Tuesday Afternoon Poster Sessions

Surface Science Division Room: East Exhibit Hall - Session SS-TuP

Surface Science Poster Session

SS-TuP1 Oxidative-Coupling Reactions via Nucleophilic Attack on Gold Surface, B. Xu, C.M. Friend, R.J. Madix, Harvard University

Metallic gold owes its centuries-old mystique and intrinsic value to its chemical inertness toward bulk compound formation. In the past decade, however, it has been discovered that the surface of gold is far from inert, and that gold can catalyze important chemical transformations - particularly with the assistance of molecular oxygen or other oxidizing agents. These processes are of particular significance because they may occur at remarkably low temperatures and pressures, suggesting the possibility of energy efficient and environmentally benign reaction conditions using metallic gold catalysts. Recently, there has been a focus on selective oxidation of alcohols to aldehydes, oxidative self-coupling of alcohols to form esters and, most recently, acylation via amine-formaldehyde coupling. Our work under ultra-high vacuum (UHV) condition on the well defined model system of Au(111) surface has unequivocally proved that surface adsorbed atomic oxygen is critical in facilitating a range of nucleophilic coupling-reactions among alcohols, aldehydes and amines. A general reaction mechanism for this class of coupling-reactions is established: surface alkoxy or amide is formed via the deprotonation of the corresponding alcohol or amine by surface atomic oxygen, which can subsequently nucleophilically attack the aldehydes (formed in situ from alkoxy or introduced directly) and produce the corresponding ester or amide. The product distribution of our low-pressure experiments match remarkably well with gas phase reactions carried out in the ambient condition as well as liquid phase reactions, proves the generality of the mechanism.

SS-TuP2 Many-Body Interactions in Quasi-Freestanding Graphene,

D.A. Siegel, C.H. Park, University of California, Berkeley, C.G. Hwang, Lawrence Berkeley National Laboratory, J. Deslippe, University of California, Berkeley, A.V. Fedorov, Lawrence Berkeley National Laboratory, S.G. Louie, A. Lanzara, University of California, Berkeley

Until recently it had been extremely difficult to experimentally address one of the most fundamental questions about graphene: How do the quasiparticles behave in neutral graphene, i.e. when the chemical potential coincides with the Dirac point energy? Here we address this question by investigating graphene on a particularly interesting substrate, the carbon face of SiC, with high-resolution angle-resolved photoemission spectroscopy (ARPES). We present the first direct measurements of the self-energy in graphene near the neutrality point, and show that the manybody physics in graphene differ from those of an ordinary metal. These exciting findings set a new benchmark in our understanding of many-body physics in graphene and a variety of novel materials with Dirac fermions.

SS-TuP3 Edge Termination of Modified Graphene Oxide during Thermal Exfoliation, *M. Acik, Y.J. Chabal*, The University of Texas at Dallas

Nanopore formation in carbon materials (e.g. exfoliated nanostacks of graphite) has been widely studied through mechanical exfoliation, intercalation, electrochemical separation, chemical or thermal exfoliation of graphite oxide (GO) via expansion with partial oxygen removal. Amongst all these methods, exfoliation of modified graphene (GO), a solutionprocessable precursor compound where aromatic and heterocyclic rings with embedded oxygen functionalities exist, by thermal processing still remains elusive for the following reasons: (1) poor control of GO composition (initial oxygen content), (2) poor understanding of the chemical composition, (3) unknown role of oxygen, adjoining oxygen interactions, and edge termination with oxygen. Infrared absorption spectroscopy coupled with in-situ thermal annealing process [1] makes it possible to examine the chemical changes taking place during thermal reduction to identify and understand interacting molecular environment and the edge functionalization. To unravel the complex mechanisms leading the removal of oxygen in GO, we have performed in-situ transmission infrared absorption spectroscopy (IRAS) measurements of graphene/graphite oxide (GO) thin and bulk films upon thermal annealing (60-850°C) in vacuum (10⁻³-10⁻⁴ Torr). Control of the edge geometry of finite-sized modified graphene flakes depends very much on the control of the processing methods. This edge reconstruction further determines electronic, electric, optical and mechanical properties of the exfoliated modified graphene flakes. Therefore, we not only perform studies deriving a thermal reduction mechanism, but also examine the edge reconfiguration with oxygen. We

report here the observation of a surprisingly strong IR absorption band that occurs only upon thermal reduction of GO. After annealing at 850°C in vacuum, the strong enhancement of the new IR active absorbance band is observed at ~800 cm⁻¹[2]. The intensity of this band is 10-100 times larger than what is expected for the oxygen content of the reduced GO, namely between 5 and 8 at.%. This band is assigned to a specific oxidation state, involving oxygen located in the basal plane (forming C-O-C bonds) and at *atomically straight* edges of reduced graphene. The large enhancement in IR absorption is attributed to the direct participation of electrons, induced by the asymmetric C-O-C stretch mode displacement. These findings open new possibilities in the field of nanoelectronics for all sensor and energy storage applications. [1] M. Acik, *et al.* J. Am. Chem. Soc. (2011), *in preparation.* [2] M. Acik, *et al.* Nat. Mater. 9, 840-845 (2010).

