Monday Morning, October 20, 2008

Surface Science
Room: 208 - Session SS+NC-MoM

Catalysis and Alloy Formation
Moderator: G.B. Fisher, Delphi Research Laboratories

8:20am **SS+NC-MoM1 Surface Structural Investigation of Ultra-Thin Films of Pd Deposited on Au(111)**, ***P.A.P. Nascente***, Federal University of Sao Carlos, Brazil, *A. Pancotti, M.F. Carazzolle, A. de Siervo,* State University of Campinas, Brazil, *D.A. Tallarico,* Federal University of Sao Carlos, Brazil, *R. Landers, G.G. Kleiman*, State University of Campinas, Brazil

Bimetallic surfaces have attracted considerable interest due to their catalytic, electronic, electrochemical, and magnetic properties. The deposition of an ultra-thin metal film on a single crystal metal substrate can produce a bimetallic surface. The interfacial interactions between the two metals can lead to preferential surface orientation, surface relaxation, surface reconstruction, order/disordered effects, and surface alloying. In this work, ultra-thin films (1 and 3 monolayers) of Pd were deposited on the Au(111) surface and then characterized by X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and X-ray photoelectron diffraction (XPD). We have considered three models: Pd overlayers on the Au(111) substrate, Pd islands covering the Au(111) surface, and a random AuxPd1-x alloy. The reliability of the theoretical simulations as compared to the experimental XPD data was measured through the R-factor analysis. The comparison between experimental and theoretical XPD results indicated that, for the 1 ML film annealed at 450 C, Pd diffused into the Au bulk, causing alloy formation, and for the thicker film, the Pd islands were, at most, 3 ML thick.

8:40am **SS+NC-MoM2 Epitaxial Growth Ag Films on Al Surfaces: Strain Relief Mechanisms**, ***R.J. Smith***, *N.R. Shivaparan, M.A. Teter, W. Priyantha, M. Kopczyk, M. Lerch, C. Pint,* Montana State University, *G. Bozzolo,* Ohio Aerospace Institute

We report the results of a characterization of 0-6 nm thick Ag films, deposited onto Al(001) and Al(110) surfaces at room temperature, using high energy ion backscattering and channeling, x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and BFS model calculations. For the Al(001) surface, measurements of the backscattered ion yields from Al and Ag atoms show that the Ag atoms occupy fcc lattice sites and shadow Al substrate atoms. However, the ion scattering yields and photopeak intensities do not follow layer-by-layer model growth curves. Together with the evolution of the Ag 3d core level binding energies and the valence band shape as a function of Ag coverage, these results support a model of Ag-Al interface alloy formation as a mechanism for strain relief in this system with ~1% lattice mismatch. For the Al(110) surface the observations are closer to those expected for layer-by-layer growth, but still show evidence of some Al diffusion into the well-ordered Ag overlayer.

9:00am **SS+NC-MoM3 Growth of Ag Islands on a Twofold Surface of a Decagonal Al-Cu-Co Quasicrystal**, ***B. Unal,*** Ames Laboratory and Iowa State University, *T. Duguet,* Ecole des Mines, France, *D. Jing,* Ames Laboratory and Iowa State University, *C.J. Jenks,* Ames Laboratory, *P.C. Canfield,* Iowa State University, *V. Fournee,* Ecole des Mines, France, *P.A. Thiel*, Ames Laboratory and Iowa State University

Quasicrystals are well ordered, but not periodic solid materials which have peculiar surface properties such as low friction and high oxidation resistance. Using a variable temperature scanning tunneling microscope (VT-STM), for the first time, we have studied the (00001) clean twofold surface of a decagonal Al-Cu-Co quasicrystal. Our STM studies have showed that annealing at ca.1000K causes the formation of two different surface phases one of which has a periodic structure while the other is aperiodic. At room temperature, we have also investigated the growth of Ag on these two different surface domains. In the aperiodic one, Ag prefers to segregate into highly anisotropic islands whose longer edges are parallel to the periodic axis (i.e. the tenfold axis). As the total coverage increases, Ag islands grow vertically while preserving their highly anisotropic shape. In the other (periodic) domain, we observe smoother, more conventional growth. These two different growth behaviors strongly indicate that the aperiodic nature of the surface has a strong effect on the growth kinetics.

9:20am **SS+NC-MoM4 Collective Migration of Cu Nanostructures on Ag(111)**, ***A.W. Signor***, *H.H. Wu, D.R. Trinkle, J.H. Weaver*, University of Illinois at Urbana-Champaign

Experimental studies of island migration, an important process in crystal growth and nanostructure synthesis, have largely been limited to homoepitaxial systems. In these systems, either diffusion or evaporation and condensation of adatoms at the island edge gives rise to a Brownian-like motion of the center of mass with size-independent barriers, and diffusivities that smoothly decrease with size according to an inverse power-law relationship. The present work with Cu-Ag(111), a lattice-mismatched system, provides compelling evidence for a strain-driven collective mechanism involving nucleation and glide of misfit dislocations. With this mechanism, the entire structure is moved by one Burger's vector as a dislocation nucleates and glides through the island and the shape is retained as the structure moves from one site to another. Quantitative analysis of island trajectories in scanning tunneling microscopy movies at multiple temperatures yields activation barriers ranging from 0.14-0.39 eV with prefactors ranging from 10^{5}-10^{18} s^{-1} for islands containing 5-30 atoms. Significantly, the barriers are very sensitive to island size and shape, and hence island diffusivities do not scale with size in the ways predicted for traditional atomistic mechanisms, greatly affecting the overall coarsening kinetics. Temperature-accelerated dynamics simulations corroborate experimental findings, showing that collective motion of sub-units within the island, due to strain effects, result in misfit dislocation nucleation and glide, with barriers that are very sensitive to size and shape.

9:40am **SS+NC-MoM5 Step Structure and Motion on an icosahedral AlPdMn Quasicrystal**, ***Y. Sato***, Lawrence Berkeley National Laboratory, *B. Unal,* Iowa State University, *K.F. McCarty, N.C. Bartelt,* Sandia National Laboratories, *A.K. Schmid, T. Duden,* Lawrence Berkeley National Laboratory, *K. Pussi,* Lappeenranta University of Technology, Finland, *T.A. Lograsso, C.J. Jenks,* Ames Laboratory, *P.A. Thiel*, Iowa State University

We have used LEEM and STM to characterize step structure and motion on a well-ordered, aperiodic icosahedral-AlPdMn quasicrystal surface. Real-time imaging capability of LEEM allows us to understand how the room temperature quasicrystal surface develops following high temperature annealing up to 910K. The way steps move on this surface at high temperature is remarkable. Two types of steps move with different velocities and cross each other. What is more, the two steps form a chicken wire-like hexagonal and rhombohedral mesh structure, as the steady-state surface morphology. From the STM step height measurement, the two steps are identified to be L and (L+M) steps, with different step heights. (L(6.8Å) and M(4.2Å) steps are two steps known to occur on this surface.[1]) When the surface is cooled, extensive mass flow from the surface into the bulk has large consequences upon the step motion dynamics and resultant step structure at room temperature. M steps hidden in the step crossings of chicken wire step–networks open up and extend, as it allows a new surface layer to be exposed, and thereby forming the brick-like step structure observed at room temperature, composed of L, M, and (L+M) steps. An obvious question is how one might understand the presence of periodic step arrays at the surface of quasicrystalline samples. One would expect the stacking of the two step heights to follow the Fibonacci sequence of the bulk quasiperiodic order.[1] By permitting localized regions of the surface where the topmost plane trades position with the near-surface plane directly underneath, we propose a construction scheme that allows a step network consistent with experimental observations. Specific planar defects observed in icosahedral AlPdMn could enable such mechanism.[2] We discuss possible ways for this "carpet" of surface layers to be connected with the underlying bulk aperiodicity.

[1] T.M. Schaub, D.E. Beurgler,and H.-J. Guntherodt, 1994 Phys.Rev.Lett. 73, 1255.

[2] M. Feuerbacher, M. Heggen, and K. Urban, 2004 Mat.Sci.and Eng. A 375-377, 84.

10:20am **SS+NC-MoM7 Reactivity Trends in CO Oxidation from UHV to Elevated Pressures: Never Mind the Gap**, ***D.W. Goodman***, Texas A&M University **INVITED**

CO oxidation on Ru, Pd, Rh, and Pt surfaces has been investigated between 10^{-8} – 10 Torr and for a variety of temperatures and O_2/CO ratios. Polarization modulation reflectance absorption infrared spectroscopy (PM-RAIRS) was used to identify the CO coverage as a function of the reaction rate for a variety of conditions up to 10 Torr. For reaction pressures less than 10^{-6} Torr, X-ray photoelectron spectroscopy (XPS) was used to measure the surface coverages of CO and O_{ads}. A clear continuum with respect to reaction rates, surface composition, and overall mechanism is apparent over the entire pressure range investigated, i.e. there is no evidence of a pressure gap.

11:00am **SS+NC-MoM9 Structural Evolution of Platinum Catalyst in Different Pressure of CO: A Study of High Pressure STM and High Pressure XPS**, ***F. Tao***, *Z. Liu, C.Y. Chung, D. Butcher, Y.W. Zhang, M. Grass, M. Salmeron, G.A. Somorjai*, Lawrence Berkeley National Laboratory

Bridging pressure gap of catalytic model studies is one of the most changeling issues to be addressed for elucidating mechanism of heterogeneous catalysis. A new high pressure STM was homebuilt for this purpose. CO adsorption and oxidation on a stepped platinum single crystal was selected as a model to study in a wide range of CO pressure from 10-9 to 1000 Torr as the adsorption and surface structure of CO on noble metals under a realistic catalytic condition is an important topic for pollution control. STM study revealed a significant pressure dependence of surface structure of CO adsorption. The clean platinum single crystal surface prepared in UHV progressively reconstruct by adsorbing CO at step sites and breaking the step edge at low pressure. At high pressure the surface reconstructs into clusters with a size of 1-3 nm. The dramatic structural evolution from low pressure to high pressure is reversible. The reversibility is confirmed with a synchrotron-based high pressure XPS. A model rationalizing the pressure dependence of CO adsorption on this catalyst is suggested.

11:20am **SS+NC-MoM10 From Near-surface to Surface CuPt Alloy: Cu Surface Segregation Induced by CO Adsorption**, ***K. Andersson***, *F. Calle, J. Rossmeisl, I. Chorkendorff*, Technical University of Denmark

Bimetallic alloys offer a way of tuning electronic structure and hence also surface catalytic properties. For example, a CuPt near-surface alloy[1] has recently been suggested as a promising catalyst for the water-gas shift (WGS) reaction, $CO + H_2O \rightarrow H_2 + CO_2$. Crucial to the catalytic performance of such alloys is the surface composition and structure under reaction conditions. Examples of segregation of one component to form a surface oxide in oxidizing environments are many. However, largely unexplored are the effects of molecular adsorbates. Using a combination of XPS, in-situ and ex-situ IR, LEED, ISS and TPD, we have studied reversible surface changes induced by elevated CO pressures and sample temperatures for surfaces with varying Cu concentrations (up to 3 ML) in the near-surface region of Pt(111). We show that at sample temperatures high enough to overcome Cu diffusion barriers (~470 K),[2] a CO pressure of 2 mbar is sufficient to induce segregation of Cu to the topmost surface layer, switching a CuPt near-surface alloy to a novel well-ordered CuPt surface alloy with very different properties. The thermodynamic driving force behind the surface changes is rationalized on the basis of the much greater bondstrength of CO to Pt surface atoms in the presence of Cu atoms in the topmost surface layer. This is observed experimentally as large, well-defined and high temperature CO desorption peaks (up to 580 K). The so-called “d-band model”[3] explains our findings.

[1] J. Knudsen et al., J. Am. Chem. Soc. 129 (2007) 6485.

[2] N. Schumacher et al., Surf. Sci. 602 (2008) 702.

[3] J. Greeley, J.K. Nørskov, M. Mavrikakis, Annu. Rev. Phys. Chem. 53 (2002) 319, and references therein.

11:40am **SS+NC-MoM11 CO Adsorption on Ru(0001) and PtRu/Ru(0001) Near Surface Alloys Using Ambient Pressure Photoemission Spectroscopy**, ***D.E. Starr***, Brookhaven National Laboratory, *H. Bluhm*, Lawrence Berkeley National Laboratory

Carbon supported PtRu alloy particles are currently used as the anode catalyst in proton exchange membrane fuel cells. Small amounts of CO, in the ppm concentration range, present in the H_2 fuel are known to poison the catalyst. The role of Ru is to increase the CO tolerance of the catalyst. Since both Pt and Ru are expensive metals, understanding the catalyst’s susceptibility to CO poisoning and the function of Ru in reducing this susceptibility are important aspects for cost reduction of proton exchange membrane fuel cells. The increased CO tolerance of these catalysts has been attributed either to CO oxidation by adsorbed OH groups on Ru or by weaker adsorption of CO on the alloy surface than either of the pure metals leading to a decrease in the steady-state coverage of CO. Direct proof of the mechanism for the alloy’s increased CO tolerance requires detailed knowledge of the surface composition under reaction conditions. As a first step towards gaining this knowledge, we have used the Ambient Pressure Photoemission Spectroscopy experiment at Beamline 11.0.2 of the Advanced Light Source to study the adsorption of CO onto Ru(0001) and PtRu near surface alloys on Ru(0001) at 300 K and pressures up to 0.5 torr. The results of this study show that at 300 K the coverage of CO on the Ru(0001) surface saturates at ~ $1x10^{-6}$ torr and remains constant up to 0.5 torr. At pressures greater than 10^{-2} torr a second peak appears in the O1s spectra indicating the presence of a second CO species. Comparison of these results to those obtained with a PtRu surface alloy formed on the Ru(0001) surface will be presented.

Biomaterial Interfaces
Room: 202 - Session BI+SS+NC-MoA

Honorary Session for Bengt Kasemo
Moderator: M. Textor, ETH Zürich, Switzerland

2:00pm **BI+SS+NC-MoA1 Self–Assembly of Organic Molecules on Surfaces Studied by STM: Dynamics, Chirality and Self-Organization**, ***F. Besenbacher***, University of Aarhus, Denmark **INVITED**

Adsorption and organization of organic molecules on solid surfaces is central to self-assembly and bottom-up fabrication within nanoscience and technology. The Scanning Tunneling Microscope allows exploration of atomic-scale phenomena occurring on surfaces: Dynamic processes can be followed by fast-scanning STM, and from data acquired at a range of temperatures; detailed information on kinetic parameters can be extracted. In the talk, a number of studies investigating dynamics and organization of organic molecules on metal surfaces will be described, addressing surface diffusion, chiral recognition chiral switching and also the interaction of molecules with chiral sites on a metal surface[1-5]. Finally, the self-assembly of Nucleic Acid (NA) base molecules on solid surfaces has been investigated. I will discuss the fact that Guanine molecules form the so-called G-quartet structure on Au(111) that is stabilized by cooperative hydrogen bonds[6]. Interestingly, cytosine molecules only form disordered structures by quenching the sample to low temperatures, which can be described as the formation of a 2D organic glass on Au(111)[7]. Molecular recognition between complementary nucleic acid (NA) bases is vital for the replication and transcription of genetic information, both in the modern cell as well as under prebiotic conditions, when a dedicated molecular machinery of evolved living organisms had not yet been developed. By means of variable-temperature Scanning Tunneling Microscopy (VT-STM) we show that on a flat metal surface, formation of complementary NA bases pairs is favoured. The C+G mixture resilience to heating is due to the formation of G-C Watson-Crick base pairs. The observation that not the oligonucleotide backbone, but a flat metal surface may be instrumental for specific WC base pairing has interesting implications for the proposed scenarios of the emergence of life.

[1] M. Schunack et al., Phys. Rev. Lett. 88, No. 156102 (2002)
[2] R. Otero et al., Nature Materials 4 779 (2004)
[3] A. Kühnle et al., Nature 415, 891 (2002)
[4] S. Weigelt et al., Nature Materials, 5 11 (2006)
[5] S. Weigelt et al., Angew. Chem. 119, 9387 (2007)
[6] R. Otero et al., Angew. Chem. Int. Ed. 44, 2270-2275 (2005)
[7] R. Otero et al., Science 319 (2008) 312-315 .

2:40pm **BI+SS+NC-MoA3 Interaction of AH Amphipathic Peptide with Lipid Bilayers and Application to the Understanding of Hepatitis C Viral Infection via QCM-D Measurements**, ***C.W. Frank***, *N.J. Cho,* Stanford University, *K.H. Cheong,* Samsung Advanced Institute of Technology, Korea*, J.S. Glenn*, Stanford University **INVITED**

Membrane association of the hepatitis C virus NS5A protein is required for viral replication. This association is dependent on an N-terminal amphipathic helix (AH) within NS5A and is restricted to a subset of host cell intramolecular membranes. The mechanism underlying this specificity is unknown, but it may suggest a novel strategy for developing specific antiviral therapy. Here we probe the mechanistic details of NS5A amphipathic helix-mediated binding to both cellular-derived and model membranes using biochemical membrane flotation and quartz crystal microbalance with dissipation. In both assays, we observed AH-mediated binding to model lipid bilayers. When cellular-derived membranes were coated on the quartz nano-sensor, however, significantly more binding was detected. Biochemical flotation assays performed with trypsin-treated cellular-derived membranes exhibited reduced amphipathic helix-mediated membrane binding, while membrane binding of control Cytochrome b5 remained unaffected. Similarly, trypsin treatment of the nano-sensor coated with cellular membranes eliminated amphipathic helix binding to the cellular membranes while that of a control lipid-binding protein remained intact. These results, therefore, suggest the effect of a protein in mediating and stabilizing the binding of NS5A's amphipathic helix to its target membrane. These results also demonstrate the successful development of a new nano-sensor technology ideal for both studying the interaction between a protein and its target membrane, and for developing inhibitors of that interaction.

3:20pm **BI+SS+NC-MoA5 Tethered Biomolecular Lipid Membranes - a Membrane Mimetic Sensor Platform*, W. Knoll*,** *I. Köper, R. Naumann, E.-K. Sinner*, Max-Planck-Institute for Polymer Research, Germany

This contribution summarizes some of our efforts in designing, synthesizing, assembling, and characterizing functional tethered lipid bilayer membranes (tBLMs) as a novel platform for biophysical studies of and with artificial membranes or for sensor development, employing, e.g., membrane integral receptor proteins. Chemical coupling schemes based on thiol groups for Au substrates or silanes used in the case of oxide surfaces allow for the covalent and, hence, chemically and mechanically robust attachment of anchor lipids to the solid support, stabilizing the proximallayer of a tethered membrane on the transducer surface. Surface plasmon optics, the quartz crystal microbalance, fluorescence- and IR spectroscopies, and electrochemical techniques are used to characterize these complex supramolecular interfacial architectures with respect to their assembly, their structure and function. We demonstrate, in particular, that these bilayers show the fluid character of a liquid-crystalline membrane with a specific electrical resistance of better than 10 MΩcm2. Then a totally novel approach for the functional incorporation of membrane proteins, i.e., by their cell-free expression and in vitro reconstitution in the presence of tBLMs is demonstrated. We focus on the yeast expression system for the synthesis of the olfactory receptor species OR5 from Rattus norvegicus. By the combination of the corresponding coding DNA with the protein synthesis machinery of a cell-extract (in vitro transcription and translation) we observe spontaneous and vectorial insertion of an interesting example for a membrane protein into a tethered bimolecular lipid membrane: the OR5 receptor as a family member of the G-protein coupled receptors.

4:00pm **BI+SS+NC-MoA7 Tethered Biomolecular Lipid Membranes - a Membrane Mimetic Sensor Pattern II**, ***E.-K. Sinner***, Max-Planck-Institute for Polymer Research, Germany

4:20pm **BI+SS+NC-MoA8 2D Self-Assembly of Annexin-A5 on Lipid Surfaces: Biological Function, Mechanism of Assembly and Biotechnological Applications*, A.R. Brisson*,** *N. Arraud, R. Bérat, A. Bouter, B. Garnier, C. Gounou, J. Lai-Kee-Him, S. Tan*, CNRS-University of Bordeaux, France **INVITED**

The self-assembly of proteins in 2D arrays at membrane surfaces is a generic strategy used by the cell for the construction of functional supramolecular edifices, e.g. bacterial S-layers, inter-membrane cadherin junctions, etc.. Annexin-A5 (Anx5) is the prototype member of the annexins, a superfamily proteins which share the properties of binding to negatively charged phospholipids in the presence of Ca2+ ions and forming various types of 2D ordered arrays at membrane surfaces. A detailed model of the structure and mechanism of formation of Anx5 2D arrays has been elaborated from EM, AFM and physico-chemical studies on various types of model membranes – liposomes in solution, lipid monolayers at the air-water interface, supported lipid bilayers.[1-4] The long-debated question of the functional role of Anx5 and annexins starts to be elucidated. The unique properties of binding and 2D self-assembly of Anx5 were exploited to develop various types of molecular tools for nanobiotechnological applications in proteomics, diagnosis or drug delivery. Chimerical proteins made of Anx5 fused to an antibody-binding moiety or linked to cell-adhesion peptides allow the construction of 2D platforms for anchoring antibodies, proteins or cells in a controlled orientation and density.[5] Gold particles functionalized with oriented Anx5 or Anx5-fusion proteins are used for labelling membrane fragments exposing phosphatidylserine molecules, such as apoptotic membranes or plasmatic microparticles, opening novel strategies for the separation and the analysis of circulating cell membrane fragments.

[1] F. Oling, W. Bergsma-Schutter and A. Brisson J. Struct. Biol. 2000, 133, 55-63.
[2] Reviakine, I., Bergsma-Schutter, W. and Brisson, A. J. Struct. Biol. 1998, 121, 356-61.
[3] Richter, R.P.; Lai-Kee-Him, J.; Tessier, C.; Brisson, A. R. Biophys. J.2005, 89, 3372-3385.
[4] Richter, R.P.; Bérat, R; Brisson, A. R. Langmuir 2006, 22, 3497-3505.
[6] Bérat, R.; Rémy-Zolghadry, M.; Gounou, C.; Manigand, C.; Tan, S.; Saltó, C.; Arenas, E.; Bordenave, L; Brisson, A. R. Biointerphases, 2007, 2, 165-172.

5:00pm **BI+SS+NC-MoA10 From Surface Science to Biointerfaces to Nanoscience*, B. Kasemo***, Chalmers University of Technology, Sweden **INVITED**

The development of surface science can, depending on ones background and focus, be regarded as a bottom up outgrowth of, e.g., solid state physics towards surfaces (structure, electron structure,..) or molecular physics towards interfaces (collision dynamics, adsorption,…), or one can alternatively see it as the result of a top down process, where technologically important areas, such as semiconductor technology, materials science, catalysis and biointerfaces [1], stimulated development of more knowledge about and better tools to study interface properties and processes. The strength of surface science originates to a large extent from the strong feed back loop between the top down and bottom up processes, connecting a manifold of interesting fundamental questions with a large diversity of applications. Historically the focus of surface science has moved from simple model systems of small molecules on metal surfaces in UHV, to more complex systems in UHV or at higher gas pressures (e.g. in catalysis), to the liquid phase (e.g. electrochemistry), and further to very complex systems (biointerfaces, tribology,…), involving also more complex materials like oxides and polymers. The evolution sketched above is here exemplified by a personal and subjective choice of examples, like surface scattering and charge transfer processes, catalysis, and biomimetic membranes. The "newest" addition on the arena is nanoscience and nanotechnology, which has connected to almost all fields of traditional surface science. Although one can claim in catalysis, and several other fields, that there has always been a "nano-" element, the control of the latter through fabrication and characterization, is what has changed dramatically over the past decade or so. Specific examples chosen here to illustrate this latter development is taken from nanotechnology for sustainable energy [2], namely (i) so called LSPR applications for solar cells and sensing, (ii) metal hydrides, and (iii) exhaust cleaning catalysis and (iv) fuel cells.

[1] Kasemo, B., Biological Surface Science. Surface Science, Vol. 500 (2002) 656.

[2] Zaech M., Haegglund C., Chakarov D., Kasemo B., Current Opinion in Solid State and Materials Science Vol. 10 (2006) 132.

Graphene Topical Conference
Room: 306 - Session GR+SS+NC-MoA

Materials Issues in Graphene from SiC
Moderator: N.P. Guisinger, Argonne National Laboratory

2:00pm **GR+SS+NC-MoA1 Ultrahigh Vacuum Growth, Electrical Characterization, and Patterning of Graphene Nanostructures on Si- and C-Polar 6H-SiC Surfaces**, ***A. Sandin***, *Z. Wang, J.L. Tedesco, J.E. Rowe,* North Carolina State University*, R.J. Nemanich*, Arizona State University

We report the growth of graphene films on both C-polar and Si-polar surfaces of 6H-SiC by thermal decomposition in an ultrahigh vacuum (UHV) chamber. Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) have been used in situ to characterize the UHV films. Following growth, focused ion beam lithography has been used to successfully etch the graphene films and control the lateral dimensions of a number of nanostructures on these graphene layers with etch rates of ~18 nm/s and lateral dimensions of ~250 to 1500 nm. Epitaxial graphene films (1-4 layers thick) have been grown on the Si face. Theoretical reports have recently addressed the bandgap engineering of graphene nanoribbons by altering the physical dimensions, edge structure, and edge atoms of the nanoribbons. However, experimental control of the growth and quality graphene nanostructures is still a challenge. Several experimental studies have shown that annealed SiC does not significantly influence the electronic quality of the epitaxial graphene overlayer. However, these studies also indicate that the thickness of graphene films can be varied by controlling the Si decomposition and carbon aggregation on the surface through control of the annealing. Graphene growth on the Si-face suffers from pit formation located at SiC atomic-height steps and the carbon nanomesh (~13x13) can be observed using LEED and STM even for our thickest Si face graphene layers. Our results for graphene film growth on the more chemically reactive C-face find more rapid growth which is difficult to control. Due to the rapid growth, graphene nucleation cannot be mapped relative to the original SiC atomic terraces on the C-face. Scanning tunneling spectroscopy (STS) current-voltage (I-V) curves have been recorded and we observe both metallic behavior and bandgaap formation, as well as the local density of states in bulk graphene and etched graphene edges. Future research will be directed to experimentally observe the proposed electronic properties of smaller (<20 nm in width) graphene nanostructures using STS.

2:20pm **GR+SS+NC-MoA2 Unique Stacking of Multi-Layer Graphene on 4HSiC(000-1)**, ***J. Hass****, J.E. Millan-Otoya, N. Sharma, M. Sprinkle, F. Ming, W.A. de Heer, P.N. First, E.H. Conrad*, Georgia Institute of Technology

Diffraction data have shown that multilayer graphene grown on the polar (000-1) face of 4H-SiC contains large, flat domains and rotational stacking faults approximately every 2 layers.[1] Such faults are particularly interesting because it has been demonstrated that rotational faults in bi- and tri- layer graphene films decouple adjacent sheets, thereby preserving the unique lattice symmetry and linear dispersion found for a single, isolated sheet.[1-3] This is in contrast with few-layer graphite, which grows in a Bernal stacking arrangement on the opposite polar (0001) face. Scanning tunneling microscopy (STM) and surface X-ray diffraction (SXRD) data exhibit a number of rotational domains in registry with the SiC substrate. Data will be presented which elucidate particular stacking orientations over micron scale domains. Scanning tunneling spectroscopy (STS) results will be interpreted in the context of symmetry breaking between sheets.

[1] J. Hass, F.Varchon, J. E. Millán-Otoya, M. Sprinkle, N. Sharma, W.A. de Heer, C. Berger, P.N. First, L. Magaud, E.H. Conrad, Phys. Rev. Lett. 100, 125504 (2008).

[2] J.M.B. Lopes dos Santos, N.M.R. Peres, A.H. Castro Neto, Phys. Rev. Lett. 99, 256802 (2007).

[3] S. Latil, V. Meunier, L. Henrard, Phys. Rev. B. 76, 201402(R) (2007).

2:40pm **GR+SS+NC-MoA3 Ultrahigh Vacuum and RF Furnace Production of Graphene on SiC***,* ***G.G. Jernigan****, B.L. VanMil, D.K. Gaskill, J.C. Culbertson, P.M. Campbell*, US Naval Research Laboratory **INVITED**

The electrical, mechanical, physical, and chemical properties of graphene have the scientific community in search of large area samples for technological applications. Since deHeer's[1] initial report of graphene formation by the thermal desorption of Si from SiC, efforts have been underway to use this method to make large area sheets of graphene. Creating graphene by desorbing Si from SiC is conceptually simple, but in practice it is very challenging to produce large area, uniform, electronic grade graphene. In this presentation, I will discuss the two processes we employ, ultrahigh vacuum (UHV) annealing (~10^{-8} mbar) and RF furnace heating (~10^{-5} mbar), to create graphene in areas ranging from 200 mm^2 to 4000 mm^2 on 4H and 6H SiC and on Si-face and C-face samples. As observed by Raman spectroscopy, both processes are capable of producing graphene, because each set of samples shows the distinctive D, G, and 2D Raman lines. Each process begins with the SiC surface being hydrogen etched to remove polishing damage and to create a uniformly stepped surface. However, the resulting graphene from each process has noticeably different characteristics. UHV production allows us to probe the graphene formation in situ with LEED, XPS, and STM. The UHV method results in single layer and few layer graphene films. Van der Pauw Hall measurements indicate the films have low mobility and the predominant carriers are electrons. AFM studies show that depending on desorption conditions (heating rate, final temperature, and cooling) the surface morphology is roughened due to formation of pits and islands. We believe this roughened surface explains the low mobility. RF furnace production allows us to form graphene in the same system that hydrogen etching is performed, thereby avoiding exposure of the sample to air. Van der Pauw Hall measurements of the RF furnace samples consistently have higher mobility than the UHV samples and the predominant carriers are holes. These films are thicker than the UHV samples and consist of multiple layers of graphene. The surface morphology does not consist of pits and islands, but instead shows lines of built up carbon along step edges. In the end, we want to produce graphene having the best characteristics of the UHV and RF furnace methods with controlled thickness (< 3 layers) and high carrier mobility (> 10,000 cm^2 /Vs).

[1] C. Berger, et al, J. Phys. Chem. B 108, 19912-19916 (2004).

3:20pm **GR+SS+NC-MoA5 Microscopic and Spectroscopic Studies of the Electronic Structure of Epitaxial Graphene on SiC (0001)***,* ***N. Sharma****, D. Oh, M. Sprinkle,* Georgia Institute of Technology*, C. Berger,* CNRS Grenoble, France*, W.A. deHeer, T.M. Orlando, P.N. First*, Georgia Institute of Technology

Growth of high quality epitaxial graphene (EG) films on the basal plane of hexagonal SiC has been demonstrated previously, providing a potential route to wafer-scale graphene electronics. To realize this promise requires a detailed understanding of the atomic and electronic structure of the EG/SiC interface. For typical EG samples, STM measurements indicate a reconstructed interface (layer 0) covered by a layer (layer 1) that images as graphene (a honeycomb pattern) at low bias voltages, but appears to partially hybridize with interface states. For this layer, we also observe a strong suppression of the 2D Raman peak (also known as D* or G') that is characteristic of graphene. For the second EG layer, a single Lorentzian-shape 2D peak is observed, which may indicate some isolation of layer 2 from the material below. Graphene films grown on the SiC (0001) surface are intrinsically electron doped. The screening response of the 2D electron gas in EG is expected to be unique due to the small carrier density and novel electronic structure. We use local defects and deposited metal islands to locally change the carrier density, and scanning tunneling spectroscopy to probe the screening response. This is of interest since the screening region in EG could include a transition from hole to electron doping, resulting in a surface PN junction that could influence electrical transport in this system.

