiO, where both intra and inter-atomic effects must be taken into account, our analysis of the CI wavefunctions shows the underlying covalent character of the main and satellite peaks. We also stress the importance of covalent mixing in the initial state in order for there to be substantial satellite intensity. We show that different degrees of covalent character in the initial states of CeO₂ and LaAlO₃ lead to very different satellite energies and intensities for the isoelectronic metal cations. Our analysis provides direct and unambiguous evidence that the inter-atomic satellite features are closely related to the covalent binding in the material.

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SS-TuP18 XPS Investigation of Volcanic Ash and Other Basalt Materials, P. Mack, T. Nunney, R.G. White, A. Wright, ThermoFisher Scientific, UK

XPS has been used to analyse the ash released from a number of volcanoes, including that from Mount St Helens, USA and Eyjafjallajökull, Iceland. The results indicate that the differences in the composition of the basalt from different regions reflect the geological structure of the region. Some of the compositional differences depend upon whether the geological plates are moving together, causing more crust material to be mixed with the lava or whether the plates are moving apart and so the lava is predominantly from sub-surface sources. Further complications arise from the fact that the ash from some eruptions (e.g. Eyjafjallajökull) also contains material from an overlying glacier. It has been found that the material from Eyjafjallajökull is richer in calcium than that from Mt St Helens.

The use of XPS to fingerprint this type of material has been investigated. The effect of ion sputtering of the material has also been investigated as a means to generate more representative data.

SS-TuP19 Combined Surface Analysis and Electrochemistry Studies on SnO₂-Pt and Sn-Pt Electrocatalysts for Ethanol Oxidation Reaction, S. Axnanda, W.-P. Zhou, M.G. White, J. Hrbek, Brookhaven National Laboratory

SS-TuP20 One-dimensional Coordination Chains of 4,4'-azopyridine on Cu(100) by Self-assembly, H.A. Lim, S.L. Tait, Indiana University

We have observed highly-ordered 1D chains of 4,4'-azopyridine (AZPY) formed by self-assembly on the pristine Cu(100) surface at room temperature. AZPY is of particular interest as a building block due to its π -conjugated system, photoactive azo site and coordinative bonding with transition metals in metal organic framework materials. Scanning tunneling microscopy shows that the APY molecules grow in one-dimensional chains, mostly starting from copper step edges, with an end-to-end pyridine-Cu-pyridine interaction. The APY chain structure, oriented along the [110] direction, is a significant departure from the side-to-side molecular arrangement in self-assembled azobenzene chains at surfaces. As the coverage increased mobile molecules are observed to be confined inside 2D APY corrals composed of a framework of intersecting chains. X-ray photoelectron spectroscopy is also used for characterization. Further studies are underway to investigate these assemblies on other surfaces as well as functionality of these systems for applications such as nano-electronics, molecular magnetism and single-site heterogeneous catalysis.

SS-TuP21 Surface Adhesion Properties of Block Copolymer Films, M. Palacio, S. Schrickler, B. Bhushan, The Ohio State University

Block copolymers are of interest as scaffold materials for cell growth and regeneration because novel, structurally diverse polymers can be synthesized from biocompatible blocks. The nanostructure and surface morphology of block copolymers can be modulated using synthetic techniques and the nanostructures can be used to affect surface mechanical behavior. We present atomic force microscopy (AFM) studies on the morphology and corresponding protein adhesion interactions of a novel class of methyl methacrylate and acrylic acid diblock and triblock copolymers. Distinct nanomorphologies were found on diblock and triblock copolymers even though their chemical compositions are identical. This has implications on the role of nanomorphology in cell-polymer interactions. Protein adhesion on a biomaterial surface is critical to understanding its biocompatibility. Bovine serum albumin (BSA) was attached to the AFM tip in order to model protein-block copolymer interactions.

SS-TuP22 XPS Organic Depth Profiling Analysis of Poly-glycidyl Methacrylate Brushes, S. Alnabulsi, J.F. Moulder, Physical Electronics, R. Barbey, H.A. Klok, Ecole Polytechnique Fédérale de Lausanne, Switzerland

The application of XPS C₆₀ sputter depth profiling to characterize synthesized poly-glycidyl methacrylate (PGMA) brush-like thin film structures will be presented. In contrast to low voltage (250 V) Ar sputtering, C₆₀ sputtering with XPS analysis was able to obtain quantitative chemical state information as a function of depth with minimal ion beam induced chemical damage. To minimize sputtering artifacts and improve interface definition, Zalar (azimuthal) rotation and appropriate instrument geometry for C₆₀ sputter depth profiling was used for this work. The XPS depth profiles show the chemical changes associated with various solutions applied to these organic films.

SS-TuP23 Particles from the Ozonolysis of Unsaturated Silane Self-Assembled Monolayers, T.M. McIntire, O. Ryder, University of California, Irvine, P. Gassman, Z.H. Zhu, Pacific Northwest National Laboratory, S. Ghosal, Lawrence Livermore National Laboratory, B. Finlayson-Pitts, University of California, Irvine

Airborne particles have well-documented effects on human health, visibility, and the chemistry of the atmosphere. Particles play a major role in climate change and are a large source of uncertainty in model predictions of global warming. A significant part of this uncertainty is the lack of understanding of the nature of the organic component. This deficiency includes the chemical speciation and the distribution of the organics between the surface and the bulk of liquid particles, as well as changes due to oxidation during transport in the atmosphere.