SS-TuP4 Electrocatalytic Surfaces: Structure, Reactivity and Nanotemplating, *X.F. Yang**, Lehigh University, *B.E. Koel*, Princeton University

Electrocatalysis in energy related applications such as fuels cells and hydrogen production impacts and possibly defines the future energy technology picture. Pt-based electrocatalysts are widely used because of their exemplary performance, but these catalysts have serious drawbacks, e.g., cost, modest efficiency, and low durability, which limit fuel cell development. Our research explores non-Pt electrocatalysts or ultrathin-Pt film electrocatalysts to gain insight and discover materials that can replace Pt or greatly red uce Pt loadings while retaining or even increasing activity and/or stability. Our approach is to using model electrocatalyst surfaces with well-defined composition and structure to simplify and exert control on the system to improve our understanding of the surface phenomena that control electrocatalytic reactions. In this work, four types of model electrocatalysts were prepared in UHV: (i) Pd₃Fe(111), (ii) Au/Pd₃Fe(111), (iii) Pt on a faceted C/Re(11-21) nanotemplate, and (iv) Pt/HfIr₃ (poly). These surfaces were characterized using LEED, XPS, LEIS, and AES, and then their electrocatalytic activity for the oxygen reduction reaction (ORR), the hydrogen evolution reaction (HER), and ethanol oxidation (EO) reaction was measured.

Significant surface segregation of Pd was discovered after clean Pd₃Fe(111) was annealed at high temperatures in UHV. The surface structure strongly depends on the annealing temperature, with the formation of an atomically smooth, random substitutional alloy by heating to 1000 K, and the formation of Pd monomer and dimer adatoms by heating to 1250 K. The annealed Pd₃Fe(111) surfaces exhibit higher ORR reactivity than pure Pt. When a submonolayer amount of Au was deposited on Pd₃Fe(111), the Au/Pd₃Fe(111) surface was found to be highly active for the ORR. The activity was strongly dependent on the Au coverage, with the highest activity found at 0.6-ML Au. A Pt monolayer deposited on a nanofaceted C/Re(11-21) surface had a catalytic activity higher than Pt(111) for the HER. In addition, a Pt monolayer on a polycrystalline HfIr₃ substrate displayed great improvement in reactivity for electrochemical ORR and EO. In summary, we have investigated a range of non-Pt and ultrathin-Pt film model electrocatalysts that are more active than pure Pt and that point to new materials that could be used to reduce cost and improve activity by nanoengineering novel electrocatalysts.

SS-TuP5 Characterization and Chemical Activity of Pt-Au and Ni-Au Bimetallic Clusters on TiO₂(110), S.A. Tenney*, B.A. Cagg, W. He, M.S. Levine, R.P. Galhenage, D.A. Chen, University of South Carolina

Oxide-supported bimetallic Pt-Au and Ni-Au clusters were studied as model catalysts for low temperature oxidation reactions. The growth, composition, and chemical activity of Ni-Au and Pt-Au clusters deposited at 300 K on TiO₂(110) were investigated using scanning tunneling microscopy (STM), low energy ion scattering (LEIS), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). The importance of the Autitania interface for low temperature oxidation was illustrated by a series of TPD and STM experiments that show a direct correlation between the number of Au-titania interfacial sites and the activity on the surface. Bimetallic clusters were grown by first depositing Ni or Pt onto the surface in order to seed the more mobile Au at existing Ni or Pt clusters. The surfaces of the bimetallic clusters are significantly enriched in Au and are almost entirely pure Au for clusters with > 50% bulk Au composition. TPD of methanol and CO on bimetallic clusters that are highly enriched in Au at the surface still show significant activity characteristic of Ni or Pt at the surface, suggesting that methanol and CO are able to induce the diffusion of Ni and Pt to the surface of the clusters. Heating the bimetallic clusters above 600 K results in the selective encapsulation of Pt or Ni by a thin film

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of titania. Pre-annealed Pt-Au and Ni-Au bimetallic clusters show promise for enhanced activity towards the conversion of methanol to formaldehyde.

SS-TuP6 Pattern Formation through Leveled Copper Etching after Dysfunctional Electropolishing, A.D. Pauric, P. Kruse, McMaster University, Canada

Electropolishing is a common industrial practice whereby a metallic surface is subjected to an anodic potential in an appropriate electrolyte to produce a microscopically smooth surface. It is typically performed in concentrated acid with cell potentials ranging from between 1.3 and 2.3V. However, little research has been conducted in the parameter space outside the electropolishing regime. Previous research in our group using deviations from electropolishing conditions has characterized a wide range of fascinating surface structures including terraces, oxide nanotubes, stripes, and dimples. Our current work involves using the copper/phosphoric acid system as a model system to study deviations from electropolishing conditions and the resultant surface features.

Upon exposing copper substrates to a high applied cell potential in concentrated phosphoric acid, etched surface patterns up to over a micron in depth are observed. Characterization of the patterns includes the use of atomic force microscopy (AFM), scanning electron microscopy (SEM), and surface enhanced Raman spectroscopy (SERS). The surface patterns evolve with variation in temperature and phosphoric acid concentration. A distinguishing feature is that the patterns are etched into rather than grown upon the copper substrate, promoting mechanical stability. Additionally, the tops of the surface features are level with respect to their surroundings. Potential applications include electrodes, current collectors for lithium ion batteries, catalysts, micro-cooling, and substrates for the fabrication of other surface morphologies.