4:00pm **GR+SS+NC-MoA7 Structural and Electronic Properties of Epitaxial Graphene on SiC(0001)**, *C. Riedl, D.S. Lee, J. Smet, L. Vitali, R. Ohmann, I. Brihuega,* MPI for Solid State Research, Germany, *A. Zakharov,* Lund University, Sweden, *C. Virojanadara,* now at: Linköping University, Sweden, *K. von Klitzing, K. Kern,* ***U. Starke***, MPI for Solid State Research, Germany

Graphene layers can be grown on a solid substrate by the controlled graphitization of SiC surfaces by high temperature annealing in ultra high vacuum (UHV). However, the exact control of the number of layers grown and their quality remains a problem. In the present work, we use angular resolved ultraviolet photoemission spectroscopy (ARUPS) from He II excitation and low energy electron diffraction (LEED) to count the number of layers continuously during the preparation procedure in the home laboratory thus avoiding laborious synchrotron experiments. The layer structure and homogeneity is further analyzed by Raman spectroscopy, core level photoemission spectroscopy (PES) and low-energy electron microscopy (LEEM) measurements. On such precisely prepared graphene samples, we investigate their electronic structure using ARUPS and scanning tunneling spectroscopy (STS). The layer dependent shifting of the energetic position of the Dirac point and the detailed structure of the π-band dispersion are analyzed both with momentum and spatial resolution.

4:20pm **GR+SS+NC-MoA8 Atomic Scale Properties of Epitaxial Graphene Grown on SiC**, ***G.M. Rutter***, *P.N. First,* Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology

Two-dimensional electron systems have been of interest to scientists for many years. From high-electron mobility transistors to novel topological quasiparticles of the fractional quantum Hall effect, the field continues to be rich in scientific possibilities and technological pay-offs. To date, most high-mobility 2D electron systems have been created at an interface between semiconductor heterostructures, making them inaccessible to the electron spectroscopies of surface science. Here we investigate graphene, a new 2D electron system that is accessible to surface studies. Our measurements use scanning tunneling microscopy and spectroscopy to elucidate the properties of epitaxial graphene, resolving heterogeneities at the level of single atoms. In this work, epitaxial graphene is created on silicon carbide wafers by thermal annealing in vacuum. Sequential scanning tunneling microscopy (STM) and spectroscopy (STS) are performed in ultrahigh vacuum at temperatures of 4.2 K and 300 K. These atomic-scale studies address the initial growth of single-layer epitaxial graphene and the role that the interface and defects play in the electronic properties of graphene. Our work shows evidence of graphene formation by mass transfer of carbon, indicated by step edge growth and the nucleation of graphene islands. STM topographic images of single-layer graphene show the atomic structure of the graphene and the graphene/SiC interface, as well as the character of defects and adatoms within and below the graphene plane.[1,2] STS of lattice defects on single-layer graphene show localized peaks in the spectra. The energy position of such localized states offers a clue to the defect's origin and composition and will be discussed.

[1] G. M. Rutter, et al., Phys. Rev. B 76, 235416 (2007).

[2] G. M. Rutter, et al., J. Vac. Sci. Technol. A in press, (2008).

4:40pm **GR+SS+NC-MoA9 Layer-Dependent Properties of Epitaxial Graphene on Silicon Carbide*+**, ***P.N. First***, Georgia Institute of Technology **INVITED**

Epitaxial graphene grown on single-crystal silicon carbide has been proposed as a platform for graphene-based nanoelectronics.[1] This new electronic material shows great potential, but also poses a number of challenges. I will discuss results from several surface characterization techniques that determine the structure and electronic properties of this system. In particular, scanning tunneling microscopy and spectroscopy are used to study the electronic and geometric structure versus the graphene layer index for epitaxial graphene on SiC(0001).[2] Additional measurements show that the structure of graphene grown on SiC(000 -1) differs dramatically from that grown on SiC(0001). Finally, results that address the physics of metal contacts to graphene will be presented.

*Work supported in part by NSF, NRI-INDEX, and the W. M. Keck Foundation. +Work done in collaboration with G. M. Rutter, J. Hass, N. Sharma, T. Li, E. H. Conrad, C. Berger, and W. A. de Heer at the Georgia Institute of Technology, and J. N. Crain, N. P. Guisinger, and J. A. Stroscio at the NIST Center for Nanoscale Science and Technology

[1] C. Berger et al., J. Phys. Chem. B 108, 19912 (2004).

[2] G. M. Rutter et al., Science 317, 219 (2007) ; Phys. Rev. B 76, 235416 (2007); J. Vac. Sci. Technol. A (in press).

5:20pm **GR+SS+NC-MoA11 Scanning Tunneling Spectroscopy of Epitaxial Graphene on SiC(0001)**, ***S. Nie***, *R. Feenstra*, Carnegie Mellon University

Over the past few years many researchers have investigated the properties of single monolayers of graphite, known as graphene. This material exhibits novel electronic properties arising from its band structure which displays linear dispersion around the band extrema, leading to high carrier mobilities and the potential for high-speed electronic devices. Using scanning tunneling spectroscopy (STS) at room temperature we have studied the electronic properties of graphene formed on the Si-face of the SiC(0001) surface. The substrate was annealed in ultra high vacuum at temperatures ranging from 1200 to 1400°C to form the graphene. With increasing temperature the surface becomes more carbon rich, showing different surface structures including 5×5, 6×6, and graphene-covered 6×6. For the highest annealing temperatures, multiple (>5) layers of graphene were formed. Low-energy electron diffraction was used to monitor the change in surface structure as a function of temperature, and scanning tunneling microscopy (STM) was used to verify the structures. Tunneling spectra were acquired on each of the 5×5, 6×6, graphene-covered 6×6, and totally graphitized surfaces. A distinct spectrum of electronic states was observed on the 5×5 and 6×6 surfaces, containing intense spectrum peaks at about –1.5, –0.5, and +0.5 relative to the Fermi-level. A conductance minimum is seen at the Fermi-level for all spectra. The observed spectra are quite similar for the 5×5 and 6×6 surfaces, indicating that the spectral peaks arise from similar surface-derived dangling bonds and/or reconstructed bonding arrangements in both cases. As graphene forms, covering the 6×6 structure, these spectral peaks diminish in intensity and their energies shift slightly. In particular, near the Fermi-level, a region of minimum intensity forms extending about 0.6 to 0.8 eV below the Fermi-level. We tentatively associate this region with the 0.8 eV band gap that is known to form for bilayer graphene, with the Fermi-level located at the top of this gap. In any case, even with this evolution in the spectra, the overall position of spectral peaks is quite close for the graphene-covered surface as compared to the 5×5 and 6×6 surfaces. We therefore interpret the features observed in the graphene spectra as primarily arising from the electronic structure at the interface between the graphene and the SiC. This work was supported the National Science Foundation, grant DMR-0503748.

Surface Science
Room: 208 - Session SS+NC-MoA

Reactivity at Oxide Surfaces
Moderator: S. Chiang, University of California Davis

2:00pm **SS+NC-MoA1 Surface Structure and Chemistry of β-Ga_2O_3 Nanoribbons**, ***V.M. Bermudez***, *S.M. Prokes*, Naval Research Laboratory

β-Ga_2O_3 is an important material with applications as a catalyst support, as a transparent conducting oxide and as a critical component in chemical sensors. Much work has been done on high-surface-area powders and on polycrystalline thin films, but little is known about the surface properties of single crystals. We have carried out a series[1-3] of computational and experimental studies of β-Ga_2O_3 nanoribbons (NRs) which are single crystals with the (100) plane as the broad face. Ab-initio periodic slab calculations verify that the (100) surface is the lowest in energy and identify which of the two possible terminations ("A" or "B") is more stable. The (100)-B is very stable, and physisorption of molecular water, methanol or formic acid on this surface is found, computationally, to be energetically favored over dissociative adsorption. On the less stable (100)-A surface, physisorption of H_2O and CH_3OH is still somewhat more favorable than chemisorption, but formation of a bridging formate species is favored for HCO_2H. Infrared (IR) spectroscopy has been used to characterize the NRs and the interface with a gold substrate. The transmission spectrum of a thin layer of NRs shows an array of randomly-oriented single crystals. IR reflection-absorption spectra (IRRAS) suggest a reaction at the oxide/Au interface during annealing. IRRAS data for the adsorption of pyridine or 1-octanol are generally consistent with the computational results. Physisorption is the dominant effect; although, some chemisorption is also observed. This could indicate the presence of defects on the (100)-B surface or the co-existence of (100)-B and -A regions. For acetic or pentanoic acid, IRRAS clearly shows the formation of stable bridging carboxylate species which suggests that organic acids may be useful for functionalizing β-Ga_2O_3.

[1] V.M. Bermudez, Chem. Phys. 323 (2006) 193.

[2] V.M. Bermudez and S.M. Prokes, Langmuir 23 (2007) 12566.

[3] V.M. Bermudez, in preparation.

2:20pm **SS+NC-MoA2 Formaldehyde Reactions Over Rutile TiO_2(110) Single Crystal**, *H. Qiu, Y. Wang,* Ruhr-University Bochum, Germany, *P. McGill,* ***H. Idriss***, University of Auckland, New Zealand, *C. Woell*, Ruhr-University Bochum, Germany

The reaction of CH_2O with perfect and defective TiO_2(110) surfaces (produced by over-annealing and Ar ion sputtering methods) was studied by thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS) and DFT calculations. Exposing the perfect

$TiO_2(110)$ surface to CH_2O at 100 K leads to the formation of physisorbed CH_2O and paraformaldehyde. The latter decomposes to CH_2O that desorbs at about 270 K. On the defective $TiO_2(110)$ surface CH_2O adsorbs more strongly on oxygen vacancy sites ultimately forming a diolate ($-OCH_2CH_2O-$) species, as demonstrated by HREELS. Upon heating to higher temperatures this species undergoes deoxygenation resulting in ethylene formation via a reductive coupling mechanism.

2:40pm **SS+NC-MoA3 Reactivity Studies on Oxide Supported Metal Nanoparticles**, ***H.-J. Freund***, Fritz-Haber-Institut, Germany **INVITED**

Metal nanoparticles supported on thin oxide films may be characterized at the atomic level. Typically it is assumed that reactions proceed on the surface of those particles. We report on results of hydrogenation and oxidation reactions where the interior as well as the metal-oxide interface participate. Several examples will be discussed on the basis of results on model systems characterized via STM, TPD, IRAS, r-NRA, molecular beam as well as high pressure studies.

3:20pm **SS+NC-MoA5 Transient Mobility of Oxygen Adatoms Resulting from O_2 Dissociation at Oxygen Vacancies of $TiO_2(110)$**, *Y. Du, Z. Dohnalek*, ***I. Lyubinetsky***, Pacific Northwest National Laboratory

The interaction of molecular oxygen with TiO_2–based materials affects many chemical and photochemical processes. We will present our recent discoveries in studying O_2 interaction with reduced $TiO_2(110)$ surface by scanning tunneling microscopy at 300K. By tracking the same surface area before and after O_2 exposure, we confirm the known O_2 dissociation channel occuring at the bridging oxygen vacancy (O_{vac}) sites, with one O atom healing an O_{vac} and other O bonding at the neighboring Ti site as an adatom (O_a). In addition, the lateral distribution and diffusion of O_a are studied. It is revealed that there are three possible configurations for the O_a in regarding to the position of the original O_{vac} site, which can not be explained by thermal diffusion. Through detailed study, we conclude that observed distribution of the O adatoms is attained through a nonthermal, transient mobility from the energy release during dissociation. Unlike for other known cases of the dissociation of diatomic molecules where both "hot" adatoms accommodate at equivalent sites, in this study, the O atoms filling the vacancies are locked into the bridging oxygen rows and only the O adatoms are relatively free to move. The transient motion of the hyperthermal O adatoms might bring an enhanced reactivity, thus affect surface chemistry.

4:00pm **SS+NC-MoA7 Direct Observation of O_2 Dissociation on Ti rows of Reduced $TiO_2(110)$**, ***Y. Du***, *Z. Zhang, Z. Dohnalek, I. Lyubinetsky*, Pacific Northwest National Laboratory

The interaction of molecular oxygen with TiO_2 plays a critical role in catalytic activity of TiO_2-based materials. It is genernally agreed that reactivity of TiO_2, partially reduced by a vacuum annealing, is greatly influenced by surface oxygen vacancy defects. In particular, at room temperature, oxygen molecules were believed to dissociate only at vacancy sites with one O atom filling an oxygen vacancy and the other O atom residing at the neighboring Ti site as an adatom. In this talk, we will show that the oxygen dissociation process is much more complicated from our scanning tunneling microscopy studies. We will demonstrate that O vacancies are not the only sites to dissociate O_2 and reveal another O_2 dissociation channel, where an oxygen molecule dissociates on rows of five-fold coordinated Ti atoms to form an oxgyen adatom pair with two lattice constants spacing. We believe the discovery of the additional O_2 dissociation channel could have a considerable impact on the TiO_2 surface chemistry. It also calls for a partial reevaluation and/or reinterpretation some of the published experimental and theoretical results.

4:20pm **SS+NC-MoA8 Reactivity of Epitaxial Vanadia on TiO_2: Are Support Interactions Required for Reactivity?**, ***M. Li***, *E.I. Altman*, Yale University

The reactivities of vanadium oxide epitaxial thin films were studied using temperature programmed desorption (TPD). The vanadia films were grown on rutile $TiO_2(110)$ using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) and were shown to exhibit the (1x1) rutile structure using reflection high energy electron diffraction (RHEED), low energy electron diffraction (LEED) while X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) showed that monolayer films contained V^{5+} while V^{4+} predominated in the bulk of multilayer films. Two reaction channels at 400 K and above 500 K were detected for submonolayer coverages for 1-propanol oxidation to form propionaldehyde. The reaction channel at 400 K persists through multilayer films and thus is designated to the deprotonation of alkoxide intermediates attached to V^{5+} surface cations; meanwhile, a comparison of the vanadia coverage and the branching ratio between these two reaction channels suggests that the reaction above 500 K might involve alkoxides atop both V^{5+} and Ti^{4+}. It is also found that the activation energy of the lower temperature channel is stable on the submonolayer film, independent of reduction and reoxidaton, while the activation energy starts to increase for the higher temperature channel upon reduction. The same lower temperature reaction channel at 400 K exists throughout multilayer films where the titania support is absent, indicating that multilayer epitaxial films retain reactivity, in contrast to prior studies where disordered vanadia films were reported to be unreactive. Comparing the branching ratio of aldehyde desorption vs. alcohol desorption on films from submonolayer to multilayer, the fraction of the alcohol that dehydrogenates is higher for the submonolayer films. Together the results indicate that the TiO_2 support increases the reactivity of vanadia by structural promotion and by aiding the initial deprotonation of adsorbed alcohols.

4:40pm **SS+NC-MoA9 The Chemistry of Volatile Organic Compounds on $TiO_2(110)$ and the Influence of Defects and Coadsorbed Species**, ***L. Benz***, *J. Haubrich, R.G. Quiller, C.M. Friend*, Harvard University

Surprisingly high reactivity has been observed over the most stable (110) surface of TiO_2 in the reactions of volatile organic compounds, in particular, in molecules containing O moieties. Ultra-high vacuum techniques such as temperature programmed reaction spectroscopy and scanning tunneling microscopy were employed in researching the fundamental underpinnings of this reactivity, including the dependence of reactivity on the presence of intrinsic surface defects. Specifically, carbon-carbon bond formation was observed, and the effect of environmentally relevant species such as water and oxygen on these reactions was examined. These reactions are of general interest in both environmental and catalytic processes.

5:00pm **SS+NC-MoA10 Tetraoxygen on Reduced $TiO_2(110)$: Oxygen Adsorption and Reactions with Oxygen Vacancies**, *G.A. Kimmel*, ***N.G. Petrik***, Pacific Northwest National Laboratory

The interaction of oxygen with TiO_2 is critical for a variety of applications including the photooxidation of organic materials, purification of water and air, and (potentially) photocatalytic water splitting. In this paper, oxygen adsorption on reduced $TiO_2(110)$ is investigated using temperature programmed desorption and electron-stimulated desorption.[1] At low temperatures, two O_2 molecules can be chemisorbed in each oxygen vacancy. These molecules do not desorb upon annealing to 700 K. Instead for $200 \text{ K} < T < 400 \text{ K}$, the two O_2 convert to another species which has four oxygen atoms, i.e. tetraoxygen, that decomposes at higher temperatures. In contrast when only 1 O_2 is adsorbed in an oxygen vacancy, the molecule dissociates upon annealing above ~150 K to heal the vacancy in agreement with previous results. These experimental results, which provide a new model for the interaction of oxygen with $TiO_2(110)$, are consistent with the recent prediction that O_4^{2-} is the most stable form of oxygen in bridging oxygen vacancies.[2]

[1] G.A. Kimmel and N.G. Petrik, PRL 100, 196102 (2008).

[2] D. Pillay, Y. Wang, and G. S. Hwang, J. Am. Chem. Soc. 128, 14000 (2006).

5:20pm **SS+NC-MoA11 Decomposition of Dimethyl Methylphosphonate on Ceria Thin Films**, ***D.A. Chen***, *J.S. Ratliff*, University of South Carolina, *D.R. Mullins, S.D. Senanayake*, Oak Ridge National Laboratory, *X. Hu*, University of South Carolina

The decomposition of dimethyl methylphosphonate (DMMP) on ceria thin films has been investigated by temperature programmed desorption and high resolution X-ray photoelectron spectroscopy. Ordered ceria films with different levels of oxidation were grown on Ru(0001), and DMMP was used as a simulant molecule for understanding the chemistry of the organophosphorus nerve agents. Methanol and formaldehyde were the major gaseous products detected from initial DMMP decomposition on the fully oxidized ceria thin films, and PO_x as well as a small amount of atomic carbon or CH_x remained on the surface after heating to 800 K. On reduced ceria, CO and hydrogen were the main desorption products with methanol and formaldehyde as minor products. DMMP chemistry on ceria was unusual because activity increased with each adsorption-reaction cycle even though phosphorus did not desorb from the surface. This increase in activity appears to be caused by the reduction of cerium oxide by DMMP itself; one possible mechanism for the redox reaction involves the formation of cerium phosphate. The chemistry of DMMP on ceria is compared with that on single-crystal $TiO_2(110)$ surfaces. Gaseous methyl and methane were the primary products from DMMP decomposition on titania. In contrast to the ceria surfaces, titania was poisoned by the byproducts of DMMP reaction and exhibited less sustained activity for DMMP decomposition after multiple adsorption-reaction cycles.

Surface Science
Room: 208 - Session SS-TuM

Dynamics at Surfaces
Moderator: A.L. Utz, Tufts University

8:00am **SS-TuM1 Gaede Langmuir Award Lecture: Probing Elementary Process in Chemical Dynamics at Surfaces*, D.J. Auerbach****, GRT Inc. **INVITED**

Chemical reactions and energy transfer processes at the gas-surface interface play a vital role in a wide range of scientific and technological problems. In the electronics industries etching and deposition are key steps in the fabrication of microelectronic components. Heterogeneous catalysis lies at the heart of many synthetic cycles in the chemical and pharmaceutical industries. Gas-surface reactions also play an important role in the environment, from acid rain to the ozone hole. Energy transfer at the gas-surface interface influences flight, controlling spacecraft drag, and the altitude of a slider above a computer hard disk. Often such processes involve a complex sequence of events. To develop a molecular level understanding we must find ways to isolate and separately study the elementary processes involved at each step. Molecular beam and laser techniques provide a remarkably rich set of tools to accomplish this decomposition into elementary steps. The method is conceptually very simple. We prepare beams of molecules with well defined properties and scatter these beams for well defined surfaces under UHV conditions. It is possible to control the chemical composition, angle of incidence, kinetic energy, electronic state, vibrational state, rotational state, and even the molecular orientation of the impinging molecules. We then make time resolved observations of the changes in these variables after interaction the surface. The observations provide signatures of the elementary dynamical processes that contribute to a given overall process. They also provide quantitative measures of the rates and cross sections involved and thus provide benchmarks for the development of theory.

8:40am **SS-TuM3 Ultrathin K/p-Si(001) Schottky Diodes as Detectors of Chemically Generated Hot Charge Carriers, *H. Nienhaus***, University of Duisburg-Essen and CeNIDE, Germany, *K. Huba, D. Krix*, University of Duisburg-Essen, Germany

The oxidation of reactive metal surfaces may lead to the emission of photons (surface chemiluminescence) and of electrons into vacuum (exoemission). This is due to the highly non-adiabatic character of the reaction. The exoemission signals are strongly influenced by the change of work function with oxidation and are, therefore, difficult to interpret. Likewise, thin-film electronic devices, e.g. metal semiconductor contacts have been used to detect the internal exoemission by measuring chemicurrents. The internal Schottky barrier acts a high pass energy filter for hot charge carriers. The barrier is much lower than the work function and stays constant during oxidation. Hence, the reaction kinetics may be studied by recording the chemicurrent transients as has been successfully demonstrated for the oxidation of Mg.[1] The interaction of oxygen molecules with alkali metal surfaces is a prototype for charge transfer reactions with strong non-adiabatic energy dissipation. To study the internal exoemission large area K/p-Si(001) Schottky diodes are prepared by evaporation of ultrathin K layers on hydrogen terminated Si(001) surfaces in the thickness range between 2 and 30 monolayers. The metal film growth at low temperatures is monitored by Kelvin probe and Auger spectroscopy. The interface properties are characterized by current-voltage measurements revealing excellent rectifying properties of the diodes. The reverse currents are extremely low and a homogeneous barrier height of approximately 0.56 eV is determined using thermionic emission theory. When the diodes are exposed to molecular oxygen a strong chemicurrent signal is observed. The current increases with exposure time, exhibits a maximum and levels off with large exposures. This behavior indicates a nucleation-and-growth type of oxide formation. The total charge detected in the diode depends on the potassium film thickness in the thin-film regime which allows for an estimate of the oxidation depth.

[1] S. Glass, H. Nienhaus, Phys. Rev. Lett. 93 (2004) 168302.

9:00am **SS-TuM4 Vibrationally Hot Precursors – Key Reactants in Catalytic Hydrocarbon Activation?, *D.F. Del Sesto***, *C.R. Thomas, D. Cook, A.L. Utz*, Tufts University

Gas-surface reactions are often classified as direct or precursor-mediated based on whether their reactivity scales with surface or gas temperature. This interpretation is rooted in the assumption that as gas temperature and kinetic energy increase, trapping probability and hence reactivity for a precursor-mediated process falls. Application of this rubric has led to the conclusion that methane dissociation generally follows a direct mechanism for reaction on a wide range of transition metals. We suggest that this classification scheme might not properly account for the role of a precursor-mediated mechanism that involves vibrationally hot molecules. In this new mechanism, the vibrational energy content (and hence reactivity) of reagents that trap on the surface would also scale with increasing gas temperature, thus clouding the distinction between direct and precursor-mediated mechanisms. If a vibrationally hot precursor mechanism exists, it could well dominate reactivity of important industrial reactions under processing conditions. Relative to the molecules typically studied in beam-surface scattering studies, the methane molecules in an industrial steam-reforming reactor have low translational energy but high vibrational energy. This is because the many vibrational degrees of freedom in a polyatomic molecule can result in a chemically significant vibrational energy content at the elevated temperatures of a steam-reforming reactor. Prior beam-surface scattering studies have not found compelling evidence for this channel in part because the low kinetic energy molecular beams used to ensure adequate trapping probabilities are generally expanded from a room-temperature nozzle source where essentially all molecules are in the vibrational ground state. Studies that quantify vibrational effects in trapping and vibrational quenching on metals, in contrast, do point to a potentially important role for vibrationally excited precursors in catalytic reactions. The presentation will detail this new mechanism for gas-surface reactivity and describe recent results from beam-surface scattering measurements that use both thermal and laser excitation of methane vibrations to assess the importance of this trapping-mediated channel for vibrationally hot molecules.

9:20am **SS-TuM5 Photoinduced Electron Transfer Chemistry of CO_2 on Pt(111): Dissociation and Desorption following Å–Scale Molecular Acceleration Towards the Surface, *I. Harrison***, University of Virginia

Ultraviolet photoinduced electron transfer from a low temperature Pt(111) surface to physically adsorbed CO_2 is shown to lead to acceleration of the newly formed negative ion towards the surface, neutralization, and a high energy collision with the surface that efficiently dissociates (ca. 30%) and desorbs CO_2. The translational energy distributions and angular distributions of photodesorbing CO_2 are compared to those of CO_2 product from the photoreaction between coadsorbed CO and molecular O_2. The similarities of the desorbing CO_2 distributions argue for similar exit channel dynamics following access to configurations near the transition state for CO_2 dissociation/CO oxidation (i.e., configurations at chemisorptive distances from the surface). Consequently, the initially physisorbed CO_2 is accelerated towards the surface following photoinduced electron transfer and can undergo “Antoniewicz bounce” photodesorption dynamics. More interestingly, the initial Å-scale molecular acceleration towards the surface generates molecule/surface collisions at chemically significant energies sufficient to dissociate CO_2.

9:40am **SS-TuM6 Femtosecond Two-photon Photoelectron Spectroscopic Study of Photodissociation of CFC on Ice-covered Ag (111) Surface**, *S. Ryu, H. Kwon, J. Chang, J. Park, **S.K. Kim***, Seoul National University, South Korea

Solvation and transfer dynamics of photo-injected electrons in thin ice film of water or ammonia co-adsorbed with a CFC (chlorofluorocarbon) molecule such as $CFCl_3$ on Ag(111) have been investigated by time-resolved two-photon photoemission spectroscopy. Water molecules were found to solvate the photo-injected electron within the first several hundreds of fs. The significant lifetime decrease upon adsorption of CFC on the ice film was attributed to dissociative electron transfer of the solvated electrons, based on the observed scission of C–Cl bonds. Furthermore, the photodissociation rate of CFC adsorbed directly on Ag(111) was observed to increase drastically owing to the transfer of the solvated electron when an ice film was overlaid. In the case of ammonia ice film, we found that the lifetime of the solvated electron was much shorter than in water ice. The solvated electron state was found to be located at 2.4 eV above the Fermi level with a binding energy of 0.7 eV at 1 ML of ammonia, and its peak intensity decreased drastically upon increasing the coverage. To shed more light on the excitation process, polarization dependence of the solvated

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* Gaede Langmuir Award Winner

electron peak was thoroughly investigated while modulating the coupling between ammonia and the substrate by use of n-octane as a spacer layer. The observed dynamics of solvation and transfer of electron and the ice layer-induced enhancement of the photoreaction demonstrate the active role of water or ammonia as an electron solvent, which should have far-reaching implications for many electron-driven chemical reactions, including, for example, the newly proposed dissociation mechanism of chlorofluorocarbons by quasi-free or loosely bound electrons on the polar stratospheric clouds.

10:40am **SS-TuM9 Dynamics of Analyte Binding onto Metallophthalocyanine Thin Films: NO/FePc**, ***S.R. Bishop***, *N.L. Tran, A.C. Kummel*, University of California, San Diego

The investigation of the gas-surface reaction dynamics of NO with different iron phthalocyanine (FePc) thin films utilizing King and Wells sticking measurements is reported. Three surfaces were studied: a flat-lying monolayer FePc/Au(111) film, a crystalline flat lying multilayer FePc film, and a thick amorphous tetra-t-butyl FePc film. The initial sticking probability is a function of both incident molecular beam energy (0.09 – 0.4 eV) and surface temperature (100 – 300 K). For monolayer FePc/Au(111), NO adsorption onto FePc saturates at 3% of a monolayer at all incident beam energies and surface temperatures suggesting that the final chemisorption site is confined to the iron metal centers. At low surface temperature and low incident beam energy, the initial sticking probability is as great as 40% and decreases linearly with increasing beam energy and surface temperature. The results are consistent with the NO molecule sticking onto the monolayer FePc via physisorption to the aromatic periphery followed by diffusion to the Fe metal center. For the multilayer crystalline flat-lying film, the sticking probabilities are greater in comparison to the monolayer for the same incident beam energy and surface temperature, while the saturation coverage for the two films is identical. More efficient trapping onto the crystalline multilayer film is consistent with NO having improved mass-matching with the multilayer FePc surface compared to the monolayer FePc/Au(111) surface. A comparison between sticking to both crystalline and amorphous multilayer thin films is also presented. The initial sticking is similar for the monolayer FePc and amorphous tetra-t-butyl FePc surfaces. Furthermore, the saturation coverage is only 2% for the amorphous multilayer while 3% for the crystalline surface. The reduced saturation coverage in comparison to monolayer FePc is attributed to the reduced coverage of metal centers with the amorphous thin films.

11:00am **SS-TuM10 "Walking Molecules": Symmetric and Asymmetric Species with 1, 2 and 4 Chalcogen "Legs"**, ***G. Pawin***, *K.L. Wong, K.Y. Kwon, L. Bartels, R. Carp, M. Marsella*, University of California, Riverside, *S. Stolbov, S. Hong, T.S. Rahman*, University of Central Florida

Since our discovery of 9,10-dithioanthracene[1] as the first molecule that violates the substrate symmetry in its diffusive motion by perambulating along a single axis on a six-(three-)fold symmetric Cu(111) surface, we have explored this phenomenon extensively and applied it to: (a) transport of cargo,[2] (b) probing of fundamental principles of physics and chemistry, and (c) multi-pronged efforts towards realization of this phenomenon at higher temperatures have been undertaken.

[1] Kwon, K.Y., et al., Unidirectional adsorbate motion on a high-symmetry surface: "Walking" molecules can stay the course. Physical Review Letters, 2005. 95(16).

[2] Wong, K.L., et al., A molecule carrier. Science, 2007. 315(5817): p. 1391-1393.

11:20am **SS-TuM11 Dynamic Processes in Metalorganic Networks Observed by Time-Resolved STM**, ***H.E. Hoster***, *A. Breitruck, R.J. Behm*, Ulm University, Germany

Upon vapor deposition of Cu, hydrogen bonded bisterpyridine (BTP) adlayers on graphite are transformed into hexagonal, long-range ordered metal organic coordination networks.[1] These are stabilized both by hydrogen bonds and metal-ligand interactions. At Cu coverages below phase saturation, we observed the formation of a chiral 2D structure that contains both Cu-free and Cu-containing BTP trimers. The Cu centers themselves are mobile, and their movement within the organic matrix goes along with local re-arrangements of the BTP molecules, which are found to appear only in a finite number of configurations. Under suitable tunneling conditions, the Cu centers are detectable by STM as bright spots. It is therefore possible to quantitatively derive the frequencies of the distinct elementary Cu hopping events by statistical analysis of long STM sequences. We show how the probability of the distinct events can be rationalized by the initial, transitional, and final local configurations of the BTP molecules surrounding the Cu atoms.

[1] A. Breitruck, H.E. Hoster, C. Meier, U. Ziener, R.J.Behm, Surf. Sci. 601 (2007) 4200.