Self-assembled monolayers (SAMs) represent a well-defined system for elucidating mechanisms of mixed gas-condensed phase reactions and serve as proxies for organic-coated airborne dust particles. Previous studies have shown that ozone reactions of terminal alkene-silane SAMs generates surface-bound acids, aldehydes, and secondary ozonide (SOZ), as well as gaseous products such as CO, CO₂, HCHO, and HCOOH. In addition, the surprising formation of large, hydrophobic organic particles was observed by AFM and Auger electron spectroscopy. A particularly noteworthy result of atmospheric interest is that the uptake of water was not increased upon oxidation of these films, despite the formation of polar carbonyl-containing

groups, and SOZ. This has important implications for particles in the atmosphere, since it is generally assumed that oxidation converts hydrophobic surfaces to hydrophilic which take up water more readily, thereby affecting visibility and cloud formation.

The goal of this work was to determine the product functional groups and the 3-D structure of particles produced from the ozonolysis of SAMs formed by attachment of 7-octenyltrichlorosilane (C8= SAM) to silica substrates. A combination of analytical techniques such as single particle FTIR, NanoSIMS, and TOF-SIMS were utilized to study the surface composition and morphology after oxidation. Atmospheric implications for the 3-D structure of SOA, SAM reactions and stability in air, ozonolysis of alkenes on surfaces, and the oxidation of alkenes on airborne dust particles will be discussed.

SS-TuP24 Temperature Programmed Desorption Study of CO on Cr(110) and Cr₂O₃(0001)/Cr(110), J.L. Walters, G. Arellano, W.A. Harrison, C.A. Ventrice Jr., H. Geisler, Texas State University - San Marcos

The adsorption kinetics of CO on Cr(110) and on Cr₂O₃(0001)/Cr(110) was investigated using temperature programmed desorption (TPD). The adsorption of CO was performed with the substrate maintained at 120 K, and a feedback control system was used to generate linear heating rates. For the Cr₂O₃(0001)/Cr(110) surface a saturation coverage of CO was measured to occur at 0.5 L. The desorption kinetics is estimated to be 1st order with an attractive lateral interaction between CO molecules. The Redhead method was used to measure the activation energy for desorption of the CO. This analysis resulted in a value of 49.2 kJ/mol ± 2.6 kJ/mol for the activation energy. For the adsorption of CO on Cr(110) no CO desorption is detected for coverage below 0.5 L. This indicates that at this coverage all of the CO is dissociating and reacting with the Cr(110) surface. Deposition of 1L CO on clean Cr(110) shows only one broad signal at 300 K. By deposition of 2 L of CO or larger, a shift of the signal to 280 K and the appearance of a second signal at 210 K can be observed. The broadening and shifting of the desorption signals can be attributed to the lateral interaction between the CO molecules and their adsorption on different binding sites on the Cr(110) surface.

SS-TuP25 Creation of NO Dissociation Sites Over the Pd/Al₂O₃ Surface, I. Nakamura, T. Fujitani, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of Rh in three-way catalysts is currently required. Pd catalysts, which have shown a high initial activity for NO reduction compared with that of Rh catalysts, have received much attention as possible substitutes for Rh. To develop high performance Pd catalysts, the nature of active sites must be clarified, as well as the effect of oxide supports on the supported Pd. In this study, we investigated the influence of an Al₂O₃ support on the electronic state and NO dissociation activity of supported Pd using a Pd-deposited Al₂O₃/NiAl(110) surface. NO was exposed at 300 K to the 2 ML Pd/Al₂O₃ surfaces annealed at different temperatures. Only molecularly adsorbed NO was observed on the Pd/Al₂O₃ surface after deposition of Pd at 300 K. In contrast, the formation of atomic nitrogen was seen on the Pd/Al₂O₃ surface annealed above 350 K, suggesting that NO dissociation sites were created after annealing. The adsorbed NO was completely dissociated over the Pd/Al₂O₃ surface annealed above 500 K. We compared the NO dissociation activity over the 500-K-annealed Pd/Al₂O₃ surface with that observed over a stepped Pd(311) single crystal surface, since the step sites on Pd surfaces are known to be active sites for NO dissociation. It was clearly shown that the NO dissociation reaction over the Pd/Al₂O₃ surface proceeded at a much lower temperature compared with that required for NO dissociation over the Pd(311) surface. We found that the active sites created on the annealed Pd/Al₂O₃ surface had a high NO dissociation ability. To clarify the nature of the Pd active sites for NO dissociation, we examined the electronic state of the Pd particles deposited on the Al₂O₃ surface. It was shown that the Pd was oxidized to Pdⁿ⁺ ($n < 2$) by lattice oxygen atoms in Al₂O₃ after annealing above 500 K. Therefore, we concluded that the positively charged Pdⁿ⁺ species created by annealing the Pd-deposited Al₂O₃ surface at temperatures higher than 500 K were effective for NO dissociation at low temperatures.

SS-TuP26 Analysis of the Characteristics of Nickel-Plating Baths, A.O. Gezerman, B.D. Corbacioglu, Yildiz Technical University, Turkey

Nickel plating processes, popularly used in Europe in the 1950s, have been increasingly employed in Turkey in recent years; as a result, industrial usage has developed rapidly. Nickel plating is the preferred process for this study because of the uniformity of the plating thickness on the plated surface and the ease with which complex components can be plated. It is also resistant to corrosion and has good hardness levels.

In this experiment, the following parameters were investigated: the effect of varying the amount of nickel, the thickness of the plating, and sheen (whether shiny or dull).

In this study, brightener and carrier agents have been used to determine the best operational parameters for the Kale Kilit Factory. The compositions of the brightener and carrier agents used in the experiment is included in this text.

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