SS-TuP7 Surface Chemistry of Atomic Layer Deposition of Manganese

Thin Films, H. Sun, X. Qin, F. Zaera, University of California, Riverside Manganese thin films can potentially be used as Cu diffusion barriers in microelectronic devices, and may possibly be grown by atomic layer deposition (ALD), to produce highly uniform thin films with good conformality in high aspect-ratio structures. Here, the early stages of film growth of two precursors, methylcyclopentadienyl manganese tricarbonyl (CH3C5H4)Mn(CO)3) and dimanganese decacarbonyl (Mn2(CO)10), were investigated by X-ray photoelectron spectroscopy (XPS) to assess their viability for ALD of manganese thin films. In most cases, only oxidized manganese could be deposited on silicon substrates covered with their native oxide layer. Only in depositions using (CH3C5H4)Mn(CO)3 at relatively high temperatures (>300°C) it was possible to detect a low binding energy feature in the Mn 2p XPS that could be assigned to metallic Mn (although it is also possible to come from manganese silicate). It was also determined that that low-binding-energy manganese species appears only after the growth of a layer of oxidized manganese, and seems to form in the sub-surface. Electron-induced deposition was also studied and compared with the thermal process. The Mn2(CO)10 precursor was much more reactive, and could lead to multilayer deposition by itself at temperatures as low as 200°C

SS-TuP8 Spin Effects on Metal Surface Reactions: O_2 on Ferromagnetic Pt, *M.C. Escano, N.T. Quang, H. Nakanishi,* Osaka University, Japan, *E. Gyenge,* The University of British Columbia, Canada, *H. Kasai*, Osaka University, Japan

We studied O_2 chemisorption on Pt surface in the need to promote O_2 activation. Activation, in this case, is defined as lowered activation barrier for O₂ dissociation but minimized O adatom (O_{ad}) binding energies; or a significantly stretched O-O bond in a loosely bound molecular O2. This kind of reaction is not easy to attain since O2 may present the same affinity to surface in its reaction path. However, such unique reaction is often sought in many electrochemical/chemical systems (i.e. fuel cell cathode catalyst, three-way automotive catalyst). Here, we show how the magnetic state of Pt can achieve this desired reaction. The model system involves a nonmagnetic Pt layer pseudomorphically laid on top of magnetic surface (M=Fe(001), Co(001)). The ab-initio calculation based on spin-polarized density functional theory, suggests that the magnetic ground state of the system is a ferromagnetically coupled Pt-M layers[1]. The induced spin moment of $0.50\mu_B$ in the Pt layer is in agreement with X-ray Magnetic Circular Dichroism (XMCD) [2]. The hybridization of Pt-5d with the M-3d states give characteristic exchange splitting similar to the spin-resolved inverse photoemission spectroscopy [3]. Using the Heisenberg spin Hamiltonian to determine the exchange interaction, we note that strong inter-layer coupling of the Pt-M spins gives a transition temperature of Pt layer higher than room temperature, in agreement with [2,3].

Potential energy surfaces obtained for O_2 dissociative adsorption on ferromagnetic Pt layer show much lower activation barrier for dissociation and also lowered O_{ad} binding energy. For molecular adsorption, the O_2

vibrational frequency is lower on ferromagnetic Pt as compared to paramagnetic Pt, despite the much lower binding energies on the former. We note that spin effects played significant role rather than charge transfer effects on the over-all structure and binding of the O_2 at transition state and on the surface [4]. This will be discussed in the meeting in terms of local density of states, charge transfer and spin density, and other parameters involved in the bonding and magnetic interactions.

References

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SS-TuP9 X-ray Diffraction Study on Hydrogen-Induced Pd(110) Surface Reconstruction, *M. Takahasi*, *S. Fujikawa*, *W. Hu*, Japan Atomic Energy Agency, *H. Tajiri*, Japan Synchrotron Radiation Institute

Absorption of hydrogen into a substrate begins with dissociated adsorption of hydrogen molecules. The mechanism of the transition from adsorption to absorption is an important knowledge for improving the performance of hydrogen storage materials. The aim of the present study is to verify the hydrogen absorption model in atomic scale through quantitative determination of structures of hydrogen-adsorbed Pd(110) by synchrotron X-ray diffraction.

Experiments were performed at a synchrotron beamline 13XU at SPring-8 using a surface X-ray diffractometer integrated with a UHV chamber equipped with a cryostat. The sample was Pd(110) single crystal which was 10 mm in diameter and 3 mm in thickness. The clean Pd(110)-(1x1) surface was prepared by electrochemical etching in HCl solution and cycles of Arsputtering and annealing at ca. 900 K in UHV. For the hydrogen adsorption experiments, the hydrogen pressure was carefully controlled with a needle valve and a nude ion gauge.

We measured five crystal truncation rod (CTR) profiles with increasing substrate temperature to room temperature from 57 K after the substrate was exposed to 10⁻⁶ Torr s hydrogen. Before and after hydrogen adsorption at 57 K, the CTR profiles changed only slightly. More distinctive changes were observed when the sample temperature reached 180 K. At room temperature, the CTR profiles were accounted for by a structure model with disordering of surface atoms. According to past Low-energy electron diffraction, He diffraction and thermal desorption spectroscopy studies, hydrogen adsorption below a substrate temperature of 120 K induced the (1x2) surface reconstruction with 1.5 monolayer (ML) hydrogen through the (2x1) structure at a hydrogen coverage of 1 ML. When the temperature is raised to 200 K, the (1x2) reconstruction returns to a low-coverage 2x1 phase without hydrogen desorption. A comparison with our X-ray diffraction results and these past studies shows that the change of the CTR profiles at 180 K corresponds to the transition from the (2x1) to (1x2) reconstructions and concomitant incorporation of hydrogen into subsurface. These results provide us with an atomic-scale picture that explains how adsorbed hydrogen is absorbed into the Pd bulk.