11:40am **SS-TuM12 Control of Scattering Potential for Hot Electrons at Ge(001) Surface**, ***F. Komori***, *K. Tomatsu*, University of Tokyo, Japan, *B. Yan, C. Wang*, Tsinghua University, China, *M. Yamada, K. Nakatsuji*, University of Tokyo, Japan, *G. Zhou, W. Duan*, Tsinghua University, China

Electron scattering in the transport through atomic-scale wires has attracted much interest, especially for possible application to functional devices. We have investigated this subject using a one-dimensional (1D) electronic system at surfaces, where we can study simultaneously the microscopic structure and electron scattering by observing topographic images and electronic standing waves in differential conductance (dI/dV) images with scanning tunneling microscopy (STM).[1] The scattering potential can be controlled by atomic manipulation by STM. Electron scatterings by impurity Si or Sn atoms inserted in a quasi-1D system were studied on a Ge(001) surface at 80 K. On the clean surface, Ge atoms form buckled dimers, which align and form a dimer row. Among the dangling bond states of the Ge dimer, an empty π^* surface electron, which localizes at the lower atoms of the Ge dimers, is quasi 1D along the dimer row. We prepared impurity dimers with Si or Sn atoms by deposition on the surface. A buckled Sn-Ge impurity dimer with Sn atom at the lower-atom position (Sn L-dimer) reflects the electrons, and a standing wave was observed in the dI/dV image. Whereas, a standing wave by a Sn-Ge dimer with Sn atom at the upper-atom position (Sn U-dimer) was too small to be observed. The standing wave amplitudes are almost the same for the Si-Ge dimers with the Si atom at the upper- and lower-atom positions (Si U-dimer and Si L-dimer). The signs of the scattering potentials by the impurity dimers were obtained by analyzing phase shift of the standing waves. The Si and Sn L-dimer, where the impurity atom is located in the conduction pathway, are potential well and barrier, respectively, for the π^* electrons. Whereas, the Si U-dimer is a potential barrier. These results are qualitatively understood by the fact that the π^* electrons propagate on the lower atoms of the buckled dimers. The Si and Sn U-dimer can be reversibly transformed to the Si and Sn L-dimer, respectively, by the bias voltage change for the STM observation as the Ge dimers[2] on the clean surface. Consequently, by switching them between U-dimer and L-dimer, we can manipulate the scattering amplitude of the π^* electrons for the Sn-Ge dimer, and the scattering phase for the Si-Ge dimer.

[1] K. Tomatsu et al Science 315 1696, 2007.

[2] Y. Takagi, Y. Yoshimoto, K. Nakatsuji and F. Komori, Surf. Sci. 559 1, 2004; Phys. Rev. B75 115304, 2007.

Synchrotron-based Spectroscopy and Spectro-Microscopy Topical Conference
Room: 310 - Session SY+SS+BI-TuM

Synchrotron-based Spectroscopy and Spectro-Microscopy
Moderator: M. Grunze, University of Heidelberg, Germany

8:00am **SY+SS+BI-TuM1 X-ray Studies of Hydrogen Bonding in Water; the Liquid Phase and on Surfaces**, ***A.R. Nilsson***, SSRL/Stanford University and Stockholm University, Sweden **INVITED**

Water and its ability to form Hydrogen bonding (H-bonding) is the basis for all life on the planet earth. The understanding of water adsorption, wetting and reactions at solid surfaces is of importance for many different areas of science such as biomaterials, catalysis, electrochemistry, corrosion, environmental science and technologies related to hydrogen as a future energy carrier. There are recent experiments that have raised the question whether we really understand the nature of H-bonding and the structure of liquid water. We have recently devoted a major effort to the development of x-ray spectroscopy measurements of water in the different aggregation forms and adsorbed on surfaces. Using x-ray absorption spectroscopy (XAS), x-ray Raman scattering (XRS), x-ray emission spectroscopy (XES), small angle x-ray scattering (SAXS) and x-ray diffraction together with density functional theory (DFT) calculations we have demonstrated the appearance of specific spectral features that can be related to two different types of water species in the liquid, tetrahedral water and asymmetric H-bond configurations. The latter species dominates the liquid. I will address fundamental questions regarding geometric structure, electronic structure, nature of surface chemical and hydrogen bonding and reactivity of water on surfaces. The connection between studies performed at both UHV and ambient conditions will be emphasized. Several examples of different water adsorption system will be illustrated such as Pt(111), Ru(001), Cu(110), Cu(111), TiO_2, Fe_2O_3 and MgO.

8:40am **SY+SS+BI-TuM3 Soft X-ray Spectroscopy of Liquids and Liquid-Solid Interfaces**, ***C. Heske***, University of Nevada Las Vegas **INVITED**

With the advent of high-brightness synchrotron radiation in the soft x-ray regime it has become possible to investigate vacuum-incompatible sample systems such as liquids using suitably designed in-situ cells. In such cells, thin membranes (e.g., made of SiC, SiN_x, or polyimide) separate non-vacuum sample environments from the ultra-high vacuum necessary for soft x-ray synchrotron beamlines. If the membranes are thin (e.g., on the order of 100 nanometer to 1 micrometer), it is possible to transmit soft x-rays with sufficient intensity for spectroscopic experiments. Two experimental techniques are of particular interest, namely x-ray absorption spectroscopy (XAS) to study unoccupied electronic states and x-ray emission spectroscopy (XES) to investigate the occupied electronic levels. The combination of the two approaches, i.e., the collection of XES spectra at variable resonant excitation (resonant inelastic soft x-ray scattering - RIXS), gives unprecedented insight into the electronic structure of hitherto inaccessible samples, such as liquids and liquid-solid interfaces. In this presentation, the experimental requirements for such studies will be discussed and it will be demonstrated how XAS, XES, and RIXS can give unique insights into the electronic, chemical, and dynamic properties of liquids (in particular water) and liquid-solid interfaces.

9:20am **SY+SS+BI-TuM5 High-Resolution X-Ray Photoelectron Spectroscopy as a Versatile Tool for the Characterization of Monomolecular Self-Assembled Films**, ***M. Zharnikov***, Universität Heidelberg, Germany **INVITED**

Self-assembled monolayers (SAMs) have recently attracted considerable interest in physics, chemistry and biology due to their ability to control wetting, adhesion, lubrication and corrosion on surfaces and interfaces and their capability to become building blocks of future electronic devices. All the above applications rely on deep understanding of properties of these systems and precise knowledge of their structure. We will review recent progress in characterization of SAMs with a chalcogen headgroup on coinage metal and semiconductor substrates by high-resolution X-ray photoelectron spectroscopy (HRXPS). As compared to conventional XPS with a laboratory X-ray source, HRXPS, which usually takes advantage of both ultimate energy resolution and tunable photon energy (synchrotron), is capable to deliver additional information on the objects of interest, including screening phenomena, homogeneity of the bonding configurations, charge transfer upon the headgroup-substrate bond formation, etc. Also, this technique is very useful when dealing with systems exhibiting a large diversity of chemical species such as, e.g., SAMs on GaAs substrates. A variety of examples will be provided. Further, it will be shown that photoemission in SAMs cannot always be described within the standard theoretical framework, which have important implications for both understanding of the XPS/HRXPS spectra of the relevant SAM-derived systems and practical applications.

10:40am **SY+SS+BI-TuM9 Chemical Imaging and Spectroscopy at Sufficiently High Spatial Resolution to Uncover Functions of Nanoscale Phenomena**, ***M. Kiskinova***, Sincrotrone Trieste, Italy **INVITED**

The complementary capabilities of different microscopy approaches in terms of imaging, spectroscopy, spatial and time resolution are strongly requested by the multi-disciplinary research programs at the synchrotron facilities and have motivated continuous investments in development of instrumentation for imaging with spectroscopic analysis. The major part of the lecture will be focused on the potential of modern x-ray photoelectron microscopes in chemical imaging and micro-spot photoelectron spectroscopy.[1] Among the selected research topics, as representative examples are (i) addressing the surface properties of the individual C and oxide nanostructures and supported catalyst micro and nano-particles (ii) mass transport driven self-reorganization processes which can introduce lateral heterogeneity in the composition and reactive properties of surfaces (iii) quantum-size effects on the local chemical reactivity measured for ultrathin films with spatially varying thickness. The final part of the lecture will briefly illustrate the most recent achievements in combining the potential of soft x-ray transmission microscopy with multiple contrast approaches and fluorescence analysis.

Günther, S., Kaulich B., Gregoratti L., Kiskinova, M.: Prog. Surf. Sci. 70, 187, 2002.

11:20am **SY+SS+BI-TuM11 Hard X-ray Photoelectron Spectroscopy up to 15 keV: State-of-the-Art and Recent Results**, ***M. Merkel,*** FOCUS GmbH, Germany, *J. Rubio-Zuazo, G.R. Castro,* SpLine Spanish CRG Beamline at the European Synchrotron Radiation Facility, France, *M. Escher*, FOCUS GmbH, Germany

Hard X-ray photoelectron spectroscopy (HAXPES) gains momentum as a new non-destructive nanoanalytical method more and more. On one hand the request for non destructive and bulk sensitive analysis methods is highly visible. On the other hand the availability of a number of suitable high energy synchrotron beam lines allows for the realization of such dedicated instrumentations. A new electron analyzer that fulfils the requirements imposed by the XRD and HAXPES techniques is presented. The analyzer of the cylindrical sector type[1] in use (FOCUS HV CSA) is a very compact and at the same time highly efficient approach for this kind of electron spectroscopy. It is capable to handle kinetic energies up to 15 keV down to a few eV with the same analyzer setup and power supply.[2] The recent implementation of a 2D event counting detector for parallel data acquisition will be described also. By means of this detector the measurement speed is increased to overcome the restrictions imposed by the reduced sample cross sections and analyser transmission at high kinetic energies. Buried layers, as they are common for a number of nanotechnological applications, are invisible with most of the known non destructive analytical methods. To demonstrate the potential of electron spectroscopy at really high kinetic energies we used thin Au layers deposited onto a Cu substrate as a model system for bulk sensitive photoemission. The comparison of the Cu3s and Au5s peaks show the energy dependence of the depth information. It is seen that substrate properties can be probed for kinetic energies ≥ 10 keV effectively. By means of such measurements we derived the energy dependence of the effective attenuation length (EAL) for electrons in Au also. For this purpose core level spectra of different energies are taken for different film thicknesses. The extracted EAL of Au shows an energy dependence of $(\mathrm{Ekin})^{0.622}$ what is in good agreement with literature data. This work was supported through the Spanish Ministry of Education and Science (MEC), grants nos. FAP-2001-2166 and MAT1999-0241-C01 and the German Ministry of Education and Research (BMBF) under grant no. FKZ 13N9033.

[1] Risley J.S, Rev. Sci. Instrum. 43 (1971) 95; Sar-El H.Z, Rev. Sci. Instrum. 38 (1967) 1210; Sar-El H.Z, Rev. Sci. Instrum. 41 (1970) 561.

[2] J.R.Rubio-Zuazo, M.Escher, M.Merkel and G.R.Castro, J. of Phys. Conf. Ser. 100 (2008).

11:40am **SY+SS+BI-TuM12 A Comparative Study of Interface Formation for Ca/PDHFV and Ca/PHF by Synchrotron Radiation Photoemission**, *Y.X. Guo, W. Zhao, X.F. Feng, L. Zhang, W.H. Zhang,* ***J.F. Zhu***, University of Science and Technology of China

Interfaces of metal/polyfluorene have attracted much research interests in both technological and scientific point of view. Polyfluorene-based light emitting devices have been proved to have a high luminescene effciency. However, the occurrence of gap states in most cases will affect the luminescence properties of organic materials. In this paper, the interface formation and energy level alighment for Ca/PDHFV and Ca/PHF have been studied by synchrotron radiation photoemission spectroscopy (SRPES) and X-ray photoelectron spectroscopy (XPS). The results imply that the chemical reaction at the interface of Ca/PDHFV is stronger than that of Ca/PHF. However, no gap states at the Ca/PDHFV interface can be observed, which is different from the observations on Ca/PHF. Both of these two interfaces display low electron injection barrier. Our findings suggest that the gap states can be removed at metal/polyfluorene interface by introducing vinylene units into polyfluorene, which may provide a new way to eliminate the gap states.

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+PS+AS+BI+SS-TuA

Plasma-deposited Polymer and Organic Surfaces in Biological Applications
Moderator: E.R. Fisher, Colorado State University

1:40pm **BO+PS+AS+BI+SS-TuA1 High Throughput Surface Chemical Analysis of Polymer Microarrays: Wettability, Protein Adsorption and Cell Response Correlations**, *M. Taylor, A.J. Urquhart,* The University of Nottingham, UK, *Y. Mei, D.G. Anderson, R. Langer,* MIT, *M.C. Davies,* ***M.R. Alexander***, The University of Nottingham, UK **INVITED**

In the search for new and improved biomaterials, combinatorial material discovery approaches are increasingly being explored. A significant development in the production of polymer libraries by parallel synthesis was the move from preparation of macroscopic samples,[1] to on-slide polymerisation as microarrays in nano-litre volumes.[2] Such microarray material libraries may readily be interrogated by automated surface analysis equipment. Recently, high throughput surface analysis of a library of 576 different acrylate copolymers in triplicate on one slide using water contact angle (WCA), XPS and ToF SIMS highlighted the difference in the bulk and surface composition of the polymer spots, and consequently the need for surface analysis data when determining structure-property relationships.[3] The complexity of SIMS data, multiplied by the number of different samples necessitates the use of multivariate analytical approaches. Using partial least squares (PLS) analysis, relationships between SIMS fragments and WCA have led to identification of moieties controlling wettability across the wide range of copolymers synthesised on one microarray.[4] Comparison of human embryonic stem cell number on the spots with SIMS spectra have identified further SIMS fragments that correlate with high or low cell-polymer affinity. Protein adsorption measurements have been undertaken in an attempt to rationalise the cell adhesion data.[5] The correlations identified, and the information on the relationship between the surface structure and cell response or wettability will be discussed in this exploration of the high throughput approach.

[1] Brocchini S et al. Structure-property correlations in a combinatorial library of degradable biomaterials. Journal of Biomedical Materials Research 1998 42 66.

[2] Anderson DG, et al. Nanoliter-scale synthesis of arrayed biomaterials and application to human embryonic stem cells. Nature Biotechnology 2004 22 863.

[3] Urquhart AJ, et al. High throughput surface characterisation of a combinatorial material library. Adv Mats 2007 19 2486.

[4] Urquhart AJ et al. TOF-SIMS analysis of a 576 micropatterned copolymer array to reveal surface moieties that control wettability. Anal Chem 2008 80 135.

[5] Taylor M et al. A Methodology for Investigating Protein Adhesion and Adsorption to Microarrayed Combinatorial Polymers. Rapid Macromol Comm 2008 (in press).

2:20pm **BO+PS+AS+BI+SS-TuA3 Plasma Medicine**, ***A. Fridman***, Drexel University **INVITED**

Novel engineering and science approaches sustaining human health, such as for example radiation biology and laser medicine, represent a significant segment of technological developments around the world. Recent breakthrough discoveries of the highly energetic but non-damaging direct treatment of living tissues with non-thermal plasma enable to create new branch of the engineering medicine, PLASMA MEDICINE, which creates qualitatively new possibilities of healing, treating of previously untreated diseases, deactivation of dangerous pathogenic organisms, development of new direct methods of medical diagnostics. New types of non-thermal atmospheric plasma discharges are able to operate directly contacting human body and other living tissues, which significantly increase effectiveness of the tissue sterilization, treatment of wounds, skin and other diseases, as well as direct medical diagnostics. Obviously success of the plasma medicine depends on deep fundamental understanding of physics, chemistry and biology of the non-thermal plasma interaction with living tissues, and engineering of the relevant non-thermal plasma discharges, which is to be discussed in the presentation. Recent achievements in plasma biotechnology also address many aspects of the challenging problem of deactivation of viruses and bacteria that cannot be disinfected by traditional methods. Disinfecting large volumes of air in buildings and hospitals economically is now possible with room-temperature atmospheric pressure plasma. Similarly, atmospheric plasma technology can be employed to sterilize medical equipment, clothing, and building walls; to disinfect living tissue without side effects, and to disinfect and preserve food and water without damage. In addition, plasma technology can also be used to create innovative tools for sensing, detection and identification of dangerous pathogenic organisms as well as to characterize success of the cleansing processes. Essential advantage of the plasma biotechnology is its potential for universal availability, due to the technology's exclusive reliance on electrical power. It avoids many logistical difficulties associated with delivery, storage and disposal that typically hinder chemical and pharmaceutical approaches to sustainable health. Plasma technology can also be easily scaled from point-of-use devices to centrally operated plants capable of cleaning massive quantities of material. The key element of recent plasma technology developments is its use as a catalyst of many natural biological processes. As such, plasma can provide highly energy efficient treatment of biological materials, which is also to be discussed in the presentation.

3:00pm **BO+PS+AS+BI+SS-TuA5 Plasma Polymer Patterning of PDMS for Microfluidic Application**, ***S. Forster***, *A.G. Pereira-Medrano, M. Salim, P.C. Wright, S.L. McArthur*, University of Sheffield, UK

Microfluidic systems are becoming increasingly important for a wide range of bioengineering applications including proteomics and protein separations. Polydimethylsiloxane (PDMS) has proved to be the most popular material for microfluidic device production in the laboratory due to its many advantages over traditional materials. However, PDMS has some fundamental problems, namely a lack of functionality present at the surface, high protein fouling and inability to retain stable surface modification due to its motile hydrophobic monomer. These factors can lead to the loss of specificity and sensitivity in many bioassays. Plasma polymerisation is a method of depositing a uniform polymeric coating onto a surface, while retaining the desired functionality of the monomer. Hence, plasma polymerisation presents a versatile approach for surface modification and patterning of device channels. The wide range of monomers available for plasma polymerisation makes this approach even more suitable for use in systems where multiple surface properties within a single device are required. The aim of this work was firstly to investigate methods to produce stable plasma polymer patterns on PDMS. The coatings chosen include acrylic acid and maleic anhydride for their functional groups and tetraglyme to reduce non-specific protein adsorption. Patterning using photolithographic techniques and subsequent specific biomolecule immobilisation was achieved. Surface characterization using XPS and ToF-SIMS was used to ensure the spatial, chemical and biomolecule resolution of the device surfaces produced. This ability to combine microfluidics with spatially defined reactive regions on a 'non-fouling' background was then used in a number of applications to show the diversity and efficiency of the devices. Protein digestion by immobilized trypsin using single flow-through experiments in PDMS devices was improved using plasma polymer functionalized channels. The results achieved using mass spectrometry showed an increase in speed and sensitivity of the digestion as well as superior device reliability. Finally, plasma functionalized channels were used to investigate the effect of ampholyte adsorption onto device walls in isoelectric focusing (IEF). By coating channels with a tetraglyme plasma polymer an increase in sensitivity and reproducibility of IEF measurement was achieved. This technique can also increase the 'lifetime' of the device by ensuring channel properties were unchanged.

4:00pm **BO+PS+AS+BI+SS-TuA8 Plasma Etching for Selective Removal of PMMA from nm-scale PS/PMMA Block Copolymers for Lithographic Applications**, ***A.E. Wendt***, *Y.H. Ting, C.C. Liu, X. Liu, H.Q. Jiang, F.J. Himpsel,* University of Wisconsin-Madison, *P.F. Nealey*, University of Wisconsin, Madison **INVITED**

Diblock copolymers films, in which polymer components segregate into nano-scale domains, have been shown to have tremendous potential in fabrication of nm-scale surface topographies. Applications range from microelectronics fabrication to the study of how topography affects the growth and behavior of living cells or microorganisms. Use of block copolymers as a template for pattern transfer requires selective removal of one polymer component, and has motivated our study of plasma etching of polystyrene (PS) and polymethyl-methacrylate (PMMA), the two components of the PS-PMMA diblock copolymer. To better understand the mechanisms of the etch process for these materials, we have surveyed the effects of etch gas mixture and ion bombardment energy (taking advantage of our capability to produce a narrow ion energy distribution at the substrate), in combination with chemical analysis of the resulting etched surfaces. Of particular interest are the mechanisms of surface roughening, which shows a complex dependence on plasma process conditions that is not easily explained. A review of the literature on factors contributing to surface roughness, such as intrinsic inhomogeneity in the film, local deposition/micro-masking, shadowing effects and redeposition will be presented. We ultimately propose a mechanism for roughening of PS that involves micro-masking by inhomogeneous modification of surface chemical composition (rather than deposition) in oxygen-containing plasmas. Support from the UW NSF MRSEC for Nanostructured Materials is gratefully acknowledged.

4:40pm **BO+PS+AS+BI+SS-TuA10 Correlation of Macroscopic Surface Qualities of Poly-Parylene with Plasma-Specific Parameters**, ***G. Franz***, *F. Rauter*, *M. Häge*, University of Applied Sciences, Germany

In the course of our research how deposition conditions teleologically influence the morphology and various physical properties of the surface of various derivates of parylene, we followed the Yasuda approach to correlate the deposition rate of polymeric films with external parameters (flow rate and power) to define three different regimes of growth.[1,2] Since external parameters, especially the pressure, influence the polymerization in an opposite manner (rising the pressure causes an increase in the collision rate, but a decrease in electron temperature) we studied the deposition of parylene vapors with and without pulsed microwave plasmas to correlate outcome parameters such as surface energy, roughness, and deposition rate with respect to plasma density and electron temperature (Langmuir and OES) by varying the molar fraction of the monomeric species, diluted by the noble gas argon, the total pressure and the power. For this end, we determined the vapor pressure of the dimer and the chemical equilibrium between the monomer and the dimer by varying the evaporation temperature and the cracking temperature, resp., and cross-checked this equilibrium by mass spectrometry. This method has been extended to explain the onset of volume polymerization which becomes manifest by slight tarnishing of the polymer. Following Yasuda, this happens when a certain ratio of number density of the monomeric species to plasma density is exceeded. After having established stable process windows, two further tracks have been followed, namely copolymerization with CF_4 (volume polymerization) and hydrophilic functionalization. Following Gogolides, the surface roughness has been correlated to contact angle measurements.[3] The super-hydrophobic character is mainly due to surface roughening (nanotexturing) in the case of normal CVD. However, plasma treatment leads to super-hydrophobic character also for smooth surfaces. Subsequent treatment with O_2 generates long-term stable hydrophilic surfaces. To calibrate the effect of momentum transfer and to separate the chemical effect of etching, this has been compared with Ar etching.

[1] H.K. Yasuda, and Q.S. Yu; J. Vac. Sci. Technol. A 19, 773 (2001)

[2] Q. Yu, C.E. Moffitt, D.M. Wieliczka, and H. Yasuda; J. Vac. Sci. Technol. A 19, 2163 (2001)

[3] A.D. Tserepi, M.-E. Vlachopoulou, and E. Gogolides; Nanotechnology 17, 3977 (2006).

5:00pm **BO+PS+AS+BI+SS-TuA11 Plasma Processing of Nanostructured Polymeric Surfaces for the Development of Immunosensors**, *A. Valsesia*, ***P. Colpo***, *I. Mannelli*, *G. Ceccone*, *F. Rossi*, European Commission Joint Research Centre, Italy

Immunosensors play a very important role for the development of Point-of-Care analysis thanks to their rapid and sensitive detection capabilities.[1] Among others, the control of the interface between the transducer and the biological probes is a crucial issue since the bio-interface is the essential element that guaranty the bioactivity of the immobilized biological probes.[2] The control of the bio-interface is typically addressed by functionalizing the surface with special chemical groups. Besides, new nanobiotechnology-based tools have led to more sophisticated approaches that use for instance nanostructured surfaces. Benefits have been already shown in terms of the improvement of immunoreaction efficiency.[3] In this work we propose a new method for fabricating nanostrucured surfaces combining the use of colloidal masks with different plasma processes. In this method, Plasma Polymerization Processes are able to produce pinhole-free functional layers with different properties. The choice of the precursor together with the appropriate plasma processing parameter ensures the production of stable functional layers which can be used for the production of the chemically contrasted nanopatterns. Also the deposition of the colloidal mask in a controlled way is essential: for example, mass sensitive detectors (like Quartz Crystal Microbalance, QCM) require the use of very large areas in order to obtain measurable signals. Also plasma etching plays a very important role: it is important to choose the suitable processing parameters enabling the fabrication of nanostructured surface which are not limited in the patterning geometry and resolution. After the optimization of the nanofabrication process, the surfaces of immunosensors have been nanostructured. In particular we transferred the nanostructures on the crystals of QCM for on-line monitoring of the protein adhesion. The nanostructures accelerate the kinetics of absorption and increase the density of absorbed molecules, resulting in higher bioactivity of the immobilized proteins and consequently in an improvement of the immunosensing performances.

[1] K. R. Rogers, Applied Biochemistry and Biotechnology - Part B Molecular Biotechnology 2000, 14, 109-129.

[2] B. Kasemo, Current Opinion in Solid State and Materials Science 1998, 3, 451-459.

[3] A. Valsesia, P. Colpo, T. Meziani, P. Lisboa, M. Lejeune, and F. Rossi, Langmuir 2006, 22, 1763-1767.

5:20pm **BO+PS+AS+BI+SS-TuA12 Use of Multivariate Analysis Techniques to Predict Cellular Response to Plasma Polymerized pNIPAM**, ***J.E. Fulghum***, *K. Artyushkova*, *A. Lucero*, *H.E. Canavan*, University of New Mexico

The primary objective of this work is to investigate the correlate structural properties of a thermoresponsive polymer, poly(N-isopropyl acrylamide) (pNIPAM), with its ability to reversibly adhere cells. PNIPAM undergoes a sharp property change in response to a moderate thermal stimulus at physiological temperatures (~32 °C). This behavior has generated great interest in the biomaterials community, and pNIPAM is being investigated as a "smart" release coating to harvest intact cell monolayers. Many techniques are used to deposit pNIPAM, including electron beam irradiation and solution deposition (e.g., silanes and self-assembled monomers). Recently, we constructed a radio frequence (rf) plasma reactor for plasma polymerization of NIPAM (ppNIPAM) from the vapor phase based on a previous design. Plasma polymerization is a sterile, solvent-free, and compatible with surfaces of any geometry or chemistry. These factors make plasma polymerization extremely useful for cell and tissue culture, which often rely on plastic tissue culture plates. Due to the inherently energetic conditions of the plasma, parameters such as maximum rf wattage, location/position of the samples in the chamber, and monomer flow have on the resulting films. In this work, pNIPAM films resulting from those varying conditions are characterized using X-ray photoelectron spectroscopy (XPS) for film composition, interferometry for film thickness, contact angles for thermoresponse, and cell detachment for cell releasing properties. Using multivariate analysis, the structural information of the films obtained at various polymerization conditions will be correlated with their thermoresponsive and cell-releasing behavior. In this way, we will predict the conditions that will optimize film composition for bioengineering applications.

Surface Science
Room: 208 - Session SS1+NC-TuA

Reactions on Gold and BiMetallics
Moderator: D.A. Chen, University of South Carolina

1:40pm **SS1+NC-TuA1 Surface-Mediated Partial Oxidation of Alcohols on Gold**, ***X. Liu***, *C.M. Friend*, Harvard University

Fundamental investigations of the chemical properties of oxygen on Au(111) will be described. These studies serve as a model for gold-based catalysis which efficiently promotes oxidation reactions of CO, alcohols, and olefins. Gold is also important in materials science more broadly because it is used for interconnects and as a substrate for self-assembled monolayers and for biological samples. Our studies of alcohol oxidation on gold single-crystal surfaces under ultra-high vacuum conditions have revealed mechanistic information for partial oxidation of alcohols that can be applied to explain the mechanism of heterogeneous catalytic processes. Furthermore, such basic knowledge is important for understanding and controlling factors that determine reaction selectivity. We have used a combination of reactivity, spectroscopic and imaging measurements in our work. These studies provide evidence that mechanistic information, established in single-crystal surface science studies, can serve as a valuable guide for understanding and designing catalytic reaction processes.

2:00pm **SS1+NC-TuA2 Selective Oxidation Chemistry on Gold**, ***J.L. Gong****, *R.A. Ojifinni*, *N.S. Froemming*, *T. Yan*, *G. Henkelman*, *C.B. Mullins*, University of Texas at Austin

The reactivity of atomic oxygen on Au(111) has been investigated employing molecular beam scattering and temperature programmed desorption (TPD) techniques under ultrahigh vacuum (UHV) conditions. We demonstrate that adsorbed O atoms (O_{ad}) facilitate $NH_{3,ad}$ decomposition even though ammonia does not dissociate on the clean Au(111) surface. The selectivity of the catalytic oxidation of ammonia to N_2 or to NO on Au(111) is tunable by the amount of atomic oxygen pre-covering the surface. Both N_2 and NO are formed via simple recombination reactions ($N_{ad} + N_{ad}$ and $N_{ad} + O_{ad}$). At low oxygen coverages ($\theta_O < 0.5$ ML), adsorbed ammonia is stripped to $NH_{x,ad}$ which decomposes to form gaseous N_2. We also present experimental and density functional theory (DFT) calculation results of formation and decomposition of the carbonate anion ($CO_3 = CO_2 + O_a$) on atomic oxygen pre-covered Au(111). A reaction probability on the order of 10^{-4} and an apparent activation energy of -0.15 eV are estimated for this reaction. The small values of reaction probability are likely part of the reason why an earlier study on Au(111) reported

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* Morton S. Traum Award Finalist

undetectable surface carbonate formation. Additionally, we have investigated partial oxidation of propanol on atomic oxygen covered Au(111). At reaction temperatures below 300 K, 1-propanol is oxidized to propaldehyde with 100% selectivity while acetone is the only products of 2-propanol partial oxidation. A small amount of CO_2 is formed at higher surface temperatures (i.e., above 300 K).

2:20pm **SS1+NC-TuA3 Model Catalysts for Steam Reforming and Water-Gas Shift Reactions**, ***J. Hrbek***, Brookhaven National Laboratory **INVITED**

The molecular hydrogen used in many large scale processes in chemical industry and for operating fuel cells is produced by these catalytic reactions. Steam reforming can provide sustainable source of hydrogen when using ethanol as feedstock; water-gas shift is used to purify hydrogen by removing CO, a catalytic poison. I will describe the preparation and characterization of model catalysts, and discuss their surface interactions with reactants under vacuum and their catalytic reactivity under higher pressures. As we have shown recently (Science 318(2007)1757; Angew. Chem. Int. Ed. 46(2007)1329)) both the model catalysts (Au or Cu on CeO2(111)) and the inverse model catalysts (CeOx or TiOx nanoparticles supported on Au(111) or Cu(111)) have significant intrinsic activity for water-gas shift at elevated pressures. Neither Au(111) nor CeO2(111) have any activity in the WGS reaction. Our photoemission data indicate that CeOx nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the CeO2 nanoparticles are inactive. Water dissociates on O vacancies of the oxide nanoparticle (the rate limiting step in the WGS reaction), CO adsorbs on Au site located near the oxide-metal perimeter, and subsequent reaction steps take place at the metal-oxide interface. Our ability to identify reaction intermediates under vacuum conditions and to link them with the structural characterization at the atomic level is critical for development of reaction models: specifically in the WGS process the oxide support is not a simple spectator and plays an essential role. I will also discuss experimental results obtained with the model catalysts for steam reforming of ethanol. This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

3:00pm **SS1+NC-TuA5 Role of the Oxide Substrate on O_2 Dissociative Adsorption on Au Nanostructures: First Principle Studies**, *S. Stolbov*, ***T.S. Rahman***, University of Central Florida

In this work we apply the density functional theory calculations to explore the mechanism of high reactivity of Au nanoparticles on oxide substrates. We test the idea that the substrate – nanoparticle interaction makes the O2 dissociative adsorption favorable on this system, in contrast to bulk Au, and then the O atoms, so adsorbed, are consumed by reactants for further oxidation. We exploit the observation that the 1.5-layer Au film on TiOx displays an exceptionally high reactivity as compared to a monolayer Au film, as well as those with 2 or more layers.[1] We calculate the eneretics of dissociative adsorption of O2 on the surfaces 1.5, 2, 2.5, 3, 4.5, and 5 Au(001) layer structures in two environments: 1) free standing layers, 2) on TiO2 fragments (modeling a substrate). For all missing row n+0.5 Au structures under consideration, the total energy is found to decrease upon the O2 dissociative adsorption. However, analysis of entire pathway for this reaction suggests that the O2 dissociative adsorption is favorable only for 1.5Au/TiO2 structure. This result along with the experimental finding[1] point to the O2 dissociative adsorption as being the main mechanism for the observed reactivity of Au nanostructures. Calculated local densities of electronic states and local charges in the system will be presented for further insights into the nature of the effect.

[1] M. S. Chen, D. W. Goodman, Science 306, 234 (2004). Work supported in part by DOE under grant # DE-FG02-03ER15842.

4:00pm **SS1+NC-TuA8 Hydrogen Splitting on Ru and Pt Nanoparticles**, *E. Fiordaliso*, ***M. Johansson***, *S. Murphy, R. Nielsen, I. Chorkendorff*, Technical University of Denmark

Here we investigate the hydrogen splitting rate as a function of particle size for Pt and Ru by measuring the rate of the H-D exchange reaction at 1 bar. The study is mainly motivated by fuel cell applications, where highly dispersed Pt is used as the anode catalyst in the Proton Exchange Membrane (PEM) fuel cell. It was found in an earlier study that at 1 bar, Ru gives a higher rate for the H-D exchange reaction than Pt.[1] The experiments are performed in an apparatus which combines an ultra-high vacuum chamber for sample preparation and surface analysis with a high-pressure cell.[2] Model catalysts in the form of spots with a diameter of 1 mm are prepared by electron-beam evaporation of metal onto a sputtered highly ordered pyrolytic graphite (HOPG) substrate. The amount of metal corresponds to an average thickness between 0.2 and 50 Å. The rate of the H-D exchange reaction for each catalyst spot is measured in the high-pressure cell with the help of a combined gas dispenser and gas sampling device. The sampled gas is analyzed with mass spectrometry. Measurements were carried out at 1 bar with a gas mixture containing 1 percent D_2 in H_2 and the temperature was varied in the range 40 to 200 °C. The model catalysts were characterized with Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM) before and after the high-pressure measurements. A simple model is used in order to extract the sticking probability for H_2 from data for the H-D exchange rate. Once the sticking probability has been obtained, the dissociative adsorption/desorption rate for H_2 can be calculated. The apparent desorption energy, E_{des}, for H_2 at the H coverage corresponding to 1 bar pressure is then extracted from data for the desorption rate as a function of temperature. It is found that at 0.2 Å average metal thickness, E_{des} is approximately 0.2 eV for Ru and 0.27 eV for Pt, and that the metals form particles with a mean diameter less than 10 Å. As the metal loading is increased, the particle size increases whereas E_{des} decreases. Above approximately 15 Å, an almost continuous metal film is formed and E_{des} becomes constant, 0.02 eV for Ru and 0.21 eV for Pt. Hence, the desorption energy for H_2 decreases with increasing particle size for both Pt and Ru, but the effect is more pronounced for Ru.

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[2] M. Johansson, J. Hoffmann Jørgensen, I. Chorkendorff, Rev. Sci. Instrum. 75 (2004) 2082.

4:20pm **SS1+NC-TuA9 Novel Pathways to Hydrogen Dissociation and Diffusion on Pd Alloys**, ***H.L. Tierney***, *A.E. Baber*, Tufts University, *J.R. Kitchin*, Carnegie Mellon, *E.C.H. Sykes*, Tufts University

Dissociation of molecular hydrogen on the surfaces of Pd-based alloys is a key step in a number of energy-related technologies, including CO_2 conversion and hydrogen separation. An understanding of the nature of H_2-surface interactions, including molecular adsorption, dissociation and surface diffusion provides a basis for the development of next-generation energy technologies. In this low-temperature scanning tunneling microscopy study we have demonstrated that individual Pd atoms in an inert Cu matrix are active for the dissociation of hydrogen and subsequent spillover onto Cu sites. The atomic-scale composition of both Pd/Cu{111} and Pd/Au{111} near-surface alloys were elucidated and H uptake was quantified. Our results indicated that H spillover was facile on Pd/Cu at 400 K but that no H was found under the same H_2 flux on a Pd/Au sample with identical atomic composition and geometry. Based on a simplistic model involving the adsorption energies of H on Pd{111}, Cu{111} and Au{111} it would appear that the barrier for H to migrate from Pd to Cu or Au is too high to occur at 400 K. DFT calculations provided insight into this unusual activity of Pd/Cu alloys for dissociation and uptake of H. The calculations revealed that the barrier for diffusion of H away from isolated Pd sites on Pd/Cu{111} alloys is lower than that of pure Pd{111}, but that this same diffusion barrier is insurmountable at 400 K on Pd/Au alloys. These results demonstrate the powerful influence an inert substrate has on the catalytic activity of Pd atoms supported in its surface.

4:40pm **SS1+NC-TuA10 Alloy Nanocluster Distinct Surface Segregation Phenomena Related to the Coordination Dependence of Bond-Energies: Introduction and Application of a New Theoretical Approach**, ***L. Rubinovich***, *M. Polak*, Ben-Gurion University, Israel

This work introduces some novel aspects concerning alloy nanocluster equilibrium surface segregation phenomena and their modeling. The first involves the extraction of the Coordination dependence of Bond Energy Variations from DFT computed surface energies (the CBEV method). In particular, polynomial functions in terms of pair coordination numbers were fitted to DFT data reported recently for energies of pure Pt, Pd and Rh surfaces and small clusters. These functions yield elemental bond energy variations pertinent to any site at the cluster surface and subsurface layers. The second novel aspect, revealed when using the bond energy variations as input in statistical-mechanical computations based on the "free-energy concentration expansion method" (FCEM[1]), concerns the finding that preferential pair-bond strengthening can lead to quite unique surface segregation characteristics. In particular: (i) In spite of the general tendency of Pd to segregate at Pt-Pd alloy surfaces, in cuboctahedron clusters certain (111) surface sites are populated by Pt, namely, a segregation reversal is predicted; (ii) Distinct Pd segregation profiles with maximal concentration at the subsurface layer are obtained for the Pt-Pd cluster (100) face, compared to subsurface oscillation in the Rh-Pd cluster (100) face. Further computations for Rh-Pd revealed inter-cluster separation involving "magic number" Pd segregated structures exhibiting various types of order. At higher temperatures atomic exchange among surface sites as well as surface-core desegregation processes are reflected in distinct configurational heat capacity peaks of the Schottky type.[2] As a test case, CBEV/FCEM computations done for the Pt-Rh(111) two-layer (oscillatory) profile show better agreement with previously reported experimental data as compared to our earlier work based on the NRL-TB/FCEM approach.[3] Using the highly efficient CBEV/FCEM method enables to explore also compositional structures and properties of Rh-Pt-Pd ternary nano-clusters.

Compared to current other approaches, this method is highly transparent, yielding better insight into the origin of surface segregation in bulk alloys and nanoclusters.

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5:00pm **SS1+NC-TuA11 Stability, Electronic, and Catalytic Properties of Supported Metal Clusters**, ***B. Roldan Cuenya***, University of Central Florida

The next generation of nanocatalysts requires detailed knowledge of the correlation between their structure and reactivity. Size- and shape-selected Au, Pt and AuFe nanoclusters with well defined intercluster distances were synthesized by diblock copolymer encapsulation. Significant changes in the electronic local density of states (LDOS) of TiC-supported Au clusters, in particular, the onset of non-metallic behavior, were observed by scanning tunneling spectroscopy with decreasing cluster size. In addition, evidence for substrate-induced modifications in the LDOS of interfacial gold atoms was found.[1] Our temperature programmed desorption (TPD) measurements indicated a size-dependency in the catalytic activity of Au/TiC for CO oxidation.[2] Furthermore, interparticle interactions were found to affect the activity and life-time of our catalysts.[3] The stability of oxidized gold species formed upon cluster exposure to atomic oxygen was investigated using a combination of temperature-, time- and CO dosing-dependent X-ray photoelectron spectroscopy and TPD.[4] Our work demonstrates the formation of surface and sub-surface Au_2O_3 on Au nanoparticles. Interestingly, the stability of these species upon thermal treatment was found to depend on the reducibility of the oxide support. Finally, the formation, surface reconstruction and high-temperature mobility of size-selected bimetallic AuFe[5] and Pt nanoclusters deposited on $TiO_2(110)$ will be presented.

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[3] L. K. Ono, B. Roldan Cuenya, Catal. Lett. 113, 86 (2007)

[4] L. K. Ono, B. Roldan Cuenya, J. Phys. Chem. C 112, 4676 (2008)

[5] A. Naitabdi, B. Roldan Cuenya, Appl. Phys. Lett. 91, 113110 (2007).

5:20pm **SS1+NC-TuA12 The Morphology and Reactivity of Metallic Nano Clusters Deposited on SiO_2 via Water Buffer Layer**, ***E. Gross***, *M. Asscher*, The Hebrew University of Jerusalem, Israel

Nanometer size gold clusters supported on metal oxide surfaces were reported as having size dependent catalytic activity. This has motivated us to prepare clusters under clean, high vacuum conditions with control over the clusters size and density. Gold nano clusters were prepared by two different growth procedures. In the first, the clusters were prepared by direct deposition (DD) of gold atoms on $SiO_2/Si(100)$ substrates. The second growth mode is based on initial evaporation of gold atoms on top of amorphous solid water as a buffer layer at 100K which separates the small gold seed clusters from the substrate. Subsequent annealing to 300K desorbs the water molecules, resulting in aggregation and growth and (cold) deposition of nano-clusters on the substrate in a Buffer Layer Assisted Growth (BLAG) mechanism. In order to increase the BLAG clusters density we have introduced a Multi-Cycle BLAG procedure (MC-BLAG). By repeating the BLAG procedure up to seven times consecutively, the cluster density can be increased by 5 fold without affecting the clusters size. BLAG clusters are more 3D in nature, have larger height to diameter ratio than DD clusters, yet their interaction with CO is very similar to DD clusters. This is reflected by the practically identical CO stretch observed on both clusters at $2106\pm2cm^{-1}$. UV-Visible absorption spectroscopy measurements have shown that differences in clusters morphology lead to variations in their surface plasmon resonance. The Multi-Cycle BLAG method also enables the growth of bi-metallic clusters. By modifying the preparation procedure either separated Au and Pd clusters or alloyed (Au-Pd) clusters can be prepared on the substrate. The catalytic reactivity of these bimetallic clusters is of great potential importance. We currently investigate the catalytic reactivity of bi-metallic clusters (such as gold and palladium or gold and copper) on dehydrogenation reactions. These reactions are of potential importance for various hydrogen energy applications, e.g. fuel cells.

Surface Science
Room: 209 - Session SS2-TuA

Dynamics and Novel Probes
Moderator: M.G. White, Brookhaven National Laboratory and State University of New York at Stony Brook

1:40pm **SS2-TuA1 Excited Electrons in Interfacial Chemistry**, ***A.M. Wodtke***, *I. Rahinov*, *R. Cooper*, University of California, Santa Barbara, *D.J. Auerbach*, GRT Inc. **INVITED**

Developing a predictive understanding of surface reactivity incorporating the possible breakdown of the Born-Oppenheimer approximation represents one of the most important challenges to current research in chemical dynamics. Furthermore, to the extent that Born-Oppenheimer breaks down, we have no predictive theory of surface chemistry. This means we are working in an exciting environment where new phenomena might be discovered through experiments and inspire new theoretical developments. This lecture will present recent experimental results from our group that bears on this topic. For example, when molecules with low levels of vibrational excitation collide with metal surfaces, vibrational coupling to electron-hole pairs is not found to be strong unless incidence energies are high. However, there is accumulating evidence that coupling of large amplitude molecular vibration to metallic-electron degrees-of-freedom can be strong and becomes more important at reduced incidence translational energies. This can occur due to charge transfer between the surface and the molecule and the high kinetic energies associated with bond compression/formation. These conditions found in these experiments simulate reaching a chemical transition-state also and we are intrigued to pose the basic question: are electronically non-adiabatic couplings important at transition-states of reactions at metal surfaces? This implies theoretical approaches relying on the Born-Oppenheimer approximation may not accurately reflect the nature of transition-state traversal in reactions at metal surfaces. In related work, we have been looking at the energy transfer processes between molecules and surfaces that enable molecular trapping, the first elementary step in “Langmuir-Hinshelwood” reactions. We find remarkably large amounts of translational energy can be channeled to a metal surface and are able to look at this for different quantum-state to state scattering channels. While our results require additional theoretical comparisons, it appears that phonon coupling may not be sufficient to explain these experimental observations.

2:20pm **SS2-TuA3 Chemicurrent Measurements using Alkali Metal Covered Pd/p-Si(001) Schottky Diodes**, ***D. Krix***, *K. Huba*, *H. Nienhaus*, University of Duisburg-Essen, Germany

Non-adiabatic energy dissipation, e.g. the creation of electron-hole pairs, plays an important role in the understanding of chemical reactions at metal surfaces. For a large number of gas-metal reactions it is possible to measure hot charge carriers produced while exposing the metal to reactive gases as chemicurrents. The method is based on depositing thin metal films on a semiconducting substrate in order to form a rectifying electrical device - i.e. Schottky diodes. Hot electrons and holes may be ballistically injected into the semiconductor for energies larger than the intrinsic barrier at the interface. Thermalising in the bulk of the semiconductor the current can not flow back into the metal other than through the measuring circuit. Therefore large area, nanometer thick Pd films were grown on wet chemically prepared, hydrogen terminated, Boron doped p-Si(001) substrates. The palladium diodes are used as a platform for further deposition of alkali metal layers. Palladium was chosen for its low barrier height (0.38 eV) on p-doped silicon, making the diodes most sensitive to low energetic hot holes while retaining excellent device characteristics. This barrier is also considerably lower than that of pure alkali-Si diodes – 0.58 eV for potassium. Chemicurrent, Auger spectroscopy, as well as Kelvin probe data are presented for the adsorption of molecular oxygen and molecular hydrogen on Pd and K/Pd surfaces at low temperatures ($T = 120$ K). During the oxidation with molecular oxygen the chemicurrents show as at least two distinct maxima. Varying the initial alkali coverage changes the relative contribution of the maxima to the chemicurrent. The overall charge detected increases monotonically with potassium coverage. After the deposition of about two monolayers of potassium a saturation is seen of about $1\mu As/cm^2$. Increasing the Pd film thickness results in a strong exponential attenuation of the observed charge. This is strong support for the identification of the detected currents as due to hot hole generation at the surface. The data give an estimate of the probability to generate a hot hole in a reaction event of approximately 1%.

2:40pm **SS2-TuA4 The Role of Surface Atom Motion in Methane Activation on Ni(111)**, ***V.L. Campbell***, Tufts University, *D.R. Killelea*, University of Chicago, *N. Chen, A.L. Utz*, Tufts University

Quantum state resolved gas-surface reactivity measurements have yielded detailed insights into how a gas phase reagent's vibrational energy promotes reaction, but our understanding of how surface vibrations influence reactivity is less complete. Here, we show that state-selected reagents, with their precisely defined internal and translational energy, are powerful probes of the reaction dynamics along other important energetic degrees of freedom, including surface atom motion. We focus on how surface atom motion influences the distribution of energetic barriers experienced by methane molecules prepared in v=1, J=2 of the ν_3 C-H stretching state and incident on a clean Ni(111) surface. Recent theoretical work suggests when a nickel atom is displaced above the (111) surface plane, the energetic barrier for reaction decreases. Within a dynamical framework, this result suggests that increasing surface temperature increases the probability that an incident methane molecule will impact on a Ni atom in this energetically favorable geometry. Statistical models of reactivity assume that energy in phonon modes is pooled to activate the reaction complex; increased surface temperature increases the pool of energy available to activate the reaction. We use state-selected reagents, with their well-defined internal and translational energies, to quantify reaction probability as a function of incident kinetic energy at a series of surface temperatures. At each surface temperature, the state-resolved reaction probability curves we obtain reveal the effective distribution of barriers along the translational energy coordinate. Changes in the shape of the effective barrier height distribution function with respect to surface temperature reveal how surface atom motion impacts reaction energetics. Our ability to prepare and control the non-equilibrium distribution of energy among the many degrees of freedom in this system permits a test of the energy pooling assumption.

3:00pm **SS2-TuA5 Low-Temperature Growth of Si/Si(111)-(7x7) by Femtosecond Pulsed Laser Deposition**, ***I.A. El-Kholy***, *H. Elsayed-Ali*, Old Dominion University

Surface morphology during the growth of Si on Si(111)-(7x7) by femtosecond pulsed laser deposition (fsPLD) is studied using reflection high-energy electron diffraction (RHEED) at different temperatures. The growth of Si on Si(111) has received considerable attention as a model system of homoepitaxy. PLD is a deposition technique that uses much more energetic species (atoms and ions) compared to other physical vapor deposition (PVD), such as in molecular beam epitaxy. In PLD, the deposition process consists of periodic bursts of laser-generated plume followed by uninterrupted surface relaxation. This periodic nature of deposition differs from other PVD methods, and this could affect the growth mechanism. The use of ultrafast lasers vaporizes the target rather than melting it, thus minimizes the formation of particulates. In this work, in situ RHEED was used to study the dynamics of PLD of Si on Si(111)-(7×7). A Ti-sapphire laser (100-fs, 800-nm, 1 kHz) was used to ablate the Si target to generate a plume that deposite on a Si(111)-(7x7) kept at varying temperatures. The experiment was performed in an ultrahigh vacuum chamber at a residual gas pressure of $5x10^{-9}$ torr. It is observed that the decay of the RHEED pattern during deposition is due to the increase in the surface roughness. Epitaxial growth of Si/Si(111)-(7x7) at temperatures as low as 350°C was observed. For this substrate temperature, no change in RHEED patterns was observed after growth, with only reduction in intensity during deposition. This indicates that the growth mechanism was step-flow.

4:00pm **SS2-TuA8 Scanning Near Field Infrared Microsocopy (SNIM) – Combining Topographical and Chemical Mapping of Bio Materials**, ***M. Havenith***, Ruhr University Bochum, Germany **INVITED**

We have set-up a scanning near field microscope (SNIM) in Bochum. As radiation source serves an Infrared Opto Parametric Oscillator (IR-OPO) and a CO laser. This allows us to cover the chemically important frequency range of the amide bands and the C-H and O-H stretching region. In 2007 our group has reported chemical imaging of microstructure self-assembled monolayers (SAMs) with nanometre resolution[1] using SNIM. This study demonstrated the extreme sensitivity of SNIM which even allowed recording the IR spectrum of a single monolayer of a specific absorbing functional group (biotin). Our measurements were carried out on a microcontact printed line pattern of a monomolecular film of biotinylated alkylthiolates. Whereas in conventional IR microscopy, about 1 µm thick layers of protein sample are required in order to record a full IR spectrum, here the IR fingerprint spectrum of approximately 30 000 biotin molecules in a 90 nm by 90nm patch of 3.7 nm height were detected. Biotin can also be considered as a model system for more complex protein systems. Further applications include the use for label-free analysis of biochips on the nano-scale. The possibility of simultaneously accessing topographic and spectroscopic information from biological nanostructures could be the basis for a new generation of nanodevices e.g. for medical diagnostics. As a proof-of-principle we demonstrate the feasibility of detecting hybridization reactions in nanostructured DNA-patches. For the DNA nanofabrication process we use nanografting which is a scanning probe microscopy based lithography technique. The nanografted single stranded nano structures can be clearly detected within the double stranded self assembled monolayers due to their distinct IR frequency response. Moreover, even nanografted double stranded nanostructures can be imaged since they have a higher packing density, yielding increased IR absorption in the corresponding amide band. This work is carried out in cooperation with the group of L. Casalis and G. Scoles at ELETTRA.

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4:40pm **SS2-TuA10 Non Statistical Patterns of Chemical Reactivity on Metals**, ***A.L. Utz***, *D.R. Killelea*, Tufts University

Facile electron- and phonon-mediated energy exchange channels on metal surfaces have the potential to support rapid and extensive energy exchange during a reactive collision, but recent state-resolved reactivity measurements of methane's dissociative chemisorption on Ni have produced clear evidence for incomplete (non-statistical) energy redistribution prior to reaction. Examples include vibrational-mode selective chemistry (in which reactivity is influenced not only by the amount of vibrational energy available, but also by the identity of the excited vibrational state), the observation that vibrational and translational energy differ in their ability to activate reaction, and even bond-selective chemistry (selective excitation of the C-H stretch in CHD_3 prior to surface impact increased the C-H : C-D bond cleavage ratio among products nearly 100-fold relative to an isoenergetic ensemble of CHD_3 whose vibrations were statistically populated). We will describe a mechanistic framework for understanding the origin of observed non-statistical reactivity and predicting the propensity for such behavior in other systems. The model builds on numerous experimental and theoretical studies of intramolecular vibrational energy flow and quenching in the gas phase, in liquids, and at surfaces, and it focuses on the timescales for key energy exchange processes relative to reaction. It provides a qualitative explanation for observed reactivity patterns, intuitive guidance for understanding and predicting reactivity patterns, and it and identifies attractive targets for future experimental and theoretical work to better understand and exploit these effects.

5:00pm **SS2-TuA11 Adsorption versus Interaction Strength: Analysis of Molecule-Surface Interactions of Organic Molecules on Pt and Pt-Sn Surfaces with HREELS and DFT**, ***J. Haubrich***, University of Bonn, Germany, *D. Loffreda, F. Delbecq, Y. Jugnet, P. Sautet*, Ecole Normale Supérieure de Lyon, France, *C. Becker, K. Wandelt*, University of Bonn, Germany

Studies on catalysis such as the selective hydrogenation of α,β -unsaturated aldehydes on transition metal surfaces represent a challenge to both experimentalists and theoreticians. In order to elucidate the underlying elementary reactions, the assignment of the adsorption structures of complex molecules on model-catalyst surfaces is a fundamental step. Insight into the molecule-surface bonding of these structures is crucial for instance to understand the different hydrogenation activities and selectivities of multifunctional molecules on various catalysts. Furthermore introducing alloying effects to catalyst surfaces can change the properties of catalysts significantly and, thereby give rise to additional modifications of the molecule-surface interaction. Here we present a complementary experimental and theoretical study on the molecule-surface interaction of different organic molecules including ethene, butadiene and the α,β-unsaturated aldehydes crotonaldehyde and prenal on Pt(111) and two ordered Pt-Sn surface alloys. With the combination of HREELS (high-resolution electron energy loss spectroscopy) experiments carried out on the three model-catalysts and complimentary density-functional theory (DFT) calculations of vibrational spectra, we identified the stable adsorption structures on Pt(111) as well as the Pt2Sn/Pt(111) and the Pt3Sn/Pt(111) surface alloys. Surprisingly, we find that the changes in the vibrational shifts for corresponding structures on the three surfaces induced by the alloying cannot be satisfactorily correlated with the changes in the adsorption energies. However, with a detailed energetic analysis of the molecule-surface bonding, new insights on the interaction strength with the substrate are obtained that allow to rationalize the behavior of the vibrational properties.

5:20pm **SS2-TuA12 Examination of Force Interactions on Surfaces with Atomic Resolution Using Noncontact Atomic Force Microscopy**, ***T.C. Schwendemann***, *B.J. Albers, M.Z. Baykara, N. Pilet, E.I. Altman, U.D. Schwarz*, Yale University

Interaction forces on the atomic scale govern the underlying physics of many fields of nanotechnology research, such as, catalysis, thin film growth, device fabrication, and tribology. Therefore, we present a method of atomic force microscopy which allows for the generation of 3D force maps of sample surfaces with atomic scale resolution. A homebuilt tuning fork based noncontact atomic force microscope (NC-AFM) facilitates the measurement of tip position and frequency shift that can be translated into force. Until recently, acquisition of surface forces on the atomic scale has been restricted to low resolution maps of single point force curves or 2D atomic resolution (xz) maps. The main difficulty in producing 3D force maps has been minimizing the drift of the instrument over the long acquisition times associated with 3D data collection. To address this issue, our low temperature ultrahigh vacuum NC-AFM was built with a high degree of thermal and mechanical stability. This stability has been demonstrated by our first 3D measurements on highly oriented pyrolytic graphite (HOPG). We chose HOPG as a test material in order to investigate the atomic scale origins of its qualities as a solid lubricant. Data was collected spanning several unit cells laterally and vertically from the attractive region to where no force interactions could be measured. A fine data mesh shows pN forces with less than 7 pm lateral and 1-2 pm vertical resolution. From this 3D data set, cuts along any plane can be plotted in 2D. Cuts in a plane parallel to the sample surface show atomic resolution. Cuts along the surface normal visualize how the atomic attractive force fields extend into vacuum. Now that this technique has been demonstrated it may serve for the further study of chemical force interactions. It is our intention to apply this technique to simple metal oxide surfaces to determine the chemical force interactions between the scanning probe tip and specific surface sites.

Surface Science
Room: Hall D - Session SS-TuP

Surface Science Poster Session

SS-TuP1 A Study of a Hydrogen Atom on Pd-Ag Alloy Surfaces Via First Principles Calculation*, **N. Ozawa**, T. Roman, H. Nakanishi, H. Kasai*, Osaka University, Japan

Technology for extracting hydrogen gas with high purity from natural gases is necessary for the establishment of a hydrogen fuel system. At present, since materials used for permeable films such as Pd are rare and expensive, a fundamental understanding about reaction processes of hydrogen on metal surfaces is necessary for developing an alternative material replacing with them. On the time, we have studied the elementary reaction processes of a hydrogen atom on Pd surfaces and its subsurface[1-4] using first principles calculations. In particular, we have given focus on quantum mechanical behaviors of the hydrogen atom motion, which appear due to the small mass of hydrogen. In this study, we investigate the quantum states of the hydrogen atom on the PdAg alloy surface and in its subsurface by calculating the wave functions and the eigen energies for the hydrogen atom motion within the framework of the variation method on an adiabatic potential energy surface (PES) obtained from the first principles calculations.[5,6] From these researches, we discuss the behavior of the hydrogen atom such as adsorption and diffusion. We find that the adsorption energy of the hydrogen atom on the surface and activation energy for diffusion into the subsurface area are smaller than on pure Pd surfaces. In this conference, we also discuss the hydrogen atom behavior on the other kinds of Pd-based alloy surfaces.

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SS-TuP2 Size-Dependent Surface Chemistry of Alumina Nanoparticles*, **P.L. Brazee**,* Smith College*, D.M. Dukes, L. Schadler,* RPI*, K.T. Queeney*, Smith College

The particle size of a number of different oxide materials has been found to influence cell adhesion and growth; specifically, nanophase (rather than conventional micron-sized) particles enhance these processes. The increased adsorption of proteins to nanophase particles has been implicated in this size-dependent phenomenon. The current study focuses on the surface chemistry of alumina particles as a function of average particle size, specifically to determine whether or not there are size-dependent differences in surface chemical species that may affect protein (and other biomolecule) adsorption. Alumina nanoparticles of varying phase and diameter were spin-coated onto silicon substrates and their uniformity characterized via SEM and XPS. The distribution of surface hydroxyl (OH) species was analyzed via transmission infrared (IR) spectroscopy. The OH stretches observed for all alumina samples are signficantly redshifted (~200 cm^{-1}) from the frequencies observed for dried alumina powders (e.g. using diffuse reflectance IR). While a common cause of such redshifting in ν(OH) peaks is hydrogen bonding with surface water, the spin-coated samples do not exhibit the concomitant peak broadening associated with this kind of hydrogen bonding. We propose that the unique ν(OH) signatures of spin-coated alumina particles arise from discrete hydrogen bonding interactions between alumina hydroxyls and surface silanols on the underlying silicon substrate. Differences in the OH-stretching peaks for different phases (e.g. γ vs. α) of alumina provide evidence that these features do, in fact, arise from the alumina particles themselves. We do in fact see a size dependence in the distribution of surface hydroxyl species, with distinct populations of different OH species arising from conventional vs. nanophase alumina of all phases studied. These differences are likely to arise from different relative populations of edge vs. facet sites as a function of particle size.

SS-TuP3 Surface Electronic Structure of Epitaxial La_2NiMnO_6 and La_2CoMnO_6 Films Grown on $SrTiO_3(100)$*, **H. Geisler**, C.A. Ventrice,* Texas State University*, Y. Losovyj,* Louisiana State University*, K. Chetry, A. Gupta*, University of Alabama

The surface electronic structure of thin films of the double perovskites La_2NiMnO_6 and La_2CoMnO_6 have been measured using ultra-violet photoelectron spectroscopy at the CAMD synchrotron. Both La_2NiMnO_6 and La_2CoMnO_6 are magnetic semiconductors with magnetic transition temperatures in their bulk phases of 280 K and 226 K, respectively. The thin films were grown on $SrTiO_3(100)$ substrates using pulsed laser deposition. To prepare the clean surfaces before photoemission measurements, the samples were sputtered with 1 keV Ar ions and annealed at ~400 °C in an O_2 atmosphere of 10^{-6} Torr. Angle-resolved photoemission measurements of both surfaces show very little dispersion of the valence emissions. Annealing the surfaces in ultra-high vacuum results in a shift of the valence features away from the Fermi level, indicating that loss of surface oxygen results in an n-type doping of these surfaces.

SS-TuP4 X-ray Photoelectron Study of Polycrystalline Samples Type $SeCuO_3$ and $SeMnO_3$ Perovskites*, **L. Huerta**, R. Escamilla,* Universidad Nacional Autónoma de México*, M. Flores,* Universidad de Guadalajara, México*, E. Morán, M. Alario-Franco*, Universidad Complutense, España

Polycrystalline samples type $SeCu_{1-x}Mn_xO_3$ perovskites were studied by x-ray photoelectron spectroscopy (XPS). The XPS spectra revealed Se, Cu and Mn oxides on the surface of the samples, mainly SeO_2, CuO and MnO. After with great periods of etching time the intensity of SeO_2, CuO and MnO decreased. The Se 3d, Me $2p_{3/2}$ (Me = Cu, Mn), Me 3d and O 1s spectral lines associated to the chemical states $SeMO_3$ were identified and they do not change with increased of etching time.

SS-TuP5 A STM Study of Pt Nanoparticles Deposited on $CeO_x(111)$ Thin Films*, **P.J. Riedel**, J. Zhou*, University of Wyoming

Ceria-supported Pt nanoparticles are widely used in many important applications, including three-way automobile emission-control catalysis and fuel cells owing to the peculiar redox properties and oxygen storage capacity of ceria as well as the synergistic effect between the Pt and ceria. Previous chemistry studies using XPS and TPD in the literature have demonstrated that the reactivity of ceria-supported Pt nanoparticles is dependent on the cerium oxidation state. To elucidate the nature of their reactivity, we investigated their structure and morphology using STM. Reducible $CeO_x(111)$ thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Our data demonstrate that surface structures of ceria thin films are dependent on the degree of ceria reduction. Fully oxidized $CeO_2(111)$ film exhibits a fairly low density of point defects due to the formation of oxygen vacancies. However, the number of surface defects increases as the ceria film is reduced. Pt particles were vapor-deposited onto ceria thin films at 300 K. The growth of Pt particles was investigated by STM as a function of metal coverage, post-deposition annealing temperatures, as well as Ce oxidation state, which were further compared to the growth of Rh and Pd. The research is sponsored by the start-up fund at the University of Wyoming and the Wyoming NASA Space Grant.