SS-TuP10 Single Molecule Force Spectroscopy Studies on Nanoclay Surfaces, B. Ozkaya, G. Grundmeier, University of Paderborn, Germany

Sequential adsorption of oppositely charged polyelectrolytes leads to multilayered thin films via electrostatic self-assembly. Incorporation of sheet-like inorganic nanoparticles is a promising method to improve barrier and ion transport properties, as well as mechanical properties in such films. The interface chemistry between the nanosheets and the polyelectrolyte segments plays a crucial role on design of thin coatings with tailored properties. In the present study, we have investigated the effects of pH and ionic strength on the adsorption of single polyelectrolyte molecules on natural clay (Na-Montmorillonite) platelets by means of AFM-based single molecule force spectroscopy (SMFS). SMFS is one of the few methods where in-situ experiments can be performed to obtain precise and quantitative information on interaction forces at a molecular level. In order to perform SMFS on clay platelets (lateral size: 50-300 nm), a heterogeneous model surface has been obtained via electrostatic immobilization of exfoliated clay platelets on template stripped ultra-flat Au(111) surfaces. Probe molecules (polyallylamine) were covalently attached to the gold coated AFM cantilever. Equilibrium desorption plateaus of constant force were obtained from the successive force-distance measurements. By adjusting the ion valency in the electrolyte, selective information from clay platelets could be obtained. In the presence of monovalent ions, desorption plateaus of constant force in the range of ~ 50 pN were obtained from pH 3 to pH 7. At pH values above the pK_b value of polyallylamine,-confirmed with polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) measurements on cast polyallylamine- no detectable desorption event took place. The constant negative surface charge of clay platelets simplifies the evaluation of effects of electrical double layer and polymer line-charge density on adsorption of the polyelectrolyte molecules. Overall, the results of pH and ionic strength dependent de-adhesion measurements provide valuable information on the interplay between surface properties and polyelectrolyte adsorption giving the basis for an improved understanding of the behavior of silicate nanoparticles in polyelectrolyte films.

SS-TuP11 Atomic Structure of Aluminum on Si(110): STM and Firstprinciples Study of "4 × 6" Reconstruction, *M. Yoshimura*, *D. Matsuoka*, Toyota Technolgocial Institute, Japan

With the miniaturization of semiconductor devices, low-dimensional structures such as quantum wires and quantum dots have recently attracted much attention. The " 16×2 " on a clean Si(110) surface has been noticed as an effective and unique substrate for the fabrication of low-dimensional nanostructures, because the one-dimensional undulated terrace structure of monatomic height and of about 2.5 nm width are formed. Because the hole mobility of Si(110) surface is about 1.5 times as large as that of Si(100) typically used as substrates of present semiconductor devices, higher speed operation is expected [1]. Thus, the interaction between Si(110) and metal is very important [2,3]. Aluminum is the typical metal forming Schottky barrier with silicon and the Al-adsorbed structures have been well examined on Si(111) or Si(001) plane [4,5]. In contrast, little is known about the structures of the Al/Si(110), particularly in real-space. In this study Al/Si(110) surfaces are investigated in real space using STM and first-principle calculation.

The experiments were carried out in an ultrahigh vacuum (base pressure: 2.0×10^{-8} Pa). First-principles calculation was performed using VASP program [6]. Aluminum was deposited on a clean Si(110)- "16 \times 2" at 600 °C for 10 min to prepare a "4 \times 6" reconstruction [7]. In the empty state, alternative arrangement of zigzag rows and straight rows is visible in empty states. In filled states, bright spots are prominent at the position of defects in the zigzag row. They are assumed to be silicon substitutional defects, as is the case for Al/Si(111) [8]. Thus we conclude Al and Si atoms formed zigzag and straight rows, respectively. In addition, the straight row of the silicon was composed of the silicon pentagon [9] as revealed by high-resolution STM. Based on the above observation, an atomic structural model is proposed and discussion will be made based on the theoretical calculation.

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SS-TuP12 Adsorption Dynamics of Ethylene on Si(001), M.A. Lipponer, N. Armbrust, University of Marburg, Germany, M. Durr, HS Esslingen, Germany, U. Hofer, University of Marburg, Germany

The functionalization of semiconductor surfaces by means of organic molecules is of great interest due to possible applications in the field of nanoelectronics. However, only little information on the reaction dynamics of these systems is available. In this work, the adsorption dynamics of ethylene on Si(001) has been investigated. With ethylene being the most simple unsaturated organic molecule, the system serves as a model system for non-activated adsorption on semiconductor surfaces. In order to investigate its reaction dynamics, we employed a supersonic molecular beam which allows for the control of the kinetic energy of the impinging molecules. Additionally, surface temperature and the excitation of internal degrees of freedom were varied when measuring the sticking coefficients as a function of relative surface coverage by means of King and Wells techniques.

With increasing kinetic energy of the impinging molecules, we find a decrease of the initial sticking coefficient as it is typical for non-activated reaction channels; the excitation of the internal degrees of freedom is shown to have a minor impact on the reactivity. With increasing surface temperature, a decrease of the initial sticking coefficient is observed. Surprisingly, the maximum surface coverage also decreases with increasing surface temperature. The results are discussed in the context of a reaction channel via a mobile precursor with long lifetime at low temperatures.