SS-TuP6 Growth and Reactivity of Pt-Au Bimetallic Nanoclusters Supported on $TiO_2(110)$*, **J.S. Ratliff**, J.B. Park, S.A. Tenney, S.F. Conner, D.A. Chen*, University of South Carolina

Pure Pt, pure Au, and bimetallic Pt-Au clusters were deposited on $TiO_2(110)$ at room temperature and studied with scanning tunneling microscopy, low energy ion scattering, and temperature programmed desorption. Pt forms smaller clusters with higher cluster densities than Au for the same metal coverage. Bimetallic Pt-Au clusters were formed by seeding Au at existing Pt clusters. The growth of Au on Pt seed clusters was confirmed by a decrease in cluster density upon dosing Au onto 0.25 monolayers (ML) of Pt. For the growth of Au on Pt seed clusters, the average cluster size increases and cluster density decreases with increasing Au coverage. Low energy ion scattering spectroscopy confirms that both Pt and Au are at the surface of the clusters, even at 300K. Carbon monoxide was used to probe the activity of the bimetallic clusters. With a constant total metal coverage, CO desorption scales linearly with the Pt percentage. Upon dosing increasing amounts of Au onto 0.25ML of Pt, CO desorption decreases but does not reach zero, even with 3ML of Au, suggesting that CO may be able to pull Pt to the surface of the clusters. CO_2 production from bimetallic clusters exposed to O_2 prior to CO exposure decreases much more rapidly with increasing Au coverage than does CO desorption due to decreased number of Pt surface sites for O_2 dissociation.

SS-TuP7 Temperature Program Desorption Study of Cu_x on Reduced $TiO_2(110)$*, **J.C. Lofaro, Jr.**,* Stony Brook University*, M.G. White*, Brookhaven National Laboratory and Stony Brook University

Copper catalysts supported on metal oxides have been used as a heterogeneous catalysts in industrial setting for various chemical processes.[1,2] Recent works have shown that copper nanoparticles supported on metal oxides (ZnO, CeO_2, TiO_2) have higher activity for the water gas shift reaction (WGSR) as well as other chemical processes.[3,4] Here, copper nanoparticles are deposited on a $TiO_2(110)$ single crystal using a homemade thermal evaporator, which is used as a model system. Auger electron spectroscopy (AES) is used to characterize the copper coverage and temperature programmed desorption (TPD) is used to probe the clusters reactivity and thermal stability. Copper coverages ranging from 0.25ML to 10ML are investigated. Probe molecules including carbon monoxide and water since those are the starting points for the WGSR, which copper is known to catalyze at high temperatures.[5]

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SS-TuP8 Photooxidation of Acetone and Butanone on Rutile TiO_2(110)

***D.P. Wilson**, D. Sporleder,* Stony Brook University, *M.G. White*, Stony Brook University, Brookhaven National Laboratory

Interest in the photooxidation of organic compounds on heterogeneous surfaces such as TiO_2 has increased in recent years. Here, acetone and butanone, two common organic ketones, are studied under UHV conditions to determine what fragmentation occurs during photooxidation and to gain insight as to the predictability of desorbing species. The data was collected using a pump-probe time-of-flight (TOF) method. Excitation occurs via exposure to 3.7 eV photons followed by ionization with 13.05 eV photons. Preheating the surface to ~200K facilitated the formation of an organic-diolate species needed for photoactivity. During butanone photooxidation, different desorption mechanisms between mass 30 and masses 27-29 are evident. Background thermal results and preliminary translational energy distributions are calculated for acetone and some butanone fragments and are presented here.

SS-TuP9 Significant Reduction in Adsorption Energy of CO on Platinum Nanoparticles on Graphite

***J.P. Oh**, T. Kondo,* University of Tsukuba, Japan*, Y. Suda,* Toyohashi University, Japan*, D. Sekiba, H. Kudo, J. Nakamura*, University of Tsukuba, Japan

Adsorption and desorption of CO on Pt vapor-deposited on highly oriented pyrolytic graphite (HOPG) have been investigated by temperature programmed desorption (TPD) of CO and in-situ helium atom scattering (HAS). Pt particles deposited on HOPG with sub-monolayer coverage are found to exhibit lower temperature desorption peak of CO at ~300 K at a heating rate of 0.5 K/sec. With increasing Pt coverage on HOPG, the desorption peak of CO at 450 K becomes dominant as observed on Pt single crystals. It was confirmed by Rutherford backscattering spectroscopy (RBS) measurements that any impurities other than carbon and Pt do not exist in the HOPG sample. These results indicate that the Pt particles deposited on a graphite surface with sub-monolayer coverage has significantly different properties for CO adsorption from that of Pt single crystal: lower adsorption energy of CO on Pt of Pt/HOPG than that for Pt single crystal. The reduction in the adsorption energy has been attributed to the interface interaction between Pt particles and graphite surface based on the separately conducted scanning tunneling microscopy experiment. Simultaneous measurement of HAS with CO-TPD indicated, the morphological change of the specific Pt particles at ~350 K. Scanning electron microscope observation before and after annealing the Pt/HOPG sample also reveals that Pt particle is mobile at higher temperatures above 350 K. However, sintering of Pt leading to an increase of particle size was not observed.

SS-TuP10 Low-Temperature Reaction of Cl_2 and C_2H_4 on ZnO(000-1) Single Crystal Surfaces

***W.H. Doh**, C.M. Kim*, Kyungpook National University, South Korea

We studied the reaction of Cl_2 and C_2H_4 co-adsorbed on ZnO single crystal surfaces. It is observed that C_2H_4 is molecularly adsorbed on ZnO at 110 K and desorbed intact from the surface when the surface temperature is increased. Cl_2 is molecularly adsorbed on ZnO at 110 K and decomposed to atomic chlorine when the surface is heated to higher than 200 K. When the ZnO surface is co-adsorbed with Cl_2 and C_2H_4, desorption of 1,2-dichloroethane is observed. We studied the mechanism of low-temperature addition of Cl to C_2H_4 on ZnO. We propose that "hot" atoms are produced in the process of Cl_2 dissociation and these "hot" chlorine atoms attack co-adsorbed C_2H_4 to produce 1,2-dichloroethane before thermodynamic equilibrium is reached.

SS-TuP11 Effect of Al_2O_3 and ZrO_2 Supports on Rh for Reaction Properties of NO

***I. Nakamura**, A. Takahashi, T. Fujitani*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of the noble metal content in the three-way automotive catalyst (Rh, Pt, Pd/Al_2O_3-ZrO_2-CeO_2) is currently required. In order to reduce noble metal loading, the enhancement of atomic efficiency and suppression of oxidation and sintering of noble metal are important subjects. To overcome these subjects, the clarification of the supported metal state is necessary. In this study, we investigated the influence of oxide support on the structure of Rh and the NO reactivity using the Rh/Al_2O_3 and Rh/ZrO_2 model catalysts. The model catalysts were prepared by deposition of Rh onto the Al_2O_3 and ZrO_2 thin films. The NO dissociation activity on the Rh/Al_2O_3 model catalyst was higher than that on Rh(111). In contrast, the activity for the Rh/ZrO_2 model catalyst was the same as Rh(111). Furthermore, the dissociation activity on the Rh/Al_2O_3 model catalyst increased by heating, but no enhancement by heating treatment was observed for the Rh/ZrO_2 model catalyst. We thus considered that the Al_2O_3 support promotes the NO dissociation activity by changing the Rh surface structure. To clarify the effect of Al_2O_3 support on Rh, we examined the NO adsorption state on the model catalysts. The IRAS peak due to NO adsorbed on bridge site was observed at 1645 cm^{-1} for the Rh/Al_2O_3 model catalyst. For the Rh/ZrO_2 model catalyst, the peak was seen at 1616 cm^{-1}, which was attributed to NO on hollow site. These results indicate that the surface structures of Rh are (100) and (111) faces for the Rh/Al_2O_3 and Rh/ZrO_2 model catalysts, respectively. We also confirmed that the exposed surfaces of Rh supported on Al_2O_3 and ZrO_2 are the (100) and (111) face from a comparison with the rate and apparent activation energy for NO dissociation on Rh(100) and Rh(111). Thus, we found that the effect of Al_2O_3 support on Rh for an enhancement of NO dissociation activity is to stabilize the surface structure of the (100) face with a high NO dissociation ability. AFM measurements confirmed that the small Rh particles with 2.5 nm diameter were formed on the Rh/Al_2O_3 model catalyst. We concluded that the Al_2O_3 support affected the morphology of the Rh surface by stabilization of small Rh particle, resulting in the enhancement of NO dissociation activity.

SS-TuP12 Au-N Synergy and N-Doping of Metal Oxide-Based Photocatalysts

***J. Graciani**, A. Nambu,* Brookhaven National Laboratory*, J. Evans,* Universidad Central de Venezuela*, J.A. Rodriguez,* Brookhaven National Laboratory*, J.F. Sanz*, Universidad de Sevilla, Spain

N-doping of titania makes possible photocatalytic activity for the splitting of water, and other reactions, under visible light. Here we show from both theory and experiment that Au preadsorption on TiO2 surfaces significantly increases the reachable amount of N implanted in the oxide. The stabilization of the embedded N is due to an electron transfer from the Au 6s levels toward the N 2p levels, which also increases the Au-surface adhesion energy. Theoretical calculations predict that Au also can stabilize embedded N in other metal oxides with photocatalytic activity such as SrTiO3 and ZnO, producing new states above the valence band or below the conduction band of the oxide. In experiments, the Au/TiNxO2-y system was found to be more active for the dissociation of water than pure TiO2 or TiO2-y. Furthermore, the Au/TiNxO2-y surfaces were able to catalyze the production of hydrogen through the water-gas shift reaction (WGS) at elevated temperatures (575- 625 K) displaying a catalytic activity superior to that of pure copper (the most active metal catalysts for the WGS) or Cu nanoparticles supported on ZnO.

SS-TuP13 Bimetallic Pt/Metal Nanocatalysts for the Decomposition of Methanol: Effect of Secondary Metal on Oxidation State, Activity, and Selectivity

***J.R. Croy**, S. Mostafa, L. Hickman, H. Heinrich, B. Roldan Cuenya*, University of Central Florida

Bimetallic Pt-Metal (Pt-M) catalysts are important in a wide range of applications including the direct methanol fuel cell (DMFC). In order to take full advantage of Pt/M systems in the design of new and efficient nanocatalysts, we must understand the structural, chemical, and electronic modifications brought about by the addition of the secondary metal M. We present here an investigation of the influence that the addition of secondary metals (M=Au, Pd, Ru, and Fe) has on the oxidation state, activity, and selectivity of ZrO_2-supported Pt nanoparticles. We use as a probe reaction the decomposition of MeOH. Size-selected bimetallic Pt nanoparticles were obtained by diblock-copolymer encapsulation and deposited on nanocrystalline ZrO_2 powder. The chemical composition of the particles was studied by X-ray photoelectron spectroscopy and structural characterization was done by atomic force microscopy and transmission electron microscopy. The reactivity of the bimetallic systems for MeOH decomposition was monitored in a packed-bed mass flow reactor by mass spectrometry. Distinct atomic segregation trends were observed upon annealing these nanoparticles in an oxygen-rich environment. The affect these trends have on the oxidation state of Pt and how this state influences reactivity will be discussed.

SS-TuP14 Reaction Properties of O_3 and CO Over Gold Surface

***T. Fujitani**, I. Nakamura, A. Takahashi*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Gold nanoparticles supported on TiO_2 exhibit high catalytic activity for CO oxidation. Although numerous investigations have been carried out to elucidate the source of this enhanced activity, there are still controversies concerning the active sites and the role of support for the Au/TiO_2 catalyst. In addition to the aforementioned studies, reactions of O_2, O_3 and CO on gold surfaces have been investigated by means of surface science techniques. Recently, we found that O_3 dissociation and CO adsorption depend strongly on the gold surface structure. Here, we report the adsorption and desorption properties of atomic oxygen produced from O_3 exposure and CO adsorption properties on gold single crystals as well as gold deposited on TiO_2(110). XPS measurements confirmed that no dissociative adsorption of O_2 occurred on surfaces of Au(111), Au(100) and Au(311). On the other hand, atomic oxygen was observed on Au(111) and Au(311) upon exposure to O_3, but no atomic oxygen was detected on Au(100). The saturation coverage of atomic oxygen on Au(311) was half of that observed on Au(111), where the exposed (111) face on Au(311) was half of that on Au(111). Furthermore, the initial formation rate of atomic oxygen for Au(311) was half of that for Au(111). These results clearly indicate that O_3 dissociation over gold surfaces proceeded selectively on the (111) face. We found that the adsorption behavior of CO also depended on the gold surface structure. PM-IRAS peaks of CO at 2070-2080 cm^{-1} were observed for Au(111) and Au(100) at CO pressures above 0.5 Torr; these peaks were assigned to the CO adsorbed on atop sites (atop-CO). In contrast, the peak due to atop-CO adsorbed on step sites was seen at 2117 cm^{-1} for Au(311) at 0.01 Torr. It was thus shown that the step sites on the gold surface were effective for CO adsorption under low CO pressure. Next, we investigated the CO adsorption state for the gold nanoparticles on TiO_2(110). PM-IRAS peak of CO adsorbed on atop sites of gold atom was observed at 2120 cm^{-1}, which was higher than the frequency of the CO adsorbed on Au(111). The CO frequency observed for the Au/TiO_2 model catalyst agreed with that on step sites for Au(311). We thus found that the TiO_2 support influences the electronic state of the supported gold, resulting in the formation of positively charged gold nanoparticles.

SS-TuP15 Formation and Thermal Stability of Gold Oxide and Platinum Oxide Shells on Nanoparticles: Size and Support Effects, ***L.K. Ono***, *J.R. Croy, B. Roldan Cuenya*, University of Central Florida

Gold and Pt nanoparticles (NPs) with two different size distributions (average sizes of ~1.5 and ~5 nm) have been synthesized by inverse micelle encapsulation and deposited on reducible (TiO_2) and non-reducible (SiO_2, ZrO_2) supports. The thermal stability of oxidized Au and Pt species formed upon cluster exposure to atomic oxygen has been investigated in ultrahigh vacuum using a combination of temperature-, time- and CO dosing-dependent X-ray photoelectron spectroscopy (XPS), as well as temperature programmed desorption (TPD). Our work on gold clusters demonstrates that (a) low temperature (150 K) exposure to atomic oxygen leads to the formation of surface, as well as sub-surface gold oxide, (b) the presence of the reducible TiO_2 substrate leads to a lower gold oxide stability compared to that on SiO_2, possibly due to a TiO_2 oxygen vacancy-mediated decomposition process, (c) heating to 550 K (Au/SiO_2) and 300 K (Au/TiO_2) leads to a near-complete reduction of small (~1.5 nm) NPs while a partial reduction is observed for larger clusters (~5 nm), and (d) the desorption temperature of O_2 from pre-oxidized Au clusters deposited on SiO_2 depends on the cluster size, with smaller clusters showing stronger O_2 binding. Preliminary data on the formation and thermal stability of different Pt oxide species (PtO_2 and PtO) on size-selected Pt clusters will be shown. Emphasis will be given to how the nature of the oxide support affects this stability. Furthermore, the distinct reactivity of similarly-sized, pure Pt and Au nanoparticles versus their oxidized counterparts will be discussed.

SS-TuP16 3D Concentration and Structure Maps of Heterogeneous Surfaces Determined by LEEM-IV Analysis, ***J. Sun****, University of New Hampshire, *J.B. Hannon*, IBM T. J. Watson Research Center, *G.L. Kellogg*, Sandia National Laboratories, *K. Pohl*, University of New Hampshire

Controlling compositional heterogeneity is important in ultrathin films growth, but determining exactly how and why heterogeneity develops is extremely challenging. The reason is that the three-dimensional compositional and structural profile of the film is difficult to measure because of the lack of surface techniques that combine high spatial resolution, subsurface sensitivity, chemical identification capability and high temporal resolution. For example, STM is not sensitive to the subsurface region and LEED averages over a large surface area. To overcome these limitations, we have developed a novel analysis approach[1] that allows us to measure the evolution of the 3D compositional and structural profile of a heterogeneous alloy surface in real time. We do this by quantitatively analyzing the pixelated intensity in the low-energy electron microscopy (LEEM) images. In the dynamical IV (intensity-vs.-voltage) analysis, a proper model for the inner potential, representing the atomic muffin-tin constant and the inelastic optical scattering, was adapted to overcome the challenges in very low-energy electron scattering. The structural and non-structural parameters are optimized simultaneously in search of the real surface structure that gives a best fit between the calculated and experimental IV curves. We have measured the composition of a CuPd surface alloy in the three topmost atomic layers, during growth, with 8.5 nm lateral resolution and monolayer depth resolution. From the 3D compositional and structural profiles, we have identified a generic step-overgrowth mechanism that leads to inherent alloy heterogeneity at steps. The heterogeneity can be traced to the difference between bulk and surface diffusion of Pd. Furthermore, Monte Carlo simulations are described to reproduce the time evolution of the compositional heterogeneity and give support to the step-overgrowth model. By the LEEM-IV analysis technique, the surface structural and compositional information measured in situ can be correlated with other surface properties, such as surface strain, diffusion mechanisms, and growth and decay processes. This work is supported by the National Science Foundation, the Department of Energy, Office of Basic Energy Sciences, and the Petroleum Research Fund.

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SS-TuP17 Reactivity of Diatomic Molecule on Bimetallic Surface: The Case of O_2 Adsorption and Dissociation on Pt/Fe, ***M.C.S. Escano‡***, *H. Kasai*, Osaka University, Japan

Bimetallic surfaces have been receiving increasing catalytic interest. Aside from using strain to tune reactivity, to a large extent, metal overlayers exhibit modified surface electronic structure due to interfacial interactions.[1,2] While dissociative adsorption of small molecules on metal surfaces has been studied extensively, theoretical studies on gas-bimetallic surface interaction have been sparse. Previous ab-initio calculations on atomic and electronic structure of Pt/Fe(001) show small lattice mismatch and a charge transfer from Pt and Fe atom sites towards Pt-Fe interface.[3] Layer by layer density of states curves against Pt(001) and Fe(001) show increase of d states at the Fermi level and a spin polarization of Pt d_{zz} states. Such changes with respect to the pure components call for investigation on O_2 surface reactivity. Spin-polarized density functional theory calculations were performed to investigate adsorption and O_2 dissociation on Pt/Fe(001). The adsorption characteristics of atomic and molecular oxygen are compared with clean Pt(001). The energetics of O_2 adsorption and dissociation are discussed in terms of two-dimensional cuts of the six-dimensional potential-energy surface. Results show "no barrier" O_2 molecule preferential adsorption on bridge with O-O axis directed towards top sites (t-b-t). A barrierless dissociation over one trajectory, O-O axis parallel and spanning over bridge-hollow-bridge (b-h-b) site, is also predicted. The potential energy decreases monotonically along this lowest energy reaction path indicative of strong O_2 interaction with the surface. A proposed pathway for dissociation may take molecular adsorption along t-b-t and a translation and dissociation towards b-h-b. Detailed analysis of the transition state reveals ease of translation towards the b-h-b. Local density of states (LDOS) of O_2 arriving over bridge for the molecular state and at the transition state support strong hybridization between O_2 p_x-states and Pt d_{zz} states. In the meeting, we will detail the mechanism of O_2 reactivity based on charge redistribution, total charge flow integrals and partial charge density plots.

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SS-TuP18 Surface Chemistry of Carboxylic Acids on Si(100)2×1, ***M. Ebrahimi‡***, *J.F. Rios, K.T. Leung*, University of Waterloo, Canada

Organic functionalization of Si(100)2x1 has attracted a lot of recent attention due to its potential applications in organic-inorganic hybrid semiconductor devices, molecular electronics, chemical and biological sensors, and optical materials. Understanding of the behaviour of organic molecules on Si(100)2×1 surface is fundamentally important, because the electronic and chemical properties and selectivity of the inorganic substrate are modified by the organic adsorbate. Among the wide range of organic functional groups, the carboxyl group is one of the key constituents of amino acids, the building blocks of peptides and proteins. Under appropriate cleaning preparation, the Si(100) surface reconstructs to the 2×1 surface, on which the dangling bonds of adjacent Si atoms pair to create surface Si=Si dimer rows. The interaction of the carboxyl group with the Si=Si dimers, composed of a full σ bond and a partial π bond, is therefore of special interest to understanding the chemical reactivity and selectivity of biomolecules in general with this widely industrially used semiconductor. The present work investigates the dissociative adsorption of acetic acid and acrylic acid on the UHV prepared Si(100)2×1 surface at room temperature using X-ray photoelectron spectroscopy (XPS), temperature programming desorption (TPD), and density-functional theory (DFT) calculation. Selectivity of the surface towards acrylic acid, bifunctional molecule, has been investigated as well. Our DFT calculation by using B3LYP/6-31++G(d,p) shows several possible adsorbate-substrate configurations (ASCs) for the adsorption of these carboxylic acids on Si(100)2×1 surface. Acetate and acrylate resulting from the O-H dissociation of the related carboxylic acid on the Si(100) bind to the surface through oxygen atom.

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* Morton S. Traum Award Finalist

Our DFT and XPS results enable the identification of the adstructures arising from bonding involving either one oxygen atom (the unidentate ASC) and two oxygen atoms (the inter-dimer and intra-dimer bidentate ASCs). Our C 1s features prove the formation of bidentate adstructure at the early stage and of both unidentate and bidentate adtructures at the saturation level of exposure. The thermal evolution of the adsorbates studied by TPD and XPS of the flash-annealed surface confirm desorption of some species detected by Q-mass spectroscopy and formation of SiC on Si.

Surface Science
Room: 208 - Session SS1+NC-WeM

Surface Structure and Morphology
Moderator: A.A. Baski, Virginia Commonwealth University

8:00am **SS1+NC-WeM1 Short vs. Long-Range Interactions: Consequences of Distributions**, ***T.L. Einstein,*** University of Maryland, *A. Pimpinelli,* University Blaise-Pascal, France and University of Maryland, *K. Kim, A. BHadj Hamouda, R. Sathiyanarayanan*, University of Maryland

In computing terrace-width distributions on vicinal surfaces, one commonly assumes a long-range repulsion between steps as the inverse square of the step separation. In many cases there may be a different short-range interaction, or the steps might be able to locally form double-height steps (inconsistent with the fermion analogy). We show that such effects can alter the apparent strength of the interaction, leading to flawed predictions of the strength of the long-range elastic repulsion while still offering a good fit by the generalized Wigner distribution. Since these are finite-size effects, we show how to deal with this problem by measuring several misorientation angles of the vicinal surface. More generally, the range of the interaction affects the form of the distribution in a remarkable way; we discuss the limiting forms and the crossover between them. We apply these ideas to other surface phenomena, such as the distribution of capture zones in island growth. Work at UMD supported by the MRSEC, NSF Grant DMR 05-20471. Visits to UMD by AP supported by a CNRS Travel Grant.

8:20am **SS1+NC-WeM2 Studies of Plasma Nitridation of Ge(100) by Scanning Tunneling Microscopy**, ***J.S. Lee***, *E. Chagarov, A.C. Kummel*, University of California, San Diego

Several recent reports on Ge MOSFET have shown the benefit of having either GeON or GeN interfacial layer between Ge and the high-k gate oxide. We have performed scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) experiments to understand the bonding and electronic structure for Ge-O and Ge-N surface species. For Ge-O, a Ge(100) surface was exposed to O_2 and annealed to form order structures. The O_2 dosing pins the Fermi level at high local coverage. Formation of Ge-N adsorbates is more challenging since N_2 nor NH_3 readily dissociate on clean Ge(100). We performed the direct nitridation on Ge(100) using an electron cyclotron resonance plasma source, and investigated the submonolayer structures of the surface using STM. The nitrided surface was annealed between 200°C and 500°C to differentiate the various adsorbate sites. By annealing the surface above the oxygen desorption temperature but below the nitrogen desorption temperature, our preliminary data is consistent with our being able to prepare Ge-N adsorbates. We are also performing STM experiments and DFT calculation to determine the electronic structure of the Ge-N adsorbates and explain why they might be superior interfacial passivants compared to pure GeO_2.

8:40am **SS1+NC-WeM3 Atom-Wide Co Wires on Vicinal Cu(111)**, ***N. Zaki***, *D.V. Potapenko, R.M. Osgood,* Columbia University, *P.D. Johnson*, Brookhaven National Laboratory

Due to stronger electron-electron interactions, 1-D systems are predicted and, in some cases, have been shown to exhibit unique and exotic electronic physical properties, such as spin-charge separation, spin-splitting in a nonmagnetic metal,[1,2] and fractional-charge phase solitons.[3] One route to the formation of 1-D systems is by self-assembly using low-index vicinal crystal surfaces. In this regard, we have successfully formed 1-atom wide Co wires using Cu(775), a 7-atom wide stepped array with (111) terraces. Contrary to a recently reported DFT prediction, the Co wires are not laterally encapsulated but are positioned exactly at the step edge. Furthermore, the wires can be relatively long; in one case, a wire measured 160 Co atoms. We will present STM studies of this system performed at room temperature and under UHV. While vicinal Cu(111) does exhibit "frizz" at the steps when scanning above cryogenic temperatures, the Co wires pin the edges, visually accentuating their presence under STM. Furthermore, we observe a lower density of states for the Co wires as compared with the Cu steps, which also serves to differentiate the two metals. Cu(111) possess a surface projected bandgap which may electronically decouple the wire electrons that reside in this gap. Correspondingly, STS measurements of these atom-wide wires will be discussed.

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[2] I. Barke, Fan Zheng, T. K. Rugheimer, and F. J. Himpsel, PRL 97 226405 (2006)

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9:00am **SS1+NC-WeM4 Surface Self-Diffusion and Structural Evolution of Pd/Cu(100) Surface Alloys**, ***E. Bussmann***, *I. Ermanoski, G.L. Kellogg*, Sandia National Laboratories

Ultra-thin films of Pd on Cu(001) are of interest both as model systems for metal-metal surface alloy formation and as potential electromigration inhibitors for Cu interconnect applications.[1] To determine how alloyed Pd, residing in the atomic layer below the surface, affects Cu surface self-diffusion, we are using low energy electron microscopy (LEEM) to study the decay of 2-D Cu islands as a function of temperature and second-layer Pd concentration. These studies are enabled by previous investigations, in which the distribution of Pd in the top three Cu layers was determined from multiple-scattering-theory fits to LEEM-IV spectra.[2] Here, we use LEEM-IV spectra in a "fingerprinting" mode to monitor the Pd concentration during deposition and island decay. Measurements of the decay rates as a function of temperature show that the activation energy for island decay increases from 0.82±0.04 eV to 1.02±0.07 eV when 0.06±0.03 ML of Pd is alloyed into the second layer. As the Pd concentration is further increased, up to 0.5 ML, we observe a monotonic decrease in the island decay rates at temperatures less than 240ºC. These measurements confirm that Pd, alloyed into the second layer, slows Cu surface transport and suggests a mechanism by which Pd could reduce the detrimental effects of electromigration. A full Arrhenius analysis was not possible at higher Pd concentrations because a significant fraction of the Pd is lost from the second layer during the measurements. We are currently using LEEM to investigate the mechanism of this Pd dissolution, which appears to involve Pd diffusion into the bulk and Cu diffusion to the surface. Work supported by the U.S. DOE, Office of BES, DMSE. Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE's NNSA under Contract No. DE-AC04-94AL85000.

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[1] C. K. Hu, et al., Appl. Phys. Lett. 81, 1782 (2002).

[2] J. B. Hannon, J. Sun, K. Pohl, and G. L. Kellogg. Phys. Rev. Lett. 96, 246103 (2006).

9:20am **SS1+NC-WeM5 Additive-Enhanced Mass Transport on Metal Surfaces: Hunting Elusive Agents of Change**, ***P.A. Thiel***, *M. Shen, C.J. Jenks, J. Evans, D.-J. Liu*, Iowa State University **INVITED**

Sulfur is well known to enhance dynamic rearrangements of single-crystal metal surfaces for the coinage metals (Ag, Cu, and Au). It has been proposed that the associated enhanced surface mass transport of metal is due to the formation and diffusion of stable metal-sulfur clusters or complexes. From scanning tunneling microscopy (STM) images of a Ag(111) surface with adsorbed sulfur below room temperature, we have been able to "see" clusters that probably contribute to enhanced transport. We propose that the imaged clusters are Ag_3S_3.[1] Our ability to see these trimeric clusters derives from the feature that they self-organize into a distinctive dot-row structure. The dot-rows are very robust, in the sense that they exist over a coverage range that spans an order of magnitude (0.03 to 0.5 monolayers). The dots are assigned as Ag_3S_3 clusters, based on DFT calculations of their energetic stability, on the calculated and measured dimensions of the dots in STM, and on experimental evidence that they incorporate Ag. We have also explored the effect of S on Ag surface dynamics by measuring the stability of Ag adatom islands produced by vapor deposition and subsequently exposed to S. By varying both surface temperature and S-coverage, we identify three regimes: At high S-coverage where a dense row-dot structure forms, the Ag islands are stable or "frozen" over long periods of time. At intermediate coverage, S serves to destabilize the Ag islands. At very low coverage (0.01 monolayer), S has no effect because it passively decorates step and island edges. Thus, S is not universally effective in accelerating mass transport, but rather exhibits complex dependencies upon temperature and coverage.

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[1] M. Shen, D.-J. Liu, C.J. Jenks, and P.A. Thiel, J. Phys. Chem. C, 112, in press (2008). .

10:40am **SS1+NC-WeM9 Growth and Evolution of Au/Ge(111) Studied by LEEM and STM**, *J. Giacomo,* ***S. Chiang***, *C. Mullet, A.M. Durand*, University of California Davis

The clean Ge(111) surface has a c(2x8) reconstruction at room temperature. Au growth on Ge(111) above 300°C occurs via nucleation. The first layer is an epitaxial $(\sqrt{3}x\sqrt{3})R30°$ phase with a coverage of 1ML. Further Au coverage results in the formation of islands. When heated to about 620°C, the $(\sqrt{3}x\sqrt{3})R30°$ Au transitions to a disordered phase. In LEEM videos, we observed domains fluctuating between the ordered and disordered phases at the transition temperature. For 2 to 10 ML of Au coverage, we have observed three dimensional islands in the LEEM images, as expected for the Stranski-Krastanov growth mode. Surprisingly, the LEEM movies show concerted hopping of islands of approximately 100 nm diameter near 300°C. Preliminary data measured by STM show additional evidence for the Stranski-Krastanov mode.

11:00am **SS1+NC-WeM10 Si Adatoms Atop the Si(111)5x2-Au Surface Diffuse in One Dimension by a Defect-Mediated Hopover Process**, *E. Bussmann,* Sandia National Laboratories*, S. Bockenhauer,* Stanford University*, F.J. Himpsel,* University of Wisconsin-Madison*, **B.S. Swartzentruber***, Sandia National Laboratories

The Si(111)5x2-Au surface has provided new understanding of the properties of one-dimensional electronic states.[1] The reconstruction includes an overlayer of Si adatoms which partly determine the surface electronic properties.[2] The chainlike surface structure naturally confines the adatoms to tracks, similar to bits in existing digital media, and previous workers have used the individual adatoms as bits in a model atom-scale memory.[3] We have characterized the thermal 1-d diffusion of the adatoms by scanning tunneling microscopy. The statistics of motion are inconsistent with diffusion by a random walk. Instead, correlations between sequential adatom jumps in both direction and time imply that the diffusion is defect-mediated. We show that the unique character of the statistics of the diffusion is consistent with a model in which each adatom diffuses by hopping over a defect localized nearby. Specifically, the measured (nonbinomial) jump length distribution, the (nonexponential) wait-time distribution, and the observed correlations are all modeled accurately over a range of temperatures (145-215° C) using a Monte Carlo implementation of our model. The effective activation barrier for adatom diffusion is found to be 1.24 ± 0.08 eV. Intuitively, defect-mediated hopover diffusion is unexpected in a strictly 1-d system, because sequential diffusion events arising from adatom jumps back-and-forth over the defect are always in opposite directions leading to zero net displacement. Work supported by the U.S. DOE, Office of BES, DMSE. Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE's NNSA under Contract No. DE-AC04-94AL85000.

[1] I. Barke, R. Bennewitz, J. N. Crain, S. C. Erwin, A. Kirakosian, J. L. McChesney, and F. J. Himpsel, Solid State Comm. 142, 617-626 (2007).

[2] H. S. Yoon, S. J. Park, J. E. Lee, C. N. Whang, and I.-W. Lyo, Phys. Rev. Lett. 92, 0986801 (2004).

[3] R. Bennewitz, J. N. Crain, A. Kirakosian, J.-L. Lin, J. L. McChesney, D. Y. Petrovykh, and F. J. Himpsel, Nanotechnology 13, 499-502 (2002).

11:20am **SS1+NC-WeM11 Influence of Si Deposition on the Phase Transition Temperature of Si(111)-7x7**, *I.A. El-Kholy, **H. Elsayed-Ali***, Old Dominion University

Reflection high-energy electron diffraction (RHEED) during the Si(111)-$(1x1)_h$ to (7x7) phase transition shows that Si deposition lowers the transition temperature. A Ti-sapphire laser (100 fs, 800 nm, 1 kHz) was used to ablate a Si target on Si(111)-$(1x1)_h$ during quenching from high temperature. To measure the transition temperature during quenching with and without Si deposition, the experiment was performed as follows: Initially, in the absence of the laser ablation plume, the Si(111) was kept at a temperature above the phase transition temperature to ensure the uniformity of the temperature throughout the surface area of the sample. The heating current was switched off and the RHEED pattern was recorded. Then, in the presence of Si laser ablation plume, the sample was kept at the same high temperature as was done without an ablation plume. The RHEED intensity was observed as the substrate was exposed to the Si plume and the Si(111) substrate was quenched at a rate of ~40°C/s. The RHEED patterns when the Si plume was present showed a shift in the transition temperature from 840°C without the plume to 820°C with the plume. We interpret this result based on the effect of adatom mobility on the nucleation of the (7x7) structure. In the vicinity of the transition temperature, the two phases coexist on the surface. When the surface temperature is lowered below the transition temperature, the reconstruction starts to grow at the step edges then expand across the terraces. Since the high temperature $(1x1)_h$ phase has higher density than the (7x7), the excess atoms, found on large terraces after quenching, are released when the lower density (7x7) is formed. The quenching process results in the cooling of the surface at a lower rate than the time needed for adatoms to diffuse across the terraces; consequently the adatoms are trapped on the surface forming secondary (7x7) nuclei on terraces, thus reducing the observed $(1x1)_h$ to (7x7) transition temperature.

11:40am **SS1+NC-WeM12 Vanadium Adsorption on Si(111)-7x7 Surface: A Combined DFT and STM Investigation**, ***F. Stavale***, Nat'l Inst. of Metrology & Federal U. of Rio de Janeiro, Brazil*, M.M. de Araújo,* Nat'l Inst. of Metrology, Brazil*, A.A. Leitão,* Nat'l Inst. of Metrology & Federal U. of Juiz de Fora, Brazil*, R.B. Capaz,* Nat'l Inst. of Metrology & Federal U. of Rio de Janeiro, Brazil*, H. Niehus,* Nat'l Inst. of Metrology & Humboldt-U. zu Berlin, Germany*, C.A. Achete*, Nat'l Inst. of Metrology & Federal U. of Rio de Janeiro, Brazil

The development of superlattices of nanodots and nanomagnetism, metals on Si substrates are of great scientific and technological importance. Consequently metal deposition on Si(111) 7x7 has been studied intensively by the surface science community. The surface diffusion energies and diffusion pathways of the adsorbates are important subjects to understand the growth mechanism of nanostructures. In this sense the scanning tunneling microscopy (STM) appeared to be a powerful technique for the study of adatom diffusion on the Si(111) 7x7 surface. In general the transition metals expose a high reactivity usually due to the formation of silicide nanostructures. Although several reports on V-Si(111)-7x7 surface system are already available a detailed and complete study of the vanadium from the very beginning adsorption stages up to high coverage cluster and island coalescence on the Si(111)-7x7 substrate has not been yet performed. In this work, we report about an investigation from the low-coverage regime up to few monolayers of vanadium deposition on Si(111)-7x7 in the range of 100K up to 850K substrate temperature. A combination of STM, density-functional theory (DFT) adsorption energy calculations and simulated STM images has been applied. In the low coverage and temperature regime we identify the most common STM signatures in this system to be: (1) substitutional vanadium atoms at silicon adatom positions and (2) interstitial vanadium atoms between silicon adatoms and rest atoms. At higher temperatures the diffusion of adatoms and clusters promote cluster coalescence into specifically shaped nanoclusters which occupy very special unit cell positions of the substrate. Such clusters are composed by vanadium and silicon atoms into an initial silicide formation. Finally, at high coverage, depending on the initial vanadium coverage and the post-annealing temperature well shaped (faceted) VSi2 clusters are formed. In conclusion a model for the adsorption, diffusion and reaction of vanadium on the Si(111)-7x7 surface is proposed.

Surface Science
Room: 209 - Session SS2+NC-WeM

Functional Metal Oxides and Quantum Metal Structures
Moderator: J.E. Reutt-Robey, University of Maryland, College Park

8:00am **SS2+NC-WeM1 Can Ferroelectric Polarization be Used to Manipulate Metal-Oxide Interactions?**, *Y. Yun, N. Pilet, U.D. Schwarz, **E.I. Altman***, Yale University

Ferroelectric polarization creates high energy surfaces that are expected to reduce their surface energy by reconstructing or adsorbing compensating charges. Because opposite charges must be screened on opposite surfaces, different surface atomic structures and reactivities are anticipated. Since the polarization can be changed by applying an electric field, this suggests switchable surface chemical properties. We previously found that this effect can be exploited to alter how strongly polar molecules adsorb on $LiNbO_3$(0001) surfaces (Y. Yun and E.I. Altman, J. Am. Chem. Soc. 129 (2007) 15684). To determine if ferroelectric polarization can alter the catalytic properties of supported metals, the interaction of Pd with $LiNbO_3$(0001) was characterized using electron diffraction, photoelectron spectroscopy (XPS and UPS), ion scattering spectroscopy (ISS), atomic force microscopy, and CO temperature programmed desorption (TPD). Positively poled $LiNbO_3$(0001) surfaces behave like many other oxides. The Pd atoms aggregate into nanoparticles, with the smallest nanoparticles exhibiting XPS peak shifts that can be associated with a size effect. CO adsorption on these nanoparticles is largely unaffected by the size of the nanoparticles, the $LiNbO_3$ support, and annealing. In contrast, preliminary results suggest that Pd behaves very differently on negatively poled $LiNbO_3$. In this case, the Pd photoemission peak shifts persist to higher Pd coverages and annealing causes the Pd peak intensity to decrease; annealing has no effect on Pd on positively poled $LiNbO_3$(0001). Further, initial findings suggest that modest heating to just 600 K severely attenuates the ability of the Pd to adsorb CO.

8:20am **SS2+NC-WeM2 Temperature Dependence of Intrinsic Nucleation in Ferroelectrics**, ***P. Maksymovych**, S. Jesse,* Oak Ridge National Laboratory*, M. Huijben, R. Ramesh,* University of California, Berkeley*, A. Morozovska,* National Academy of Science of Ukraine*, S. Choudhury, L.-Q. Chen,* Pennsylvania State University*, A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Nucleation of domains is central to understanding and applying ferroelectric materials. In bulk ferroelectrics, the number of ferroelectric nuclei grows rapidly with temperature, verifying the involvement of thermal fluctuations, which are widely interpreted as a result of defect, modified local barriers. In homogeneous, low defect thin films, a local voltage source can produce intrinsic switching domain without the influence of defects. We have examined the temperature depended of intrinsic domain nucleation for the first time using Piezoresponse Force spectroscopy of model oxide materials, $BiFeO_3$ and $Pb(Zr_{0.2}Ti_{0.8})O_3$ from 34 to 300 K. Measurements were performed in ultra high vacuum, which allowed cryogenic cooling but also precluded the presence of water known to significantly affect ferroelectric phase stability. The key finding is that the temperature dependence of ferroelectric switching initiated by a scanning probe tip is small and amounts to only a 20 percent increase in the nucleation voltage upon cooling of the films to the lowest temperature. These results are in stark contrast to previous reports for ferroelectric switching in the capacitor geometry where the coercive field increases by at least a factor of five over a similar temperature range. To complement the experimental data, a theoretical analysis was carried out based on two models, the rigid ferroelectric model and phase-field simulations. The temperature dependence predicted by the phase-field modeling is small and in good agreement with the experiments, while the rigid ferroelectric model overestimates it considerably. We conclude that the intrinsic ferroelectric switching induced by scanning probe experiments involves minimal contribution from thermal fluctuations. PM was supported as a Eugene P. Wigner Fellow at ORNL. Research was performed at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, and supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

8:40am **SS2+NC-WeM3 Catalysis of M-YSZ(100) Model Anodes for Solid Oxide Fuel Cells**, ***R.G. Green***, *J.B. Giorgi*, University of Ottawa, Canada

Solid oxide fuels cells (SOFC's) convert chemical energy directly into electrical energy through a reaction involving the oxidation of fuels, such as hydrogen or natural gas. The oxidation reaction occurs at the anode which is typically composed of a nickel-yttria-stabalized-zirconia (Ni-YSZ) cermet. This composition provides the active triple phase boundary where gas (fuel), the active catalyst (metal) and the oxide ion provider (YSZ) meet. We will discuss a model system of this complex catalyst which has been studied under ultrahigh vacuum. To create this model, we deposit an active transition metal (Pd, Ni, Co) in the form of nano-particles onto single crystal YSZ (100). The defective YSZ surface offers a range of meta-stable nanostructures that can interact with the metal component. Additionally, the surface shows high reactivity toward carbon at high temperature. These properties add difficulty and complexity to the model systems. Results of catalytic activity toward methane as a function of metal composition and particle size will be discussed. The catalysts have been studied in-situ using photoelectron spectroscopy, scanning probe microscopy, as well as thermal desorption spectroscopy and reaction techniques.

9:00am **SS2+NC-WeM4 Structure of Au and Ag Clusters on Al_2O_3/FeAl(110)**, ***M.C. Patterson***, *O. Kizilkaya, R.L. Kurtz, P.T. Sprunger*, Louisiana State University

We present ultraviolet photoemission and STM studies of Ag and Au clusters deposited on both clean and oxidized FeAl(110). Preliminary DFT calculations indicate that deposition of Ag or Au results in the formation of bilayer islands with Ag(110) or Au(110)-like structure, due to the almost perfect match between the adsorbate and substrate lattice constants. This is concordant with studies of Ag growth on the similar intermetallic alloy NiAl(110).[1] High coverage levels of either adsorbate do not wet the FeAl surface, which can be seen by the presence of distinctive FeAl(110) valence band, Al 2p core level, and Fe 3p core level features at all levels of coverage. Angle dependent photoemission shows no dispersion in valence band features as a function of emission angle, and confirms that adsorbate, Fe, and Al are all present in the surface region. Additionally, some evidence of Al-Au alloying is observed in the Al 2p core level and Au 5p features in the Au/FeAl(110) system.

[1] B. Unal, F. Qin, Y. Han, D. Liu, D. Jing, A. R. Layson, C. J. Jenks, J. W. Evans, and P. A. Thiel, Phys. Rev. B. 76, 195410 (2007).

9:20am **SS2+NC-WeM5 The Effect of Water and Surface Order on Reactivity**, ***R.G. Quiller***, *L. Benz, T.A. Baker, M.E. Colling, C.M. Friend*, Harvard University

Understanding the effect of hydrating or hydroxylating a surface is an important aspect of interfacial chemistry. Intermolecular interactions including hydrogen bonding between water, hydroxyl groups, and oxide species play a crucial role in determining products and reaction rates in a range of heterogeneous reactions. Using surface science techniques such as temperature-programmed reaction and infrared reflection absorption spectroscopy, we studied the effects of such interactions on a number of catalytically and environmentally relevant systems on both Au and TiO_2 single crystal surfaces. We found that in addition to changes induced by water-related interactions, defects and surface ordering also played an important role in surface reactivity. Our results, therefore, emphasize the role of surface preparation and water coverage. These results help determine the role of intermolecular interactions on gas-oxide reactions and have implications in heterogeneous catalysis and environmental chemistry.

9:40am **SS2+NC-WeM6 Engineering Thin Film Superconductivity Toward Single Atomic Layer: A Scanning Tunneling Microscopy/Spectroscopy Study**, ***S.Y. Qin***, *J.D. Kim, A.A. Khajetoorians, C.K. Shih*, University of Texas at Austin

Ultra-thin Pb films on semiconductor substrates have exhibited many intriguing phenomena manifested by the quantum confinement of electronic states. Quantum stability has been a topic of interest for many years. Recently, it was shown that quantum confinements also play an interesting role on superconductivity. Oscillations of superconductivity gap and Tc as a function of film thickness have been observed in Pb/Si(111) and Pb/Ge(111) systems. Moreover, it is found that the superconductivity remains very robust even for films as thin as 5 ML. An interesting question arises as to what extent the robustness of superconductivity remains in even thinner regime. By using a different surface template, namely Pb/Si(111) root 3 surface, we have grown uniform Pb films down to 2 ML. The film shows preferred thicknesses of 2ML and 4ML, presumably a manifestation of the quantum stability. While superconducting gap remains robust down to 4ML and shows BCS-like temperature dependence, superconductivity of 2ML Pb film exhibit several interesting features. First of all, the superconducting transition temperature is significantly lower. Moreover, we find that even with nearly perfect 2ML films, the magnitude of superconducting gap is strongly suppressed by a minute concentration of hole defects. On the contrary, the gap is not affected by distribution of small excess nano-islands.

10:40am **SS2+NC-WeM9 Effect of Quantum Well States on the Formation of MnCu c(2x2) Surface Alloy**, ***W. Kim***, Korea Research Institute of Standards and Science, *I. Kim*, Chonnam National University, Republic of Korea, *C. Min*, Seoul National University, Republic of Korea, *H.-D. Kim*, Pohang Accelarator Laboratory, Republic of Korea, *C. Hwang*, Korea Research Institute of Standards and Science

The formation of quantum well states in metallic thin films under a certain boundary condition cause the sharp change in the intensity of electron density of states(DOS) at Fermi level of the thin films as the film thickness varies. This thickness dependence of DOS at Fermi level is the origin of quantum size effects found in many physical properties of the metallic thin films. In this study, we carried out the experiments to examine the effect of the quantum well states in the Cu/fcc Co(001) system on the formation of a surface alloy. It is well known that deposition of a half monolayer Mn on the Cu(001) leads to the formation of a very stable single layer MnCu c(2x2) surface alloy, and the origin of this process has been attributed to the magnetic energy of enhanced surface magnetic moment of Mn atom.[1] As the first step of the experiment, we examined the evolution of the Mn core level photoemission spectra with increasing Mn thicknesses, comparing the low energy electron diffraction(LEED) pattern for each Mn thickness. From the obtained spectra. we found out that there exist the features which are closely related to the surface alloy formation. Based on this spectroscopic evidence of surface alloying, we investigated the effect of quantum well states on the formation MnCu surface alloying. We deposited half monolayer Mn atoms on the wedge shaped Cu layers formed on the fcc Co(001) surface, and measured Mn core level photoemission spectra for the different Cu thicknesses. The observed spectra show overall correlation with the oscillating behavior of DOS at Fermi level as the thickness of Cu layers changed. Judging from the changes of Mn core level spectra, we could conclude that the lower electron density of states at Fermi level enhanced the formation of MnCu ordered surface alloy. This conclusion was also confirmed by the direct observation of the intensity of the half order spots of c(2x2) LEED pattern of MnCu surface alloy formed on the Cu/fcc Co(001) system with selected thicknesses of Cu layer. The results of our study strongly support the previous interpretation of the formation of stablized MnCu surface alloy.

[1]. M. Wuttig et al., Phys. Rev. Lett. 70, 3619 (1993).

11:00am **SS2+NC-WeM10 Adsorption of the Thiol Molecule $(SCH_3)_2$ on a Metallic Quantum Well System**, ***L. Tskipuri***, *R.A. Bartynski*, Rutgers University

We have studied the bonding of the thiol molecule dimethyldisulfide $(SCH_3)_2$ on ultrathin Cu and Co films that exhibit metallic quantum well (MQW) states using inverse photoemission (IPE), reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). This thiol is similar to more complex organic molecule that exhibits the self-assembled properties on metal surfaces. After a room temperature exposure of the Cu surface to the thiol molecule at a dose of ~ 2.5 L, a c(2 x 2) low energy electron diffraction (LEED) pattern confirmed that the adsorbate forms an ordered overlayer. A large sulfur signal is observed in Auger electron spectroscopy (AES) and the C-H stretch mode was observed in IR with a frequency of 2915 cm^{-1} confirming molecular adsorption. Changes in the IPE spectrum upon adsorption are dominated by suppression of the substrate-related features, although some weak adsorbate-induced peaks are also observed. Both experimental and theoretical evidence indicates that electronic orbitals involved in molecule-surface bonding are in the same energy range as the MQW states of the substrate and the possible influence of MQW states on molecular adsorption and self-assembly of the thiol molecule will be discussed.

11:20am **SS2+NC-WeM11 Adsorbate Dynamics under Nanoscale Confinement**, *Z. Cheng, G. Pawin, D. Sun, M. Luo, D. Kim, Y. Zhu,* ***L. Bartels***, University of California at Riverside

The diffusion of isolated adsorbates at extended low-index metal surfaces has been studied by scanning tunneling microscopy at many places, yet the behavior of isolated molecules may significantly differ from that of molecules at higher coverages and in confined structures such as nanometer-size metal clusters. We investigate the behavior of coverages of CO molecules confined to 4nm pores formed on Cu(111). While high-coverages form ordered patterns, in which vacancy diffusion and the behavior of dislocation lines can be studied, intermediate coverages aggregate to disordered islands or disperse completely across a pore, thus resembling a 2D liquid and gas, respectively. Isolated molecules show different diffusive behavior at the perimeters of the pore and at their center, revealing the importance of substrate confinement for the molecular behavior.

11:40am **SS2+NC-WeM12 Charge Carrier Separation and Transport at Organic Semiconductor Interfaces**, ***X.-Y. Zhu***, University of Minnesota **INVITED**

Charge carrier generation and transport are central to the operation of all organic electronic and optoelectronic devices, such as organic light-emitting diodes (OLEDs), field effect transistors (OFETs), and photovoltaic cells (OPVs). A fundamental distinction from their inorganic counter parts is the localized nature of charge carriers and electronic excitations in organic semiconductors. Localization is a fundamental character resulting from the narrowness of the electronic band, the flexibility of the organic molecule, the deformability of the van der Waals bonded lattice, and the low dielectric constants of organic solids. This is in addition to the prevalence of structural and chemical defects that form the bulk of charge carrier traps in organic semiconductors. We study the exciton dissociation and charge carrier localization problem in organic semiconductors using femtosecond time-resolved two-photon photoemission (TR-2PPE) spectroscopy to follow the formation and decay of excitons and small polarons in organic semiconductors. These experiments are beginning to answer the following critical questions: How do charge carriers separate at organic heterojunctions in an OPV? How does an electron localize to form a small polaron?

Energy Science and Technology Focus Topic
Room: 203 - Session EN+AS+TF+VT+NC-WeA

Energy: Tools and Approaches
Moderator: T.A. Dobbins, Louisiana Tech University and Grambling State University

1:40pm **EN+AS+TF+VT+NC-WeA1 Continuous, In-Line Processing of CdS/CdTe Devices**, ***W.S. Sampath***, Colorado State University, *R.A. Enzenroth, K.L. Barth*, AVA Solar Inc., *V. Manivannan*, Colorado State University, *K. Barricklow, P. Noronha*, AVA Solar Inc. **INVITED**

A continuous, in-line process suitable for high throughput manufacturing of CdS/CdTe photovoltaic devices has been demonstrated. Utilizing this process, devices with efficiencies of 13% has been fabricated with a low iron soda lime glass (3”x3”) with ant-reflection coatings. The process has been extended to large area devices (16” x16” substrate size). After $CdCl_2$ treatment, devices showed $V_{oc} > 700$ mV and $J_{sc} > 20$ mA/cm^2. This performance is similar to the performance of small area devices which showed good stability. Also we have employed many methods including Spectroscopic Ellipsometry (SE) as a non-destructive tool to characterize CdS/CdTe heterojunction specifically studying the effects of processing on the optical properties of the thin-film layers.

2:20pm **EN+AS+TF+VT+NC-WeA3 Molecular Dynamics and Experimental Investigations of Reversible Absorption of H_2, CH_4, and CO_2 in Calixarenes**, ***J.L. Daschbach***, *P.K. Thallapally, B.P. McGrail, L.X. Dang*, Pacific Northwest National Laboratory

Molecular solids based on calix[4]arenes have been shown to exhibit reversible absorption of small gas molecules, and remain stable, at temperatures above 400 K. As such, they are interesting as prototypical molecular systems for storing guests like hydrogen and methane, and potentially selectively trapping carbon dioxide in hydrocarbon based systems. We have conducted high-pressure and temperature gas absorption experiments with low density p-tert-butylcalix[4]arene (TBC4) in which calixarenes are slightly offset to form a skewed capsule with an estimated free volume of 235 Å^3. Hydrogen and methane absorption near 300 K were 1.0 and 2.2 wt% respectively. Carbon dioxide is absorbed at a 1:1 loading per TBC4 molecule at 3 atm. In recent work we have shown that the high density form of TBC4 will absorb CO_2 at 3 atm, undergoing a phase transformation in the process, and it can be reversibly cycled between these states using moderate combinations of temperature and pressure. Somewhat surprisingly, we have found that TBC4 can be loaded with up to two CO_2 per TBC4 molecule. We have used empirical molecular simulation techniques to study the dynamics of CO_2 and CH_4 in TBC4. The rattling motion of the absorbed small molecules have been characterized using velocity autocorrelation. The coupling to the host lattice is probed by temperature dependent calculations. The effects of increased loading are studied up to the 2:1 loading of CO_2, and clearly show differences in the host-guest coupling for molecules outside the cavities relative to the cage entrapped molecules. The free energy of absorption of CH_4 and CO_2 is studied under range of conditions by thermodynamic integration. These data support the experimental observations that these molecules can be reversibly absorbed at moderate pressures and temperatures.

2:40pm **EN+AS+TF+VT+NC-WeA4 Sustainable Energy and the Role of Advanced Electron Microscopy**, ***D.J. Stokes***, *B. Freitag, D.H.W. Hubert*, FEI Company, The Netherlands

Advanced electron microscopy, using the latest aberration-corrected and monochromated (scanning) transmission electron microscopes (S/TEM) is helping to bring new scientific and technological insights that are advancing progress in areas such as health, energy and the environment. Specifically, with global energy resources under increasing pressure, great efforts are being made to develop new nanomaterials that will lead to renewable energy sources and increased efficiency, to sustain energy supplies into the long term future whilst helping to preserve and protect the Earth’s environment. To get there, we are being taken to atomic realms such that, to tailor new nanomaterials for specific functions, it is essential to precisely understand, accurately control and truly visualize structure-property relations at an unprecedented level. The atomic structure of nanomaterials and the energy needed for their function can be optimized by the fundamental understanding of catalytic behavior of nanoparticles and by a better understanding of the physical properties on the atomic level of systems such as solar cells, fuel cells and light sources (LEDs). This requires advanced tools that allow us to see down to the individual atoms and sense their chemical environment. It means having the ability to perform experiments in situ, to follow specific chemical reactions and physical processes, and there is a need to be able to do this in multi-dimensions, both spatial and temporal. We discuss and demonstrate the role of advanced electron microscopy in answering some of the most challenging and fundamental scientific questions in the field of catalysis, ranging from electron tomographic 3D reconstruction of the crystal facets of catalyst nanoparticles and aberration-corrected imaging correlated with density functional theory for elucidating precise atomic positions, to in situ studies of catalytic reactions for visualization of otherwise unseen intermediate nanostructures. These examples relate the nanostructures investigated to the property manifested by that particular structure, enabling us to gain new information about catalytic function.

3:00pm **EN+AS+TF+VT+NC-WeA5 Investigation of Low Temperature-Annealed TiO_2 Electrodes Prepared by Sol-Gel Technique for the Fabrication of Dye-Sensitized Solar Cells**, *M.F. Hossain, S. Biswas, M. Shahjahan, A. Majumder*, ***T. Takahashi***, University of Toyama, Japan

Dye sensitized solar cells (DSCs) are considered as a low cost alternative to conventional p-n junction solar cell devices. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO_2 electrode. Among the various techniques for the preparation of TiO_2 photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates, and also it is a low temperature process. Crystallinity is one of the key factors behind the photovoltaic performances of TiO_2; therefore achievement of better crystallinity at relatively low temperature is an important issue. In our present study, the titanium dioxide porous films were deposited on SnO_2:F coated glass by sol–gel technique; where, an alcoholic solution of tetra-buthylorthotitane was hydrolysed in a water/alcohol/acetic acid mixture. These films were transparent and crack free. For this investigation; annealing temperature and number of coating layers were varied. All the films were annealed at different annealing temperatures, ranging from 350 to 500°C. Sufficiently good crystalline samples were obtained by annealing at 350°C. The X-ray diffraction patterns of all TiO_2 films confirmed the anatase structure. The surface morphology of the films has been observed by atomic force microscope and field emission scanning electron microscope. The morphology of TiO_2 thin films strongly depends on annealing temperatures and number of coatings. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different TiO_2 thin films to evaluate the economic viability of this technique. It has been observed that the photoelectric conversion efficiency of DSCs increases with the optimization of annealing temperature as well as with the increase of the numbers of layers.

Surface Science
Room: 208 - Session SS1-WeA

Structure of Oxide Surfaces and Oxide Heterostructures
Moderator: Ch. Wöll, Ruhr-University, Germany

1:40pm **SS1-WeA1 Tuning the Properties of Metals on Oxides: Au on MgO a Case Study**, ***T. Risse***, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

This contribution will focus on the recent efforts to characterize the properties of Au atoms and particles on well ordered MgO films and the ability to tune these properties by modifying the oxide film. The studies are embedded in the current endeavor to correlate the properties of oxide supported Au deposits with their catalytic activity. In this respect the charge state of Au particles has come under scrutiny, in particular after combined theoretical and experimental evidences suggested that nucleation of Au clusters at point defects of MgO leads to a charging of the particles which in turn was made responsible for the enhanced catalytic activity in low-temperature CO oxidation. More recently theoretical calculations predicted that not only defects sites might be able to induce charging of Au atoms and cluster, but the film thickness may serve a suitable parameter to control charging.[1,2] In this contribution we present a combined low-temperature scanning tunneling microscopy/spectroscopy (STM/STS), infrared (IR), and electron paramagnetic resonance (EPR) spectroscopic investigation on the properties of gold atoms and clusters adsorbed on well ordered MgO films. These studies aim at providing experimental evidences for the presence of negatively charged Au atoms and particles on these oxide surfaces. First we will focus on the impact of color centers. To this end STM/STS and EPR spectroscopic results will be discussed which can be used to characterize these centers and prove the adsorption of Au particles on them. In combination with IR spectroscopy it possible to show that color centers are indeed capable to donate charge onto Au particles. As a second part we want to discuss the question if the MgO film thickness is a suitable parameter to tune the charge state of Au deposits as predicted theoretically. Thereto low temperature STM experiments of Au atoms and clusters deposited on 3 ML and 8 ML thick MgO films will be discussed to find evidences for a charge transfer for 2-3 ML thick MgO films.

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[2] D. Ricci, A. Bongiorno, G. Pacchioni, and U. Landman, Phys. Rev. Lett. 97,036106 (2006).

2:20pm **SS1-WeA3 Shape Transitions of Anatase Islands during Epitaxial Strained Layer Growth**, ***M.S.J. Marshall***, *M.R. Castell*, University of Oxford, UK

It is well established that misfit strain between epitaxial islands and their substrates significantly influences the shape evolution of the islands as they increase their volume during growth. We have studied the growth of anatase islands on $SrTiO_3$ surfaces. Extended annealing in UHV causes the surface region of single crystalline $SrTiO_3(001)$ to become enriched with TiO_2. This results in the formation of epitaxial islands of anatase TiO_2 (001). These islands are studied using UHV scanning tunneling microscopy (STM) and UHV scanning electron microscopy (SEM), which reveals the changes in morphology during growth induced by misfit strain. Screw dislocations observed with STM on some of the islands enable the rapid growth of micron-sized square islands. Starting from a square island, two types of shape transitions are observed. In the first, above 1000°C, the square anatase islands elongate in length and narrow in width. This growth behavior follows the established Tersoff and Tromp model of strain relief in epitaxial islands.[1] In the second growth mode, below 1000°C, the islands relieve strain by the formation of trenches in the middle of each side of the square, thereby evolving into crosses. This shape arises because a lower annealing temperature imposes a kinetic constraint on the detachment of growth units necessary for island narrowing. While it might be expected that the growth of the notches would proceed to form four squares, each of optimal dimension, this does not occur. The shape transitions occur because the strain energy term in square islands increases more rapidly with volume than the surface and interface energy terms. In our system the islands are widely spaced, thus avoiding inter-island interactions, but there are still substantial differences between the theoretically predicted critical island size of a few 10s of nm edge length and our observed 1μm length. This can probably be explained because of partial strain relief due to dislocations in the anatase islands.

[1] J. Tersoff, and R. M. Tromp, Phys. Rev. Lett. 70, 2782 (1993).

2:40pm **SS1-WeA4 SEM Controlled STM Characterization of Cu/ZnO Nanoparticles**, ***A. Birkner***, *V. Schott, Z. Wang, Ch. Wöll*, Ruhr-Universität Bochum, Germany

The investigation of Cu deposits on ZnO substrates is of significant importance for understanding methanol synthesis using $Cu/ZnO/Al_2O_3$ catalysts. The role of the Cu is still under debate. Whereas some authors propose that the active sites are on the surface of bare Cu particles, others suggest that under reaction condition the surface in fact is covered by a thin layer of ZnO. In order to resolve this issue we have investigated temperature induced morphology changes of Cu islands deposited on ZnO substrates. We have extended the STM investigations of Kroll and Köhler[1] by additionally employing scanning electron microscopy (SEM). Our combined SEM/STM instrument allows to investigate Cu nanoparticles directly after deposition and heating and after exposure to reactants at pressures up to 1 bar. With the help of the SEM the very same Cu particle can be addressed before and after gas-phase exposure. By additionally employing Auger spectroscopy we can determine the composition of the surfaces of the Cu particles. We will also present first STM measurements of Cu clusters deposited on ZnO powder particles.

[1] M. Kroll, U. Köhler, Surf. Sci. 601 (2007) 2182.

3:00pm **SS1-WeA5 Preparation of TiO_2 Nanocrystals by Oxidation of Ti-Au Surface Alloys**, ***D.V. Potapenko***, *R.M. Osgood*, Columbia University

The formation of TiO_2 nanoparticles on a non-reactive, single-crystal noble metal substrate is useful for studies of nanocatalytic reactions. The formation of Ti-Au surface alloy on Au(111) surface and the growth of TiO_2 nanocrystals from the surface alloy have been studied with scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS) and Auger electron spectroscopy (AES). In our study, titanium was vapor deposited on Au(111) surface at 200 K. STM images show that Ti nucleates at the elbows of the surface herringbone reconstruction. At low Ti coverages (< 0.3 ML) extensive surface alloying occurs already at 400 K through island – substrate atomic exchange. Yet even at 900 K some amount of Ti stays near the surface. The exposure of the sample at 900 K to the flux of O_2 leads to oxidation of this sub-surface Ti and to growth of TiO_2 nanocrystals. At low initial Ti coverages (< 0.1 ML) the majority of the crystallites have triangular shape and at higher coverage, we observe hexagonal and ridge-like crystallite formation. The results of our experiments form an interesting comparison to recent studies of TiO_2 nanocrystals formed via reaction of vapor-deposited Ti on water multilayers on Au(111).