SS-TuP13 Surface Characterization of Polymeric Materials using TOF-SIMS and XPS, J. Lee, K.-J. Kim, Korea University, Republic of Korea, Y. Lee, Korea Institute of Science and Technology, Republic of Korea

TOF-SIMS and XPS are very useful techniques for the analysis of solid surfaces composed of organic and polymeric species. In order to widen the application of TOF-SIMS and XPS to archeology and plasma process, we analyze the dyed fabrics and the fluorocarbon thin films. First, the fabrics dyed with natural dyes and synthetic dyes were investigated with TOF-SIMS and XPS. Dyes investigated belong to various chemical groups, which include indigo, carthamin, crocin, shikonin, curcumin, purpurin and alizarin. TOF-SIMS and XPS spectra for the dyed textiles showed specific molecular ions and fragment ions from organic dyes as well as elemental ions from metallic mordants. Several ancient fabrics were also analyzed to identify the natural dyes. Secondly, Fluorine-containing hydrophobic thin films were obtained by two different plasma methods : inductively coupled plasma (ICP) and pulsed plasma (PP). Three kinds of fluorine-containing gases such as C₂F₆, C₃F₈, and c-C₄F₈ were used to generate hydrophobic plasma polymer films. Process parameters for plasma polymerization such as gas ratio, gas pressure, pulse frequency, and processing time were investigated. Surface analytical instruments such as TOF-SIMS, XPS, and AFM were used to characterize the fluorocarbon thin films generated by ICP and PP. In this work, TOF-SIMS was used to provide useful information about the chemical properties including surface composition and XPS was used to examine the chemical structure of dyed fabrics and fluorocarbon films.

SS-TuP14 Links Between the Surface Atomic Arrangement and Catalytic Properties of Bimetallic Alloys: A First Principles-based Investigation, J.A. Stephens, H.C. Ham, G.S. Hwang, University of Texas at Austin

Catalysts composed of more than one metallic element often exhibit remarkable activity and selectivity compared to their monometallic constituents. These synergistic properties often can be explained in terms of two kinds of effects: modification of catalyst electronic structure due to interactions between dissimilar metal atoms (ligand effects) and the presence of mixed-metal surface sites that, because of their size and shape, promote some chemical reactions more than others (ensemble effects). Understanding in detail how ligand and ensemble effects operate in particular cases is an important step toward realizing the longer term goal of rational catalyst design. Experimental study has provided valuable insight into this problem, but progress has been hampered by the difficulty of studying reacting systems with atomic resolution. We employ the tools of molecular simulation in a two-pronged approach to complement these efforts. First, we use density functional theory to explore how particular atomic arrangements in the surfaces of bimetallic alloys influence their catalytic function. We have found, for example, that the experimentallyobserved ability of Au-Pd catalysts to promote the direct synthesis of hydrogen peroxide may depend on the presence of surface Pd monomers surrounded by Au. Our calculations indicate that on larger Pd ensembles, O-O bond scission can more readily occur, leading to the formation of water. We have similarly studied the oxygen reduction reaction and carbon monoxide oxidation on Au-Pd alloys. In the second prong of our work, we attempt to predict how the metal atoms in catalyst surfaces are actually arranged using a combination of density functional theory, the cluster expansion method, and Monte Carlo simulation. From these simulations, we have obtained the temperature- and composition-dependent ensemble size and shape distributions for the (111) and (100) surface facets of Au-Pd and Au-Pt alloys. Our results are in good agreement with available experimental observations.

SS-TuP15 Nitrogen-Rich Heterocycles and Stimulus-Induced Switching Imaged by Liquid STM, B.E. Hirsch, K.P. McDonald, A.H. Flood, S.L. Tait, Indiana University

Supramolecular motifs that provide controllable functionalization of surfaces on a nanometer scale offer significant advances in organic solar cells and other surface supported systems. Based on recent advances in twodimensional organic self-assembly at the liquid/solid interface, we are developing complex surface architectures based on versatile nitrogen-rich heterocycles. This work focuses on the molecular design and subsequent adsorption of this class of compounds onto graphite (HOPG) utilizing liquid scanning tunneling microscopy to resolve the packing of the individual molecules. Current molecular design includes extended alkyl chains and other substituents including amide linkages to facilitate intermolecular ordering. Exploration of photo-activated, tip-induced, and chemically stimulated switching of these molecules is underway to enable manipulation of patterning and packing. SS-TuP17 Electrical, Physical, and Chemical Properties of the Metal to Amorphous Hydrogenated Boron Carbide Interface, M.S. Driver, S. Karki, A.N. Caruso, University of Missouri - Kansas City

Boron carbide (BC), as a semiconducting material, has been under scrutiny for several decades for its use in heterostructure devices toward applications in solid-state neutron detection and thermoelectric energy conversion. The heterostructure devices are typically heterojunctions in which p-type amorphous hydrogenated boron carbide $(a-B_5C:H_x)$ is deposited onto n-type Si, and a Cr/Au contact is applied at the $a-B_5C:H_x$ surface. Traditionally it has been believed that Cr forms an ohmic contact at the a-B5C:Hx interface and that the heterostructure current-voltage rectification is a classical function of the p-n junction. However, we have found through photoemission studies of Cr overlayers on a-B₅C:H_x that a complex series of interfaces is formed, involving various oxides and borides, which are likely convoluting-and could be dominating-the observed rectification. To follow up the Cr findings, we have explored Al, Cu, Au, Ag, and Ti using the same set of studies. This talk will provide an overview of the electronic, physical, and chemical interfaces between the above metals and $a-B_5C:H_x$ in the context of understanding the I(V) characteristics of the presumed p-n junction.

SS-TuP22 Electron Stimulated Reactions on Graphene-Coated Ru: Relevance to Extreme Ultraviolet Lithography (EUVL), B.V. Yakshinskiy, R.A. Bartynski, Rutgers University

The contamination of optical surfaces in EUVL exposure tools, operating at 92 eV photon energy, results in degradation of the mirror reflectivity. We report studies of the thermal and electron-induced interaction of benzene and toluene vapors, typical background gases, with the Ru surface, as model cap layer for multilayer mirrors (MLM), using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS), electron stimulated desorption (ESD), low electron energy diffraction (LEED), and scanning tunneling microscopy (STM). A low energy electron source (100 eV) is used to simulate radiation excitations on the surface produced by EUV photons. Heating of adsorbed hydrocarbons leads to a stepwise dehydrogenation and buildup a selflimited carbon monolayer. Electron bombardment of the bare Ru surface in the presence of gas phase hydrocarbons inevitably results in rapid accumulation of 1 ML of carbon or carbonaceous species. Subsequent contamination growth is determined by the electron-stimulated surface chemistry on the graphitized surface. Graphene monolayer and bilayer formation on Ru(0001) by hydrocarbon pyrolysis or by carbon segregation from the sample bulk is examined as a possible way to reduce the surface contamination rate. Graphene buildup has been confirmed by the presence of corresponding superstructures in LEED patterns and STM images. The binding energy of the hydrocarbon molecule is found to be smaller on a graphene layer than on disordered carbon. Electron irradiation of both bare and graphene covered Ru surface in the presence of benzene and toluene vapors leads to C-buildup. However, in a case of low irradiation density, when the electron flux is rate-limiting parameter, graphene monolayer exhibits its protective properties by slowing down carbon accumulation initially, until sufficient thick overlayer is formed. But in a case of high electron flux, when the adsorption of hydrocarbons is rate-limiting parameter, the carbon accumulation rate is invariant to the surface morphology.

The work is supported by Intel and DOE.

SS-TuP23 Photoelectron Spectroscopy Studies of Superconducting **Mo₂B and Mo₂BC**, *L. Huerta*, Universidad Nacional Autonoma de Mexico, *R. Falconi*, Universidad Juárez Autónoma de Tabasco, Mexico, *M. Flores*, Universidad de Guadalajara, Mexico, *A. Duran*, *R. Escamilla*, Universidad Nacional Autonoma de Mexico

The effect of carbon in the structure of Mo_2B is increasing the superconducting transition temperature from 5.8 K to 7.5K. Polycrystalline samples of the Mo_2B and Mo_2BC were synthesized by the arc melting technique. The samples were characterized by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). XRD results shown that when carbon atoms are added to the structure of the Mo_2B compound a transition structural from body centered tetragonal to face centered orthorhombic is induced forming the Mo_2BC compound. XPS spectra revealed the presence of the Mo 3d, C 1s, and O 1s core levels associated to the chemical states Mo_2B and Mo_2BC . In order to explain the increase of transition temperature in the Mo_2B doped with carbon, we measured the valence band spectra (XPS and UPS), the results were compared with the density of states at the Fermi level $N(E_F)$ of Mo_2B and Mo_2BC .

SS-TuP24 Electrical and Photo-Functional Properties of Copper Oxide Thin Films Prepared by Reactive Magnetron Sputtering, A. Shukur, H. Shukur, M. Sato, I. Takano, Kogakuin University, Japan

Copper oxide-based materials have been widely investigated due to their potential application in many technological fields. Cupric oxide (CuO) is a monoclinic n-type semiconductor with a band gap of 1.2-1.5 eV, whereas cuprous oxide (Cu2O) is cubic p-type semiconductor with a band gap of 2.0 eV [1]. Copper oxides have been employed as a heterogeneous catalyst for several environmental processes, e.g. NO selective reduction, CO oxidation and NO2 decomposition and it is a very promising material for the development of photovoltaic devices like solar cells.

Copper oxide thin films were prepared by reactive magnetron sputtering. Firstly the sputtering chamber was pumped down to $1.2 \times 10-5$ Pa. The substrate was a corning glass (#1737) and mirror finishing stainless steel (304ss). The Ar gas was kept at 15sccm and the substrate temperature was kept at 300oC. The amount of oxygen flow rate was varied at 0-10sccm and also the deposition power was varied at 10-40W in order to prepare films with different structures. The structure of the deposited films was measured by X-ray diffraction method (XRD: MAC Science. Co, Ltd). The surface morphology was observed by atomic force microscopy (AFM). The resistivity, mobility and carrier concentration were measured by employing the Hall Effect measurement system. The optical properties of the films were determined by a UV–VIS spectrophotometer (Shimadzu).

In this study, the copper oxide thin films were deposited by a reactive DC magnetron sputtering method. Single Cu2O and CuO phase can be obtained by controlling the sputtering power. The p-type Cu2O thin films were prepared with 30-40W. The n-type CuO was observed at power 10-20W. Low electrical resistivity of 90.18 Ω m was obtained for the thin film formed at sputtering power of 30W. The thin film was showed a band gap of 2.5eV attributed to Cu2O at sputtering power 30W whereas the band gap of 10w is 1.9eV. Our experimental investigation indicated that the sputtering power and oxygen flow rate has a significant influence on the electrical properties and optical band gap of the films.

SS-TuP25 Influence of Crystal Structure for Electrochromism of WO₃ Thin Films Prepared by Reactive Magnetron Sputtering, *H. Suzuki*, *H. Shukur, S. Ibrahim, I. Takano*, Kogakuin University, Japan

WO₃ is known as the material with an n-type semiconductor characteristic showing electrochromism (EC). The amorphous WO₃ thin film especially is used for a display device or a high-speed reaction sensor using electrochromism. WO₃ thin films for electrochromism have been fabricated by various film formation methods such as reactive sputtering and vacuum evaporation. The relationship between Ar gas and O₂ gas introduced during the film formation is the important condition for the structure of WO₃ thin film. The structure decides the electrochromic characteristic of the WO₃ thin film. In the reactive sputtering method Ar/O_2 gas flow rate especially induces the structure change of WO₃ thin film and the surface morphology.