4:00pm **SS1-WeA8 Interface and Electronic Characterization of Thin Epitaxial Co_3O_4 Films**, ***C.A.F. Vaz***, *H.-Q. Wang, C.H. Ahn, V.E. Henrich, M.Z. Baykara, T.C. Schwendemann, N. Pilet, B.J. Albers, U.D. Schwarz,* Yale University*, L.H. Zhang, Y. Zhu,* Brookhaven National Laboratory*, J. Wang, E.I. Altman*, Yale University

The oxides of the 3d transition metals form an important class of materials with properties that depend sensitively on the cationic oxidation state and the electronic environment. As a consequence, these compounds display a multiplicity of magnetic, electronic and catalytic behavior, which makes them interesting from both fundamental and practical perspectives. In this work, we study the interface and electronic structure of thin (~20-74 nm) $Co_3O_4(110)$ epitaxial films grown by oxygen-assisted molecular beam epitaxy on $MgAl_2O_4(110)$ single crystal substrates. Using several real and reciprocal space techniques, we show that the surface and bulk properties of [110]-oriented Co_3O_4 thin films depend sensitively on growth conditions and post-growth annealing. The as-grown film surfaces are found to be relatively disordered and exhibit an oblique low energy electron diffraction (LEED) pattern associated with the O-rich CoO_2 bulk termination of the (110) surface. Post-annealing is found to improve considerably the film characteristics; in particular, the film surface displays sharp rectangular LEED patterns, suggesting a surface stoichiometry of the alternative Co_4O_4 bulk termination of the (110) surface. Non-contact atomic force microscopy demonstrates the presence of wide terraces separated by atomic steps in the annealed films that are not present in the as-grown structures; the step height of ~2.7 Å corresponds to two atomic layers and confirms a single termination for the annealed films, consistent with the LEED results. Finally, magnetic susceptibility measurements show that antiferromagnetic order is present at low temperatures, with an ordering temperature close to 47 K for the as-grown films and of about 30 K for the annealed films. Such well characterized and high quality surfaces could be employed as templates for the growth of other materials or as a model system for the study of exchange bias.

4:20pm **SS1-WeA9 Surface Structure of ZnO(0001) Nanolayers on Pd(111)***, *G. Weirum,* Karl-Franzens University Graz, Austria*, R. Schennach, A. Winkler,* Graz University of Technology, Austria*, I. Bako,* Chemical Research Centre of the Hungarian Academy of Science, Hungary, ***S. Surnev***, *F.P. Netzer*, Karl-Franzens University Graz, Austria

Zinc oxide has attracted a significant scientific and technological interest since it is widely used in catalysis, gas sensing, and in the fabrication of optoelectronic devices. When the wurtzite ZnO crystal is cleaved parallel to the basal plane (0001), two structurally and chemically different surfaces are created on each side of the crystal, which are Zn- and O-terminated. The structure stabilisation mechanism of these two polar surfaces has been extensively investigated,[1,2,3,4] but consensus models have not evolved yet. When prepared in a nanolayer form (1-2 monolayers thick), ZnO has been shown to adopt a hexagonal boron–nitride structure, where the Zn and O atoms are arranged in a trigonal planar (i.e. non-polar) configuration.[5] Here we have studied the surface structure by scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED) of ZnO nanolayers grown on a Pd(111) surface as a function of the Zn coverage and the oxygen pressure. ZnO layers have been prepared either by reactive evaporation of Zn in oxygen atmosphere ($5x10^{-8}$–$5x10^{-6}$ mbar) onto the Pd substrate or by post-oxidation of Zn metal deposits, both methods yielding similar results. In the submonolayer coverage range two two-dimensional hexagonal ZnOx phases coexist on the Pd(111) surface: one of them exhibits an open honeycomb structure with a surface periodicity of ~ 11 Å, whereas the other one has a close-packed structure with a lattice constant of 3.3 Å, which is close to the bulk value of ZnO(0001) surfaces (3.25 Å). The latter phase becomes dominant at higher oxygen pressures and also at higher Zn coverages. The first ZnO monolayer on Pd(111) contains the hexagonal close-packed layer phase only and displays a (6x6) Moiré structure. At higher coverages the flat film morphology is maintained, but two different terminations are resolved in STM, which are found to show pronounced oxygen pressure dependence.

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[2] O. Dulub et al, Phys. Rev. Lett. 90, 016102 (2003)

[3] B. Meyer and D. Marx, Phys. Rev. B67, 035403 (2003)

[4] F. Ostendorf et al., Phys. Rev. B77, 041405 (2008)

[5] C. Tusche et al., Phys. Rev. Lett. 99, 026102 (2007)

[*] Supported by the Austrian Science Funds (FWF) via the Project P19198-N02 and the National Research Network "Nanoscience on Surfaces".

4:40pm **SS1-WeA10 Growth of Au on Single Crystalline Anatase TiO_2(101) and (001): Probing Under-Coordinated Sites with Core Level Photoelectron Spectroscopy**, ***L.E. Walle,*** Norwegian University of Science and Technology, Norway, *S. Plogmaker,* Uppsala University, Sweden, *A. Borg,* Norwegian University of Science and Technology, Norway, *A. Sandell*, Uppsala University, Sweden

Gold has for a long time been regarded as an inert surface of little use as catalyst. However, in the last decade gold particles have begun to garner attention for their unique catalytic properties.[1] Supported gold particles on metal oxides have been shown to be effective catalysts for several processes, including CO oxidation at remarkably low temperatures, down to 200 K. Most intriguing is the strong size dependence, particles below 5 nm in size are far superior to larger particles in terms of catalytic activity.[2] The detailed mechanism behind the CO oxidation process on the Au/TiO_2 system is still largely an enigma. Many studies have suggested under-coordinated Au atoms and the Au-TiO_2 interface as reactive sites. A fundamental understanding of the growth mechanism of Au clusters on TiO_2 and the nature of the Au/TiO_2 bond is thus of great importance. Up till now most experimental studies of Au particles on single crystal TiO_2 have been done on the rutile phase, due to the good availability of rutile single crystals. On the other hand, the anatase TiO_2 polymorph seems to be the preferred phase when forming nanosized particles. In the last couple of years good quality anatase single crystals have become commercially available which has triggered an increased research interest. In this contribution we present a study of Au growth on single crystalline anatase TiO_2(101) and TiO_2(001) surfaces under UHV conditions using core level photoelectron spectroscopy. The data were obtained at the Swedish National Synchrotron Facility MAX II. A preliminary analysis gives that Au nucleates at steps on both surfaces. Regarding the (101) surface this is in agreement with a recent report by Gong et al.[3] In addition, we have studied subsequent adsorption of CO at 120 K on the Au particles. Adsorption of CO induces a shift of the Au 4f core level by 1 eV, which is easily observed. The relative amount of Au atoms that can bond to CO varies with the amount of deposited Au. Since CO only bonds to under-coordinated Au atoms at 120 K the results thus give information regarding the geometrical properties of the Au particles.

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[2] M. Valden, X. Lai, and D. W. Goodman, Science 281, 1647 (1998).

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5:00pm **SS1-WeA11 Growth of CeOx Nanoparticles on TiO_2(110)**, ***J.B. Park***, *D.J. Stacchiola, J. Graciani, S. Ma, A. Nambu,* Brookhaven National Laboratory, *J.F. Sanz,* Universidad de Sevilla, Spain, *J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

Catalysts containing nanoparticles of ceria supported on titania exhibit a high activity for the water-gas shift reaction and the CO oxidation. It has been suggested that this catalytic activity is related to the easy reversible change of the oxidation states of ceria (Ce^{3+} and Ce^{4+}), but very little is known about the ceria-titania interactions and the growth mode of ceria on titania. In this work, the growth of CeOx on rutile TiO_2 (110) have been investigated by STM and PES in UHV. The deposition of CeOx changes the morphology of TiO_2 (110), creating several layers deep steps. At low coverages (less than 0.3ML of Ce), CeOx nanoclusters are preferentially nucleated on the in-plane oxygen atoms of TiO_2 (110) and exhibit diagonal arrays along the [001] direction by sharing bridging oxygens. At high coverages, extended rectangular islands of CeOx are observed. XPS studies show that the diagonal arrays of CeOx nanoclusters and their coverage-dependent morphological changes are associated with changes in the oxidation states of the CeOx nanoparticles. The DFT calculations provide the detailed atomic structures for CeOx on rutile TiO_2 (110).

This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

5:20pm **SS1-WeA12 Experimental Band Dispersions and Surface Morphology of the Wide Band Gap Oxide Semiconductor β-Ga_2O_3 With and Without Mn Doping**, ***T.C. Lovejoy***, *J. Morales, E.N. Yitamben,* University of Washington, *N. Shamir,* Nuclear Research Center - Negev, Israel, *S. Zheng, S.C. Fain, F.S. Ohuchi, M.A. Olmstead*, University of Washington

Experimental studies of the wide band gap semiconductor β-Ga_2O_3 have been conducted on bulk single crystals using angle resolved photoemission (ARPES) and scanning tunneling microscopy (STM). This system exhibits interesting electronic and optical properties including electroluminescence and resistivity changes upon gas adsorption. In addition, the resistance can vary over many orders of magnitude with annealing and/or electric field treatment of the transparent crystal. Measured valence band dispersion relations are in qualitative agreement with previously reported theoretical calculations. The observed local surface structure is similar to that previously reported for thin films, but the larger scale morphology is characterized by rectangular pits or islands a single unit cell high with lateral sizes varying on the 10-100nm scale. Preliminary experiments with transition metal (Mn) doping reveal changes in electronic structure and surface morphology that may be relevant for application of Mn:Ga_2O_3 as a dilute magnetic oxide. Work supported by NSF grant DMR-0605601. TCL was supported by an IGERT Fellowship, NSF/NCI DGE 0504573; ENY was supported by an IBM Fellowship. Some experiments were performed at the Advanced Light Source, Berkeley, supported by DOE contract DE-AC02-05CH11231.

Surface Science
Room: 209 - Session SS2-WeA

Electrons and Electronic Spectra at Surfaces
Moderator: R.M. Osgood, Columbia University

1:40pm **SS2-WeA1 Electron Dynamics at a Metal-Organic Interface**, ***C.H. Schwalb***, *M. Marks,* Philipps University Marburg, Germany, *S. Sachs, A. Schöll, F. Reinert,* University Würzburg, Germany, *E. Umbach,* Forschungszentrum Karlsruhe, Germany, *U. Höfer*, Philipps University Marburg, Germany

The injection of charge carriers at a molecule-metal interface plays a decisive role in the performance of organic semiconductor devices. Especially new electronic states that may develop due to the interaction of the adsorbed molecules with the metal substrate can alter the injection mechanisms drastically. We present a recent study for a well characterized model system of epitaxial 3,4,9,10-perylene tetracarboxylic acid dianhydride (PTCDA) thin films on a Ag(111) substrate. Two-photon photoemission (2PPE) displays a dispersing unoccupied state between the metallic Fermi level and the lowest unoccupied molecular orbitals (LUMO) of PTCDA with an effective electron mass of 0.39 m_e at the Γ-point. Its energetic position in the band gaps of both the Ag(111) substrate and the PTCDA overlayer identify it as a genuine interface state, a result that is corroborated by model calculations. Time-resolved measurements show that the lifetime of electrons excited into this interface state is 55 fs. This is a relatively small value for an unoccupied state located only 0.6 eV above the Fermi level and is indicative for a large penetration of the wavefunction into the projected sp-gap of Ag(111). In order to investigate the role of the interface state for carrier transport between the organic semiconductor and the metal we populate the LUMO of PTCDA by absorbing 2.4 eV photons in films of varying thickness up to 100 ML and simultaneously record fluorescence and angle-resolved photoemission spectra. We observe a long lived component in the 2PPE intensity close to the Fermi level which clearly correlates with film thickness and fluorescence lifetime.

2:00pm **SS2-WeA2 Electronic Structure and Charge Separation at a Planar Molecular Heterojunction Probed by Two-Photon Photoemission**, ***G. Dutton***, *D.B. Dougherty, S.W. Robey,* National Institute of Standards and Technology, *W. Jin, W.G. Cullen, J.E. Reutt-Robey*, University of Maryland, College Park

The molecular donor-acceptor interface performs a critical function in the operation of organic photovoltaics as the sole site of charge separation. Understanding the electronic structure and exciton/polaron dynamics at these interfaces is crucial for developing the understanding of the relevant diffusion, dissociation and recombination processes necessary for achieving enhanced efficiencies. We have employed photoemission techniques, primarily two-photon photoemission spectroscopy (2PPE) and time-resolved pump-probe measurements, to examine these issues for thin organic films and heterointerfaces of pentacene and copper phthalocyanine with C60 fullerene. This talk will concentrate on results for interfaces between copper phthalocyanine and C60 formed on Ag(111). Using a combination of visible 1.75eV pump, corresponding to the phthalocyanine Q-band absorption maximum, and 5.25eV UV probe, we observe the ultrafast population dynamics of the C60 LUMO electron-polaron at 0.3 eV above the Fermi level. Preliminary analogies of corresponding physical molecular structures at this interface will also be presented based on STM results for the similar zinc phthalocyanine:C60 interface.

2:20pm **SS2-WeA3 Quantitative Three-dimensional Spin-Polarimetry in ARPES**, ***J. Osterwalder***, University of Zurich, Switzerland, *H. Dil, F. Meier,* University of Zurich and Paul-Scherrer-Institut, Switzerland, *J. Lobo,* University of Basel, Switzerland, *L. Patthey*, Paul-Scherrer-Institut, Switzerland **INVITED**

An angle-resolved photoelectron spectrometer has been equipped with a full three-dimensional spin polarimeter by using two orthogonal Mott detectors.[1] The unique capability of the instrument has made it possible to introduce a new two-step fitting routine that provides absolute spin polarization vectors for each individual band intersected in a particular

ARPES spectrum or momentum distribution curve.[2] This procedure is crucial when analyzing strongly overlapping peaks or weak signals sitting on a large unpolarized background. It is robust against strong intensity variations due to matrix element effects because it references the spin polarization contribution of each band to the measured peak intensity. The method is applied to two-dimensional systems where spin-orbit effects lead to complex momentum-dependent spin structures.[3] Two prototypical systems, Bi/Ag(111) $(\sqrt{3}x\sqrt{3})R30°$ and Pb/Ag(111) $(\sqrt{3}x\sqrt{3})R30°$ were investigated. We confirm that the surface states experience a large spin splitting. Moreover, we find that all surface states are 100% spin polarized, and that for some states, spin polarization vectors rotate out of the surface plane. With the photoelectron spin as an additional tag in the measurement, spin-split bands with splittings far below the measured line width can be resolved. This has allowed us to see such splittings in quantum well states within ultrathin Pb layers on Si(111). Comparable to surface states, the space inversion symmetry is broken in these films, and the spin degeneracy of the valence electrons is lifted. The effect is much smaller though, and we measure energy splittings as small as 15 meV.

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3:00pm **SS2-WeA5 A New Spin on Chirality: Reactions Induced by Polarized Secondary Electrons from a Magnetic Substrate[1]**, ***R.A. Rosenberg****, M.J. Abu Haija,* Argonne National Laboratory, *P.J. Ryan*, MUCAT, Ames Laboratory

Since nearly all biological compounds are homochiral, any model of the origin of life must be able to incorporate a mechanism that could lead to preferential chirality. Since chiral molecules have a certain handedness, many researchers have investigated the possible influence of circularly polarized UV photons and longitudinal spin-polarized electrons in creating an enantiomeric excess.[2-4] However, in general the demonstrated effects have been small and/or on the order of the experimental error. In the present work we hypothesize that a previously unappreciated source may play a role in chiral-selective chemistry: low-energy (0-20 eV) spin-polarized secondary electrons, produced by photon,[5] electron,[6] or ion[7] irradiation of a magnetic substrate. To test this theory we have performed detailed x-ray photoelectron spectroscopy measurements of the reaction rate for x-ray induced, secondary electron photolysis of a model chiral compound, R- or S-2-Butanol, adsorbed on a magnetized permalloy ($Fe_{0.2}Ni_{0.8}$) substrate. Our results show an enhancement of ~10% in the rate of C-O bond cleavage that depends on the chiraltiy of the molecule and the spin polarization of the secondary electrons. Not only do our results demonstrate a chirality enhancement well above that of most previous work, but, since this mechanism only requires a magnetic substrate and ionizing radiation, it should be viable in a wide variety of possible prebiotic environments.

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4:00pm **SS2-WeA8 The Temperature-Dependent Dynamic Solvation of Excess Electrons at the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide/Ag(111) Interface**, ***M.L. Strader***, Max Planck Institut für Metallforschung, Germany

Interest in room temperature ionic liquids (RTIL's) has increased rapidly in the last decade, fueled by the potential of RTIL's as environmentally friendly 'designer solvents'. The unusual, highly ionic character of RTIL’s has motivated study of their fundamental physical properties. The dynamic solvation responses of various RTIL’s have been studied in bulk, and extension of study to the interface could prove useful to electrochemical applications. Two-color, angle-resolved, two-photon photoemission (AR-2PPE) has been used to study interfacial solvation dynamics in ultrahigh vacuum (UHV) for a number of systems. Thin films of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide were epitaxially grown on Ag(111) and studied with AR-2PPE. The well-known low vapor pressures of RTIL's afford the rare opportunity to study interfacial solvation dynamics at electrochemically relevant temperatures in the liquid phase. A pronounced increase in solvation at elevated temperatures is observed.

4:20pm **SS2-WeA9 Novel Acoustic Plasmons on Metal Surfaces**, ***K. Pohl****, B. Diaconescu,* University of New Hampshire, *G. Vercelli, L. Vattuone, M. Rocca*, CNISM, IMEM-CNR and Università di Genova, Italy

The recent discovery of a fundamentally new sound-like plasmon on a bare metal surface of beryllium may introduce a new research direction in the area of plasmonics.[1] While conventional surface plasmons are optical modes and have a finite excitation energy of a few eV, the novel acoustic mode can be excited with very low energies of a few meV. This allows, in principle, for a coupling with visible light for signal processing and advanced microscopies as well as new catalysts on metallic surfaces. In order to show that this novel excitation is a general phenomenon on closed-packed noble metal surfaces, as predicted by our theoretical collaborators,[2] we have measured the dispersion of the acoustic surface plasmon on Cu(111) by electron energy-loss spectroscopy for a parallel momentum-transfer range from 0 to 0.20 1/Å. We can report that the dispersion is indeed linear (acoustic) with a slope (sound velocity) in good agreement with theory,[2] and energy values that extend up to 1 eV. We will shown that the novel acoustic surface plasmon, ASP, is a general phenomenon on metal surfaces that support a partially occupied surface state within a wide bulk energy gap. It is caused by the non-local screening of the surface electrons due to bulk electron. The adsorption of about 0.25 ML of oxygen on the surface removes the surface state on Cu(111) and indeed destroys the ASP.

This work was supported in parts by the NSF under Grant No. DMR-0134933 and DMR-0753467, by the visiting scholar program of CNISM and by Compagnia S. Paolo.

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4:40pm **SS2-WeA10 Exploring Adsorption through Surface Resistivity Measurements**, *C. Liu, **R.G. Tobin***, Tufts University

Surface resistivity – the increase in the electrical resistivity of a thin metal film due to surface defects or impurities – is a simple and readily measured property that provides a window into complex nonequilibrium surface processes. It originates in the diffuse scattering of the metal’s conduction electrons by the localized potential created by the surface modification, and depends in complicated fashion on the local electronic structure of the scatterer. The variation of surface resistivity with coverage, for both single adsorbates and coadsorption systems, gives insight into the effects of surface defects and neighboring adsorbates on the electron-scattering probability. We report on several surface resistivity studies that reveal different aspects of adsorption. All are carried out on 50 nm thick epitaxial Cu(100) films grown on H-terminated Si(100) substrates. CO adsorption on these films exhibits striking differences in electron-scattering cross section for adsorption on different sites, with CO on defect sites exhibiting near-zero net scattering.[1] Studies of oxygen and sulfur adsorption reveal the effects of interadsorbate interactions. Individually adsorbed oxygen and sulfur show very different coverage-dependences, with oxygen atoms acting as independent non-interacting scatterers while at high coverages sulfur strongly suppresses scattering by nearby sulfur atoms.[2] Sulfur has a similar effect on coadsorbed oxygen, reducing its effective scattering cross-section essentially to zero when the two atoms are adsorbed on adjacent lattice sites.[3] We suspect that the apparently zero differential resistivity observed for defect-bonded CO and for adsorption of O or S near a pre-adsorbed sulfur atom results not from zero electron scattering by the added adsorbate but from cancellation of the new adsorbate’s added scattering by a reduction in scattering from the defect site or preadsorbed sulfur. These results can be analyzed qualitatively in terms of the behavior of adsorbate-derived orbitals near the Fermi level.

[1] C. Liu and R.G. Tobin, J. Chem. Phys. 126, 129705 (2007).

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

[3] C. Liu and R.G. Tobin, J. Chem. Phys., in press.

5:00pm **SS2-WeA11 Dependence of Surface Properties on Adsorbate-Substrate Distance: Work Function Changes and Binding Energy Shifts for I/Pt(111)**, ***P.S. Bagus***, University of North Texas, *Ch. Wöll*, Ruhr Universität Bochum, Germany, *A. Wieckowski*, University of Illinois at Urbana-Champagne

A detailed analysis of the character of the bond of I adsorbed at on-top and three-fold sites of Pt(111) is presented. At both sites, the bonding is dominated by an ionic interaction supplemented with some covalent character due to donation from the adsorbed I anion to Pt. The way in which the I-Pt interaction affects observed properties, including the anomalous work function changes induced by the adsorption of I and the shifts of I core level binding energies, will be described. The surprising fact that a negatively charged adsorbate leads to a work function decrease, rather than the increase expected solely due to the charge of the adsorbate, arises from electronic reorganizations that cancel the dipole due to the charged adsorbate.[1] Furthermore, the contributions that lead toward an interface dipole that lowers the work function are larger as the adsorbate moves closer to the surface. Thus, the magnitude of the change in the interface dipole can be directly correlated with the distance of the I adsorbate from the Pt surface. A similar distance dependence is also found for the shifts of the I core level binding energies. In effect, these shifts can be interpreted to indicate adsorbate height. In particular, the shifts provide a new way to distinguish I adsorption at on-top and three-fold sites of Pt(111) since the distance of I from Pt(111) is different for these two sites. Furthermore, the effects important for the shifts of the interface dipole in the simpler case of

I/Pt are also relevant for the charge transport barrier between a metal substrate and an organic adsorbate.[2] Thus the distance dependence demonstrated here for I/Pt may also provide information helpful for understanding these more complex systems.

[1] P. S. Bagus, D. Käfer, G. Witte, and C. Wöll, Phys. Rev. Lett., 100, 126101 (2008).

[2] G. Witte, S. Lukas, P. S. Bagus, and C. Wöll, Appl. Phys. Lett., 87, 263502 (2005).

5:20pm **SS2-WeA12 Influence of Quantum Well States on Apparent Tunneling Barrier Height in Ultra Thin Pb Films**, ***J.D. Kim***, *S.Y. Qin, C.K. Shih*, The University of Texas at Austin

The thickness dependence of tunneling decay constant (κ) for ultra thin Pb films is studied with various sample biases by using low temperature STM. It is found that quantum well states (QWS) have a strong influence on κ. While the decay constant versus layer thickness (κ vs. L) clearly shows bilayer oscillations, we found that the apparent contrast in κ vs. L also show strong bias dependence. This result shows that κ-oscillation does not necessarily imply the work function oscillation. We further show that in this case, the parallel component of crystal momentum plays a critical role in tunneling process and is largely responsible for the observed phenomena. On the other hand, at large negative sample bias, the measured decay constants shows less bias dependent. Nevertheless, at small negative biases (less than 0.3 V below), the measured κ is strongly influenced by location of QWS near Fermi energy.

1NSF-IGERT DGE-0549417; NSF-FRG 26-1126-8750.

Surface Science
Room: 207 - Session SS1-ThM

Growth and Etching on Surfaces
Moderator: A.A. Baski, Virginia Commonwealth University

8:00am **SS1-ThM1 Step Etching and Restructuring on Cl_2-exposed, Cl-saturated Si(001)-(2x1)**, ***R.E. Butera***, *J.H. Weaver*, University of Illinois at Urbana-Champaign

We use scanning tunneling microscopy and density functional theory to investigate the etching of rebonded step atoms and the concomitant restructuring of the B-type step for Cl_2-exposed, Cl-saturated Si(001)-(2x1) at 675 K $\leq T_S \leq$ 725 K. Previous studies have shown that these exposure conditions allow uptake beyond "saturation," providing inserted Cl moieties, Cl_i, that lead to novel etching patterns without regrowth structures. Using surfaces with narrow terraces, we show that Cl_i diffuses to the rebonded S_B step and our calculations identify a stable adsorption configuration that bridges the rebonded and non-rebonded step atoms. Step etching removes the rebonded step atoms and results in the formation of an atom-wide vacancy line (AVL) along the step. Step restructuring begins with AVL diffusion into the terrace and ends with step retreat by one dimer unit to reestablish the rebonded S_B step structure. We use theory and experiment to show that restructuring is driven by the reduction of step energies and adsorbate-adsorbate repulsion. These results identify the rebonded step structure as the most energetically favored step structure on Cl-terminated Si(001)-(2x1).

8:20am **SS1-ThM2 Ion Scattering from Au Nanoclusters formed by Buffer Layer Assisted Growth**, ***S. Balaz***, *J.A. Yarmoff*, University of California, Riverside

Ion scattering is used to probe the atomic and electronic structure of Au nanocrystals grown by Buffer Layer Assister Growth (BLAG). Amorphous solid water (ASW) was adsorbed as a buffer layer onto SiO2/Si(111) at liquid nitrogen temperature. Au was then evaporated onto the buffer layer to form nanoclusters. The samples were subsequently annealed to room temperature, causing the water to desorb and the clusters to deposit directly onto the substrate. Time-of-flight (TOF) spectroscopy was used to measure 2 keV 7Li+ and 39K+ ions scattered from Au atoms both at low temperature when the clusters reside atop the buffer layer, and after desorbing the water. Small Au depositions yielded a sharp single scattering peak that indicates single layer structures. Following larger depositions, multiple scattering features were present indicating the formation of multilayer nanoclusters. The neutral fraction of scattered K+, which provides an indication of the filled quantum states, starts at ~50% for small Au coverages and decreases with further deposition, indicating changes in the quantum state occupancy with cluster size.

8:40am **SS1-ThM3 Competition Between Particle Formation and Burrowing: Gold on Bismuth**, ***P. Swaminathan***, *J.S. Palmer*, *J.H. Weaver*, University of Illinois at Urbana-Champaign

We discuss Au nanoparticle formation on Bi films under conditions where burrowing of the formed Au particles into the film is competitive to growth. Burrowing occurs because the surface free energy of Bi is lower than that of Au, the Au-Bi interface energy is small, and the kinetics, in terms of high surface and grain boundary diffusion rates, are favorable. The negligible solid solubility of Au in Bi at low temperatures means that alloy formation effects can be neglected. By changing deposition temperatures and rate, we show the effect of burrowing on the final size distribution. These results are supported by kinetic Monte Carlo simulations that include atom impingement, surface diffusion, and burrowing rates as parameters. Burrowing broadens and splits the size distribution as small particles are removed from the surface continuously and those that remain grow to larger sizes by adatom capture. These results are important for systems where nanostructures are assembled on low surface energy substrates, and they specify the conditions where growth is affected by burrowing.

9:00am **SS1-ThM4 Optical Anisotropy Induced by Oblique Incidence Ion Bombardment of Ag(001)**, ***H. Wormeester***, *F. Everts*, *B. Poelsema*, University of Twente, The Netherlands

Oblique incidence ion sputtering has become a widely used method for the creation of highly regular patterns of lines and dots. On a Ag(001) surface oblique incidence sputtering creates a ripple pattern that exhibits plasmonic features. The photon energy of this plasmonic feature depends on the ripple periodicity. The development of these anisotropic features is measured in-situ with the optical technique Reflection Anisotropy Spectroscopy (RAS). The ion induced nanopatterns are prepared using 2 keV Ar ions with a flux of a few Ma/cm^2 in a temperature range of 300 - 420K. With RAS, a periodicity of ripples above 200 nm is measured by a shift in photon energy of the plasmon resonance. Features with a smaller periodicity show a plasmon resonance around 3.65 Ev. For very grazing incidence sputtering, 80° polar angle of incidence, only a resonance feature around 3.65 Ev is observed. High resolution LEED measurements after sputtering confirm the formation of 1D nanoripples. For a polar angle of incidence of the ion beam of 70° a shift in the maximum of the plasmon resonance feature is observed. These spectra can be well described within the Rayleigh-Rice description for scattering from a slightly rough surface. The formation of nanoripples, i.e. a 1D roughening of the surface perpendicular to the direction of the ion beam, suffices to describe the measured optical data. The evolution of the rms, wavelength and wavelength distribution of the ion bombardment induced nanoripples is obtained from in-situ measurements. For a polar angle of the ion beam of 61° we find that also the roughening in the direction along the nanorippels has to be taken into account to describe the optical spectra.

9:20am **SS1-ThM5 Producing Ultraflat Si(100) Surfaces with Aqueous Etching: STM and FTIR Yield Mechanistic Insights**, ***M.A. Hines***, Cornell University **INVITED**

The production of atomically flat Si(100) surfaces is a long-standing technological challenge, as Si(100) is the basis for today's microelectronic devices. From a chemist's standpoint, the study of etch morphologies yields fascinating insights into surface chemistry, as etching reactions literally write a record of their reactivity on the etched surface. We use a combination of STM and vibrational spectroscopy to show that a simple aqueous etchant can produce Si(100) surfaces of surprising and unprecedented smoothness. The etched surface is characterized by long rows of H-terminated silicon atoms. This structure is favored because it minimizes interadsorbate repulsion on the surface. A new technique for the analysis of surface infrared absorption spectra[1] is used to deconvolute the well-known vibrational spectrum of the etched H/Si(100) surface. This analysis yields a relatively simple picture of the structure of the etched surface -- a picture that is much simpler and much smoother than previous analyses. The significant effects of interadsorbate strain on the spectrum will also be discussed. Finally, the influence of gas evolution on the mesoscale roughness of etched surfaces will be discussed. Again, the fascinating patterns that form during etching yield new insights into the chemistry of etching.

[1] I. T. Clark, B. S. Aldinger, A. Gupta, and M. A. Hines, J. Chem. Phys. 128, 144711 (2008).