In this study, WO₃ thin films were deposited by reactive magnetron sputtering with a W target in the condition of changing an Ar/O_2 gas flow rate. In the condition the WO₃ thin films with various crystal structures were fabricated. The relationship between the crystal structure and the electrochromic property were investigated with the great interest.

The WO₃ thin films were deposited by the multi process system with the helicon sputtering source on an Indium-tin oxide (ITO) coated glass and stainless steel (304SS) used as a substrate. The formation conditions of the WO₃ thin film were changed from 5 to 10 sccm in Ar gas flow rate and from 10 to 20 sccm in O₂ gas flow rate under a constant DC source power. The substrate temperature was kept at 473 K using an infrared lamp. The crystal s tructure and electrochromic property were investigated by X-ray diffraction (XRD) and UV-VIS spectrometer respectively. The crystal structure turned from the WO₃ thin film with the peak (112) to the WO₃ thin film with the peak (02), (112) and (022) with increasing Ar gas flow rate, while increase of O₂ gas flow rate gradually turned up the main peak (112). The maximum efficiency of electrochromic property was obtained at 7.5 sccm in Ar gas flow rate and 15 sccm in O₂ gas flow rate.

SS-TuP26 The Friction Properties of F-Doped DLC Thin Film Prepared in a C_7H_8 Atmosphere by the Ion-Beam Assisted Method, *M. Kurosu, I. Takano*, Kogakuin University, Japan

DLC (Diamond-Like Carbon) is known as amorphous carbon including hydrogen and has a characteristic between graphite and diamond. DLC film has been prepared by various methods of chemical vapor deposition (CVD) or physical vapor deposition (PVD) including the sputtering method. The property of DLC shows wear resistance, high hardness and low friction coefficient. DLC is applied in various fie lds such as motor parts, tools and molds.

In this study, DLC films were prepared by the ion-beam assisted method that was the PVD method allowing a low-temperature formation. In this

method the mixing layer which led to high adhesion was formed between the substrate and the DLC thin film. PTFE-Doped DLC (F-DLC) films were prepared by He⁺ ion irradiation in the toluene (C₇H₈) gas. He⁺ ion beam was irradiated at a current density of 5 μ A/cm² with a constant accelerating voltage of 5 kV. PTFE doping was performed by using the electron-beam deposition method with PTFE evaporation rate from 0.05 to 0.2 nm/sec. The film thickness measured using QCM was kept at 200 nm. Film composition and microstructure were investigated by X-Ray photoelectron spectroscopy and Raman spectroscopy, respectively. The hardness was measured by an indentation method with a Knoop indenter. The friction coefficient was measured for an SUJ2 ball with a constant load of 0.98 N until the sliding distance reached to a length of 100 m. The friction coefficient property under the vacuum was measured in 5 x10⁻⁴ Pa.

Frictional properties changed under the vacuum and the atmosphere. Friction coefficient of the F-DLC thin film with PTFE deposition rate of 0.2 nm/sec showed 0.25 at a sliding distance of 100 m. Friction coefficient property of the F-DLC thin film under a vacuum showed 0.12 at a sliding distance of 100 m. It was found that F-DLC indicated a low friction coefficient in a v acuum. F-DLC can be expected to be used as one of space materials in the future.

SS-TuP27 Photo-functional Properties of Cu-Added Titanium Dioxide Thin Films Prepared by Reactive Magnetron Sputtering, S. Arahara, H. Shukur, M. Sato, I. Takano, Kogakuin University, Japan

TiO₂ has been known as one of a promising photocatalyst and is already used in various practical applications, such as the degradation of environmental pollutants and the self cleaning of glasses. Furthermore, the surface of TiO₂ exhibits high hydrophilicity under ultra-violet (UV) light irradiation. A crystal form of TiO₂ is classified according to structure as anatase, ruttile and brookite. TiO₂ shows relatively high reactivity and chemical stability under UV light whose energy exceeds the band gap of 3.2eV in the anatase crystalline phase. The sun can provide an abundant source of photons. However, UV energy accounts for only a small fraction (~5%) of the sun's energy compared to the visible region (45%). Many techniques have been examined to improve this problem by the doping of transition metals into TiO₂.

In this study, TiO₂ films were prepared by reactive magnetron sputtering using a Ti target in an Ar/O₂ gas mixture. Cu addition was performed by Cu sputtering onto those TiO₂ films. It was considered that the charge separation between an electron and a hole was improved by adding Cu to the TiO₂ surface. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic change of a methylene blue solution was applied to a photocatalytic property. Light irradiation to TiO₂ films in a methylene blue solution was carried out by using a commercial sterilizing lamp as ultraviolet light and an artificial sun light as visible light. Transmittance of a methylene blue solution was measured by a spectrophotometer. Furthermore, photocurrent between the TiO₂ film and a platinum electrode was measured by a volt-ampere characteristic using an unresisted ammeter in a KCl solution of 0.5 mol/ ℓ .

The crystal structure of TiO₂ turned from a rutile type into an anatase type with increase of O₂ gas flow rate. Photocatalytic property and photocurrent property of an anatase type of TiO₂ showed the high value. The effect of the Cu addition exhibited different behavior according to each crystal structure. As for the photocatalytic property, the effect of the Cu addition was observed in rutile type, while on the photocurrent property the effect of the Cu addition was observed in anatase type. It was considered that the charge separation between an electron and a hole was enhanced by adding Cu to the TiO₂ surface.

SS-TuP28 Deviation from Wulff Structures for Pt Nanoparticles Supported on TiO₂(110): A STM Study, F. Behafarid, B. Roldan Cuenya, University of Central Florida

This study reports the shape of micellar platinum nanoparticles (NPs) supported on TiO₂(110) resolved by scanning tunneling microscopy (STM). Since micellar NPs are initially spherical in shape at room temperature, the 3D faceted shapes obtained after high temperature annealing display structures typical of thermodynamic equilibrium, in contrast with kinetic shapes of physical vapor deposited NPs, which are normally 2D and dominated by the diffusion of metal atoms on the support. All of the NPs resolved show an epitaxial relationship with the support, evident by TiO₂(110)[001] direction being one of the symmetry axis of the NPs. Analyzing these shapes reveals that in addition to hexagonal top (type A) and square top (type B) NPs reported for evaporated NPs, there are two additional categories of shapes observed for micellar NPs (Type C and D). Type A and B consist only of 111 and 100 facets at the interface with the support and the free top surface. However, type C and D feature also 110 facets either at the interface with the support or at the free surface. This facet orientation was not observed before in other studies due to its instability and high surface energy. The ratio of 100/111 facets obtained for these shape deviates from the Wulff structure. This deviation could be attributed to size effects, interface-induced strain, and/or possible TiOx adsorbates on exposed facets.

SS-TuP29 Slope Selection in Au Growth Fronts by Protrusion Interactions, J.L. Sacedón, A. González González, J.A. Aznárez, E. Rodríguez Cañas, E. Vasco, Consejo Superior de Investigaciones Científicas, Spain

Growth fronts of polycrystalline films composed by paraboloid-like surface protrusions (SPs) have been recently decomposed into elemental paraboloidal meridian zones, which allow a comprehensive statistical analysis of the film surface [1]. Using this analysis, local height distribution curves have been synthesized [2] and the interface width expressed as function of the statistical parameters [3]. The method evidences that the average value of the slopes obtained at the SP border remains constant during the growth [2]. The analysis of distribution curves of the terrace width (~ the inverse of the slope) at the SP borders provides three terracewidth limit values [4]: two of them in close agreement with the predicted ones within the frame of the standard slope selection theory, which is based on the balance between downhill/uphill surface currents for the A,B flanks of preferential (111) fcc growth (an intra-SP mechanism); and the third one has been interpreted as a result of an external interaction between SPs and the borders of crystalline plates on which the SPs grew. In the selected slope theory formalism, the surface current balance is the condition to keep constant a characteristic terrace width along a straight infinite flank formed by uniform terraces. In this work, we show that is possible to obtain limit terrace-width values close to those observed experimentally for limited and curved profiles by using, at the SP border terraces, an external interaction parameter and upward "Pav" coefficients predicted by the theory [5]. Finally, we will propose a general self-organization formalism, which applied as an inter-SP mechanism to the over-growing and under-growing protrusions, allows to predict limit values of terrace widths for the A and B flanks, in a reliable agreement with the experimental ones.

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SS-TuP30 UV Induced Photodesorption of O₂ on Rutile TiO₂(110): An Angular Imaging Study, *D.P. Wilson*, *M.D. Kershis*, Brookhaven National Laboratory, *M.G. White*, Stony Brook University and Brookhaven National Laboratory

The binding states of oxygen on TiO2(110) are important for many reactions, including the degradation of organic compounds and photodesorption. Experimental data and theoretical calculations have shown many different configurations for O₂ on TiO₂(110), including O₂⁻, O₂²⁻, and O4. Defect sites in titania (bridging oxygen vacancy, Ti3+ interstitial), while necessary for the adsorption of oxygen, also play a role in the initial binding states. In this experiment, the angular distributions and images of oxygen photodesorption from a rutile TiO₂(110) surface are studied under UHV conditions using a pump-probe Time-of-Flight (TOF) detection scheme to help determine the initial binding states of oxygen on this surface. Excitation occurs via exposure to 3.7 eV photons followed by one-photon ionization using 13.05 eV photons. The delay time between the lasers can be varied according to the maximum desorption velocity of the oxygen molecules. Ions were detected using a dual microchannel plate and a phosphor screen. A CCD camera positioned behind a phosphor screen captured the light emission of the phosphor, allowing for the imaging of the desorbing neutral O2 molecules. SimION 3D was used to simulate the motion of the ions through a Time-of-Flight (TOF) mass spectrometer to generate a probability distribution for detection that was used to compare images at different delays.

Previous experiments on the oxygen velocity distribution on TiO_2 (110) showed 3 different "channels" for desorption, with two being "fast" and one being "slow". The velocity distribution for the slow channel tracked with surface temperature, indicating that a trapping desorption mechanism dominated this channel. The two "fast" channels, however, did not depend on temperature and were attributed to two different oxygen binding states on TiO_2 (110). Many different binding states of oxygen have been predicted and it is unclear which state is responsible for which channel. Images of the

fastest channel and comparisons at different coverage and photon flux are shown.

The methyl radical velocity distributions from 4 different ketones (acetaldehyde, acetone, butanone, and acetophenone) were also investigated. For ketones where methyl radical desorption is not the preferred pathway (butanone), a 2+1 REMPI scheme was used for signal enhancement. Using these model systems allows for direct comparison of different properties of each molecule.

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