10:40am **SS1-ThM9 Focused Ion Beam (FIB) Patterning and Selective Decomposition of III-V Semiconductors**, ***K.A. Grossklaus***, *J.M. Millunchick*, University of Michigan

The use of focused ion beams (FIB) has been identified as a method by which III-V substrates may be modified in a variety of ways for subsequent film growth. Presented here are the initial results of research exploring the use of FIB to modify III-V semiconductor surfaces and directly mill 3-D square array and hole patterns. Studies thus far have examined the FIB response of GaAs, InAs, and InP wafer substrates, along with AlAs layers grown on GaAs substrates. Each of these materials has been found to respond differently to the ion beam. Through use of the FIB to chemically decompose selected sample areas, group III nanostructures have been produced in patterned areas on InAs, GaAs, and InP, while AlAs has been shown to be resistant to metal nanostructure formation. The appearance and distribution of these nanostructures has been found to depend on the ion dose used for patterning. Nanostructure size and distribution on InP in particular has been shown to vary with ion dose and time from milling. It has been shown that ridge-like features act as preferential sites for the self-assembly, providing a method for the regular placement of metallic nanostructures. The causes for the different FIB response of each material will be discussed relative to their different material properties and predicted ion beam response. Proposed routes for controlling or eliminating the formation of group III nanostructures and the results of preliminary attempts to do so will be presented. The FIB patterning conditions and the patterns created thus far will be discussed in terms of their suitability for the creation of modified substrates upon which low defect density lattice mismatched films may be grown. As part of this additional patterning types and geometries for future examination and film growth experiments will also be discussed.

11:00am **SS1-ThM10 Electron Induced Deposition of Amorphous Carbon Nitride Films**, ***H. Fairbrother***, *J.M. Gorham, J.D. Wnuk*, Johns Hopkins University

Nitrogen doped carbonaceous films have attracted intense experimental and theoretical interest due to the beneficial effects that nitrogen incorporation has on the wear resistance, adhesion characteristics and optical/electronic properties of amorphous carbonaceous films. Motivated by a desire (i) to understand the structure of amorphous carbon nitride films deposited by electron beam induced deposition (EBID) and (ii) to better understand the role that electrons play in moderating the microstructure and film growth of plasma deposited nitrogen doped carbonaceous films, we have studied the deposition of amorphous carbon nitride films from a 1,2-diaminopropane precursor molecule exposed to low energy (< 5keV) electrons. Our experimental approach involved initially depositing nanometer-scaled thin films of the precursor at low temperatures under ultra-high vacuum (UHV) conditions. The influence of electron irradiation on the chemical composition and bonding within the deposited film was then probed using reflection absorption infrared spectroscopy (RAIRS) in combination with x-ray photoelectron spectroscopy (XPS), while complementary data of the gas phase species evolved during electron irradiation were studied with mass spectrometry (MS). The electron stimulated decomposition of adsorbed 1,2-diaminopropane proceeded with the loss of both C-H and N-H bonds and the formation of an amorphous carbon nitride film. Upon more prolonged electron beam irradiation, nitrile (C≡N) species were formed. This observation suggests that electrons may play an important role in moderating the chemical structure of plasma deposited carbon nitride films. Hydrogen was the principal gas phase product evolved during film deposition. The loss of C-H and N-H bonds from the film, as well as the hydrogen evolution, were modeled by a first-order kinetic process with a rate constant that increases linearly with electron fluence. This information obtained under UHV conditions will also be compared with data obtained from the growth kinetics and structure of amorphous carbon nitride films grown using EBID of vapor phase 1,2-diaminopropane, studied using a combination of auger electron spectroscopy and atomic force microscopy. Results will also be presented on the role that the incident electron energy and the substrate exert in determining reaction rates and growth kinetics.

11:20am **SS1-ThM11 Low Energy Electron Induced Decomposition of Adsorbed Methylcyclopentadienylplatinum(IV)-trimethyl**, ***J.D. Wnuk***, *J.M. Gorham,* Johns Hopkins University, *W.F. Van Dorp,* Rutgers, the State University of New Jersey, *C.W. Hagen,* Delft University of Technology, The Netherlands, *T.E. Madey,* Rutgers, the State University of New Jersey, *D.H. Fairbrother*, Johns Hopkins University

Electron beam induced deposition (EBID) of volatile organometallic precursors has emerged as an effective and versatile route to creating 2-D and 3-D metallic nanostructures. In an effort to better elucidate the process by which these structures are formed, we have studied the effect of low energy (500eV) electrons on sub-monolayer coverages of methylcyclopentadienylplatinum(IV)-trimethyl (MeCpPtMe$_3$) adsorbed onto gold substrates in situ under ultra-high vacuum conditions using a combination of mass spectrometry, reflection absorption infrared spectroscopy (RAIRS) and x-ray photoelectron spectroscopy (XPS). Electron beam irradiation produces a carbonaceous film that contains Pt atoms in an oxidation state which is intermediate between metallic Pt and the parent Pt(IV) species. XPS analysis of the Pt(4f) region indicates that the conversion of Pt species follows first order kinetics, with a rate constant proportional to the target current. Electron stimulated decomposition of adsorbed MeCpPt(IV)Me$_3$ is also accompanied by the evolution of gas phase methane and hydrogen as well as the loss of the C-H bonds associated with the parent MeCpPt(IV)Me$_3$ compound. The kinetics of methane and hydrogen production and the loss of C-H groups from the adsorbate layer can all be described by first order kinetics, with calculated reaction cross-sections comparable to the XPS-measured value. In conjunction, XPS, RAIRS and MS data suggests that a single electron event is responsible for decomposition of the parent compound and the formation of the platinum containing carbonaceous film. Electron beam irradiation also results in a reproducible change in the film's Pt/C ratio, whose magnitude is consistent with the idea that electron beam decomposition is initiated by a single Pt-CH$_3$ bond cleavage event. The average cross-section for the electron stimulated decomposition of adsorbed MeCpPt(IV)Me$_3$ via the different pathways at a specific electron beam energy of 500 eV is measured to be 1.5x10^{-16} cm^{-2}. Results from this study, carried out under well-defined reaction conditions where changes in the gas phase composition and the film's surface composition can be monitored simultaneously, provide new insights into the EBID process.

11:40am **SS1-ThM12 A Study of the Surface Chemistry and Cross Sections for Electron Induced Dissociation using Temperature Programmed Desorption**, ***W.F. Van Dorp***, Delft University of Technology, The Netherlands, *S. Zalkind, B. Yakshinksiy, T.E. Madey,* Rutgers, the State University of New Jersey, *J.D. Wnuk, J.M. Gorham, H. Fairbrother,* Johns Hopkins University, *C.W. Hagen*, Delft University of Technology, The Netherlands

Electron beam-induced deposition (EBID) is a technique where adsorbed precursor molecules are dissociated by a focused beam of electrons to define metallic or semi-conducting patterns. Control over the process has developed to the extent that the amount of deposited material can be controlled (nearly) to the level of single molecules.[1] However, the purity of the deposits is not yet well controlled due to lack of knowledge of the precise nature of the precursor dissociation. Therefore, we study the adsorption behaviour of $(CH_3)_3$-Pt-$C_5H_4CH_3$ (a typical EBID precursor) and the dissociation cross section as a function of incident electron energy using Temperature Programmed Desorption (TPD).[2,3] TPD experiments using a Au(110) sample as substrate indicate that the first monolayer in contact with the substrate has a higher desorption temperature than condensed multilayers. The adsorption energy for the monolayer in contact with the Au is estimated to be 55 kJ/mol. The desorption behaviour in the first monolayer is first order and multilayers do not form until after the first monolayer has formed; the precursor desorbs molecularly. The precursor desorbs (nearly) completely below 0 °C. To study the adsorption behaviour in a condition more typical of an EBID experiment, we deposited a several nm thick carbon/Pt containing layer on the sample. TPD measurements using this "realistic" surface show that the desorption behaviour is similar to that on clean Au(110). The peaks have their maxima in the same range of temperatures, although the peaks are wider. Using this "realistic" C/Pt surface, we studied the effect of broad beam electron irradiation on the TPD spectrum of a single monolayer of precursor. As the total electron dose increases, the area under the TPD peak for m/z = 289 decreases. Cross sections for dissociation can be calculated from the reduction in the area under the TPD peak and are about 10^{-16} cm^2 for electron energies between 40 eV and 3 keV, comparable to those for electron induced dissociation in the gas phase.

[1] W.F. van Dorp, C.W. Hagen, P.A. Crozier, P. Kruit, Nanotechnology 19 (2008) 225305.

[2] N.S. Faradzhev, C.C. Perry, D.O. Kusmierek, D.H. Fairbrother, T.E. Madey, J. Chem. Phys. 121 (2004) 8547.

[3] C. C. Perry, N. S. Faradzhev, D. H. Fairbrother, T. E. Madey, Int. Rev. Phys. Chem. 23 (2004) 289.

Surface Science
Room: 208 - Session SS2+NC-ThM

Catalysis on Nanoclusters
Moderator: J. Hrbek, Brookhaven National Laboratory

8:00am **SS2+NC-ThM1 Hybrid Nano-Oxide System for Oxidation of Methanol at Lower Temperatures**, ***A.S. Karakoti***, *A. Vincent, T. Spalding,* University of Central Florida, *D. Patel,* NJ Institute of Technology, *S. Seal*, University of Central Florida

Paradigm shift in the global energy policy towards cleaner and alternate fuels, arising out of uncontrolled green house emissions and rapid depletion of fossil based fuels, paved the way for various challenging areas of research. Among the various alternatives, direct oxidation of alcohols to hydrogen offer one promising alternative to primary fuels. Hydrogen produced from the alcohols can be used as a primary fuel source for DMFCs. Preliminary work on conversion of methanol to hydrogen and other byproducts, in presence of noble metals such as platinum and gold as catalysts, has shown promising results. However, the use of noble metal catalysts makes the conversion an expensive deal. Nanomaterials such as titanium oxide (titania), zirconium oxide (zirconia), cerium oxide (ceria) have been tried as active catalyst supports in varying range of particle sizes and molar ratios of noble metals with limited success. To overcome the hurdles in the existing systems, we have focused on the hybrid ceria-titania nanostructures synthesized using sol gel and co-precipitation methods for optimizing the efficiency of the catalyst in methanol oxidation. The percent conversion of methanol to various species was studied using an in-house built catalytic reactor coupled to a mass spectrophotometer for analysis of gaseous reaction products. The selectivity and efficiency of the hybrid nano-oxide system as a catalyst support was studied as a function of mixture concentration, percent loading of the noble metal catalyst and the phase structure. Experimental results were normalized with respect to the surface area of the supporting catalysts. The adsorption characteristics of methanol and byproducts on the catalyst surface were evaluated using Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS). Powder samples were characterized using X-ray Diffraction (XRD) and Transmission Electron Microscope (TEM) for determining the phase, particle size and shape of the particles in mixed systems. X-ray Photoelectron spectroscopy (XPS) was used to verify the oxidation state of the metal catalyst as well as mixed ceria-titania supports as a function of molar concentration of the constituents. Preliminary results have shown that the onset temperature for methanol decomposition was as low as 150^{o}C and both the onset as well as complete conversion temperature varies as a function of molar ratio of ceria to titania.

8:20am **SS2+NC-ThM2 Decomposition of Methanol on High Surface Area Titanium Carbide Films**, ***D.W. Flaherty***, *N.T. Hahn, C.B. Mullins*, University of Texas at Austin

We are investigating the surface chemistry of small alcohols on novel, high surface area, titanium carbide films using a combination of temperature programmed desorption, molecular beam reactive scattering, and infrared absorption spectroscopy. High-surface area catalytically active films can be synthesized by glancing angle deposition of a metal onto a cold surface in a low ambient pressure of gas. The subsequent surface reaction of the two components results in the growth of nano-porous films with controllable stoichiometry and morphology. We have employed this technique, referred to as reactive ballistic deposition (RBD), to deposit nano-structured, high surface area films of metal carbides. It is well known that transition metal carbides have catalytic properties similar in some respects to platinum group metals, with the added benefits of comparatively low cost, high thermal stability, and mechanical durability. Building on our knowledge from the previous investigation of high surface area TiO2 films, we are developing high surface area, porous, transition metal carbide films for the purpose of studying their physical properties and chemical reactivity. Our current work has focused on the deposition and physical characterization of titanium carbide (TiC) films deposited using the RBD technique. Auger electron spectroscopy is used to investigate the stoichiometric dependence of the films on growth conditions. The specific surface area and distribution of binding site energies of the films are measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption (TPD) of chlorodifluoro-methane. Results from TPD studies suggest that TiC films grown using the RBD technique have specific surface areas of at least 100 m^2/g and are thermally stable to nearly 1000 K. The combination of high surface area and thermal stability suggest that these films could be effectively utilized for heterogeneous catalysis.

8:40am **SS2+NC-ThM3 Catalysis by Atomic-Size Centers**, ***H. Metiu***, University of California, Santa Barbara **INVITED**

We perform density functional calculations to explore the properties of two new classes of catalysts, both consisting of atomic-size active centers. In one class the cation at the surface of an oxide is replaced with another cation which we call a dopant. By an appropriate choice of the dopant-oxide pair we can weaken the bond of the oxygen atoms at the surface of the oxide and make the system a better oxidant and a better oxidation catalyst. Other choices of dopant-oxide pairs will cause the dopant to adsorb oxygen and weaken the O-O bond to activate oxygen for oxidation reactions. A second class of catalysts with atomic-size active center consists of small oxide clusters supported on a different oxide (for example, a VO_3 cluster supported on TiO_2). Some of the oxygen atoms in the cluster end up bridging two different cations (for example, V-O-Ti) and if the two cations are well chosen, the bridging oxygen becomes active in oxidation reactions. We study the mechanism of methanol oxidation to formaldehyde by VO_3 supported on TiO_2 and plan to screen a large set of oxide clusters on an oxide for hydrocarbon activation.

9:20am **SS2+NC-ThM5 The Oxidative Dehydrogenation of Methanol by Vanadia Particles Supported on Ceria Thin Films**, ***H.L. Abbott***, *A. Uhl, M. Baron, D.J. Stacchiola, S.K. Shaikhutdinov, H.-J. Freund*, Fritz Haber Institute of the Max Planck Society, Germany

Vanadia particles and monolayer or submonolayer coverage vanadia films supported on metal oxide surfaces have shown high activity for the selective oxidation of alcohols. In particular, methanol oxidative dehydrogenation to formaldehyde occurs readily on ceria-supported vanadia. Although support and coverage effects are known to be important for this reaction, questions remain about the relationship between the structure and the reactivity. Here, a well-defined model system, consisting of vanadia nanoparticles deposited on thin ceria films, has been employed. X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRAS), and temperature programmed reaction (TPR) were used to characterize the VO_x/CeO_2 model system. XPS measurements indicated that the oxidation state of the vanadium atoms increases with decreasing coverage. Under low coverage conditions, STM images revealed the presence of isolated vanadia species. Vanadyl stretching vibrations detected by IRAS vary between 1000 and 1050 cm^{-1}, depending on the coverage and the annealing temperature. Two TPR peaks, corresponding to the selective oxidation of CH_3OH on VO_x, were observed, including a new low temperature peak at ~350 K that is believed to correlate with isolated species.

9:40am **SS2+NC-ThM6 Photochemistry of $(NO)_2$ Layers on Alumina-Supported Ag Nanoparticles: Size and Excitation Influences**, *D. Mulugeta, K.H. Kim, K. Watanabe,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, ***D. Menzel***, Fritz-Haber-Institut der Max-Planck-Gesellschaft and Technical University Muenchen, Germany, *H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The unique electronic and optical properties of metal nanoparticles (MNPs) are caused by their small size compared to typical interaction lengths with photons and electrons, the confinement of excitations in them, and their specific excitations, in particular the Mie plasmon which causes strong field enhancement.[1] Modifications of photochemical reactions occurring on them are expected. We have investigated the photochemical reactions in $(NO)_2$ layers on AgNPs deposited on alumina films, using ns laser pulses off and on the plasmon resonance, and for varied NP size. Photoexcitation of $(NO)_2$ leads to photodesorption of NO as well as photochemical conversion to N_2O and to chemisorbed NO. Results include total removal and conversion efficiencies, desorbed species and their cross sections, and mean translational energies of photodesorbed NO. Excitation in the plasmon resonance strongly enhances yields and cross sections, compared to off-resonance excitation and to Ag(111) surfaces. The similar (nonthermal) translational energies of desorbed NO in all cases indicate a common mechanism believed to proceed via temporarily trapped hot electrons forming transient negative ions (TNI) which leads to desorption and reaction. Recent results obtained for variable sizes of the AgNP (2 - 10 nm) have shown that characteristics of both thermal and photochemical reactions depend on size. To explain these results, the influences of the size dependences of a number of excitation and decay processes, based on knowledge of the photophysics of the AgNPs, will be discussed. Time permitting, the changes introduced by the use of fs laser pulses will also be presented. These examples show some important consequences of the small dimensions of NMPs, size-dependent confinement effects, and influences of plasmon excitations.

[1] K. Watanabe, D. Menzel, N. Nilius, and H.-J. Freund, Chem. Rev. 106 (2006) 4301.

10:40am **SS2+NC-ThM9 Effects of Nanocluster Surface Chemistry on Electrocatalysis**, ***B.L. Abrams***, *P.C.K. Vesborg, S. Dobrin, D. Mowbray, I. Chorkendorff*, Technical University of Denmark

Nanocluster catalysts in the small size regime (<10nm) offer the opportunity for enhanced catalytic reactivity due to increased active site availability. This reactivity is also materials dependent and related to how tightly or weakly the nanocatalyst binds the reactants of interest such as hydrogen for the hydrogen evolution reaction (HER).[1,2] Corresponding to the decrease in size is an increase in nanocatalyst surface area. The high surface to volume ratio of nanoclusters in this small size regime thus allows for the ability to impact their catalytic properties by altering their surface chemistry. In this work we alter the cluster surface chemistry by varying the type of surfactants present on metal and metal alloy nanoclusters such as Pt, Au, AuPt, AgPt. These nanoclusters are synthesized using a modified inverse micelle[3] technique where the presence of surfactant molecules (non-ionic or cationic) is crucial to maintaining the nanocluster monodispersity. Following synthesis in the solution phase, the nanoclusters are evaluated electrochemically as a function of surfactant type and amount. In the case of Pt nanoclusters stabilized by a non-ionic surfactant, the HER activity is comparable to standard polycrystalline Pt. The negligible suppression of HER indicates that the surfactant may not significantly block the active sites necessary for HER. In relation to the activity measurements, we have studied the attachment mechanism of the surfactants to the cluster surface utilizing density functional theory (DFT) calculations. An evaluation of the charge transfer processes and reactions as revealed by electrochemical measurements will be presented for each material as a function of surface chemistry alterations. Preliminary result for other reactions of interest to fuel cells such as the hydrogen oxidation reaction will also be discussed.

[1] J.K. Nørskov,et al.,"Trends in the Exchange Current for Hydrogen Evolution" J. Electrochem. Soc. (152), J23 (2005).

[2] Greeley,J.,et al.,"Computational High-Throughput Screening of Electrocatalytic materials for Hydrogen Evolution", Nature Materials, 5,909-913(2006).

[3] Wilcoxon, J.P; Abrams, B.L., "Synthesis, Structure and Properties of Metal Nanoclusters" Chemical Society Reviews, 35,1162-1194(2006).

11:00am **SS2+NC-ThM10 Size-Dependent Structure of MoS_2 Nanoclusters**, ***J. Kibsgaard****, *J.V. Lauritsen*, University of Aarhus, Denmark, *S. Helveg, H. Topsoe, B.S. Clausen,* Haldor Topsoe A/S, Denmark, *F. Besenbacher*, University of Aarhus, Denmark

Within the area of nanomaterials it is well know that "small is different", which implies that nanostructures may have new functional properties.

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* Morton S. Traum Award Finalist

Properties like conductivity, color, reactivity, magnetism, and melting point may thus be entirely different for the nanomaterial compared to the same properties for materials with macroscopic dimensions. The dimension of a material is therefore an important parameter to consider in the development of new nanomaterials. Not least in catalysis where the active materials today is confined to a limited number of metals, tuning the size of the catalytic particles may help in the development of new and better catalysts. The MoS_2-based desulfurization catalyst constitutes one of the most important environmental catalysts as it removes sulfur from fossil fuels. Without this removal, the sulfur would cause massive acid rain problems such as forest decline. The recent focus on environmental problems and a stricter legislation concerning the sulfur content in fossil fuels have generated great interest in understanding and improving the desulfurization catalyst. We have used atom-resolved Scanning Tunneling Microscopy (STM) to follow the structural progression of triangular MoS_2 nanoclusters as a function of their size, and analyse how the equilibrium structures are altered when the cluster size is reduced. A comprehensive analysis of the size distribution reveals that certain “magic” clusters are favored. The analysis reveals that a rearrangement of the sulfur atoms terminating the cluster edges influences the stability and that the requirement to optimize the sulfur excess relative to molybdenum drives a striking reconstruction of the cluster edge.

11:20am **SS2+NC-ThM11 Size-Selected Deposition of Transition Metal Sulfides**, ***M.J. Patterson***, StonyBrook University, *M.G. White*, Brookhaven National Laboratory, StonyBrook University

Supported MoS_2 nanoparticles are known for their ability to catalyze a wide array of heterogenous reactions and work done in our laboratory is geared towards understanding the role of size, structure, composition and support interactions of the particles in these reactions. This problem has not yet been resolved due to the inhomogeneity of commercial catalysts. We therefore focus on preparing homogenous samples in ultra high vacuum that can serve as model systems for catalytic reactions such as hydrodesulfurization. A recently constructed cluster beam apparatus in our laboratory uses magnetron sputtering in order to make a variety of transition metal cluster compounds. We are currently investigating the size dependent and substrate dependent properties of these systems in particular $Mo_xS_y^+$ clusters (x=2-8, y= 6-12) on single crystal surfaces (i.e. Au(111), Al_2O_3/NiAl(110)). Characterization of the clusters are carried out using surface sensitive techniques such as Auger, photoemission spectroscopy, and thermal desorption. Preliminary work on the reactivity of these clusters with small sulfur containing molecules will also be discussed.

11:40am **SS2+NC-ThM12 Ligand-Spacer Controlled Size Selectivity of Gold Nanoclusters and the Effect of the Ligand on Cluster Geometry and Electronic Structure**, ***G. Shafai***, *S. Hong*, University of Central Florida, *M.F. Bertino*, Virginia Commonwealth University, *T.S. Rahman*, University of Central Florida

We have carried[1] out calculations based on the density functional theory in the projector augmented wave scheme (PAW) and the pseudopotential approach, to examine the effect of the size of the diphosphine ligand spacers on the stability of Au clusters containing 8 and 11 atoms, through evaluations of the cluster total energy and proper correction of spurious interactions between charged supercells. We find that Au11+3 is indeed preferred by ligand L3 rather than L5, while Au8+5 is preferred by L5 rather than L3, in agreement with experimental data.[2] The size selectivity induced by the ligand is found to be a purely electronic effect via coupling of the d-band of Au and p-band of the ligand. We have also examined the effect of the ligand on the geometric and electronic structure of Au clusters. For Au13, for example, we find bare cluster to form a flat flake, in agreement with previous theoretical calculations. On the other hand, Au13 cluster covered with ligands of phosphine (PH3) forms a stable spherical structure (icosahedron), in agreement with experimental findings,[2] which is 0.08 eV lower in energy as compared to the flat-flake complex. If the phosphine is replaced by H, the spherical structure is no longer stable, but it still maintains a 3 dimensional form, signifying the effect of the ligand in stabilization of the structure. We observe a narrow d-band for gold atoms in the flat-flake complex, while in the icosahedron structure the d-band is wider. We also find a stronger overlap between the p orbitals of the P atom with d orbitals of gold atoms in the icosahedron complex.

[1] Work supported in part by by NSF Grant CHE-0741423.

[2] M. Bertino et al. Jour. Phys. Chem. B Lett. 110, 21416 (2006).

Surface Science
Room: 207 - Session SS1+NC-ThA

Water-Surface Interactions
Moderator: M. Salmeron, Lawrence Berkeley National Laboratory

2:00pm **SS1+NC-ThA1 Structure and Kinetics of Nanoscale Amorphous and Crystalline Ice Films on Various Substrates, *B.D. Kay*,** *J.L. Daschbach, Z. Dohnálek, G.A. Kimmel, J. Matthiesen, N.G. Petrik, R.S. Smith, T. Zubkov*, Pacific Northwest National Laboratory **INVITED**

Molecular beam scattering, programmed desorption (both TPD and isothermal), and vibrational spectroscopy are used to study the chemical kinetics and reaction dynamics of molecular processes occurring both on the surface and within the bulk of amorphous and crystalline ice films. Molecular beams are used to synthesize chemically and structurally tailored thin films on various substrates including Pt(111), Pd(111), C(111) and FeO(111). These films can have morphologies ranging from dense and smooth, to highly porous depending on growth conditions. The precise control of the film structure allows physiochemical processes such as densification, crystallization, diffusion, isotope exchange, solvation, and dewetting to be studied in detail. The experimental methods, results, and their relevance to supercooled water, astrophysical icy bodies, wetting phenomena and nanoporous materials will be presented. Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

2:40pm **SS1+NC-ThA3 Iron Phthalocyanines on Au(111) and their Interaction with Water**, *C. Isvoranu, E. Ataman, K. Schulte,* Lund University, Sweden, *A. Rienzo, G. Magnano, J.N. O'Shea,* University of Nottingham, UK, *J.N. Andersen, **J. Schnadt***, Lund University, Sweden

Phthalocyanines are an extensively studied class of molecules due to their chemical and thermal stability and high polarizability. These characteristics make the phthalocyanines and related molecules interesting for a wide range of applications such as in molecular electronics, gas sensing devices, or as cathode and/or anode materials in fuel cells. Often, in such applications the molecules will be in contact with either liquid water as an important component of the application or with water from the ambient atmosphere. In spite of the ubiquity of the water – molecule interaction, investigations of the atomic-scale properties of the interaction of organic and organometallic molecules with water in general and of phthalocyanines with water in particular are scarce. Here, we have studied the adsorption of iron phthalocyanines on Au(111) by x-ray photoelectron and x-ray absorption spectroscopies at both sub- and full monolayer coverages and we have characterized the interaction of the different preparations with small amounts of water. For the water-free preparations, the results indicate that the full monolayer is dominated by a single molecular species, while several distinct species are observed for the submonolayer coverages. Tentatively, these different species are assigned to structures previously observed by scanning tunnelling microscopy (STM).[1] The present results show clearly that the interaction between the substrate and adsorbate differ strongly between the submonolayer and full monolayer structures, with the interaction appearing considerably stronger for the submonolayer structures. Iron phthalocyanine monolayers on Au(111) are inert to water with no change observed in the spectral characteristics of the molecular layer when exposed to water. Quite in contrast, the submonolayers exhibit strong modifications of the spectral appearances, which can be assigned to an interaction between the molecular adsorbates and water. Surprisingly, the observed chemical shifts point to a more subtle interaction of water with the iron phthalocyanines than a mere hydrogen bond formation between the water and the phthalocyanines.

[1] Z.H. Cheng, L. Gao, Z.T. Deng, N. Jiang, Q. Liu, D.X. Shi, S.X. Du, H.M. Guo, and H.-J. Gao, J. Phys. Chem. C 111 (2007) 9240.

3:00pm **SS1+NC-ThA4 Water Diffusion on Pt(111) Terrace, Kink and Steps: Density Functional Theory Study of Water Interaction and Diffusion**, ***L. Arnadottir**, E.M. Stuve,* University of Washington, *H. Jónsson*, University of Iceland

Density functional theory (DFT PW91) calculations were used to study diffusion of water molecule on a flat Pt(111) terrace as well as on kinks and step edges. Diffusion on the (111) terrace is predicted to become active on the time scale of seconds at 74 K in reasonable agreement with experimental results (Daschbach et al. J. Chem. Phys. 120 (2004) 1516). The binding of water at steps and kinks on Pt(111) surface is substantially stronger than at the flat terrace, by 0.16 eV and 0.25 eV, respectively. The diffusion barriers of a single water molecule moving along the flat terrace up to a kink site or moving along the step edge are all comparable, while the barrier of diffusion up to a step edge is significantly lower then all of the other barriers calculated. Consequently, the barrier for diffusion from the step edge down to the terrace is substantially larger than for diffusion along the flat terrace. At low coverage, clusters of water molecules would, therefore, be expected to align along the upper side of step edges. This is consistent with experimental STM images taken by Morgenstern et al. (Morgenstern et al. Phys. Rev. Lett. 77 (1996) 703).

3:20pm **SS1+NC-ThA5 Growth of Ice Multilayers Studied with STM**, ***K. Thürmer**, N.C. Bartelt*, Sandia National Laboratories

Much progress has been made in the past few years in determining the structure and morphology of ice films on Pt(111). In our work we use STM to explore how metal-water interactions determine the ice–film morphology by tracking the film evolution during growth and annealing. We find that ice films as many as 30 molecular layers thick can be imaged with STM when negative sample biases of <-6(±1)V and sub-picoamp tunneling currents are used. As reported before by others, we observe that water deposited onto Pt(111) below 120K forms amorphous films, whereas metastable cubic ice appears between 120 and 150K. At 140K the first layer of water wets the Pt(111) substrate. At a mean film thickness of ~1nm the film consists of individual regularly-shaped 2-3 nm high crystallites, embedded in a one bilayer high wetting layer. We analyze the annealing behavior of these crystallites and report[1] that their dewetting is limited by the nucleation of new molecular layers on their top facets. By measuring nucleation rates as a function of crystallite height we estimate the strength of the driving force for dewetting. Upon deposition of additional water the crystallites coalesce and eventually, at ~5-10 nm mean thickness, the film becomes continuous, with the exception of a few remaining pinholes. A common, but not well understood observation is that ice grows between 120 and 150K in its metastable cubic 1c variant rather than in its equilibrium hexagonal form ice 1h. We find evidence for ice 1c in thicker films and suggest that it is a consequence of the mismatch in the atomic Pt-step height and the ice-bilayer separation. We propose a mechanism of cubic-ice formation via growth spirals around screw dislocations.

[1] K. Thürmer and N. Bartelt, Phys. Rev. Lett. 100, 186101 (2008).

4:00pm **SS1+NC-ThA7 Ice Nanoclusters on Au(111): Formation of a Unique Double Bilayer**, ***D.J. Stacchiola**, J.B. Park, S. Ma, P. Liu, J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

The nucleation of water into ice on solid surfaces has far reaching consequences in physical and biological systems. We have used ice multilayers grown on gold surfaces to prepare oxide nanoparticles. Profound differences on the nanoparticle nucleation pattern were observed when a different oxidant, such as NO2 multilayers, was employed. To gain insight into the origin of this nucleation behavior we have studied the formation of ice nanoclusters on Au(111) combining STM, TPD and IRAS results with DFT calculations. The nucleation of single water molecules in the elbows of the herringbone reconstruction of Au(111) has been previously reported, as well as the study of the initial formation of small clusters, with 6 or more water molecules, on other hydrophobic surfaces such as Ag and Cu. However, not detail studies on the initial formation of water multilayers on Au(111) surfaces have been reported. In the case of a hydrophilic surface such as Pt(111), where a wetting bilayer is formed in the interface, it has been very recently shown that the growth of thicker layers leads to the formation of isolated ice islands on top of the interfacial bilayer, with 5 or more bilayers of water per island. We will show in this presentation that in the case of Au(111) no wetting interfacial bilayer is formed, due to the gold hydrophobic character and large lattice mismatch with ice Ih, and the initial growth of multilayers proceeds through the formation of isolated ice clusters with a unique double bilayer structure. An absence of dangling hydroxyl groups on the ice clusters points to participation of all hydrogens in hydrogen bonding within and between the two bilayers, and renders the surface of the double bilayer hydrophobic.

This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

4:20pm **SS1+NC-ThA8 Isotopic Effects in the Mixing Between Surface and Bulk Molecules at the Surface of Amorphous Solid Ice Studied by FTIR and DFT Calculations**, ***P. Uvdal**, J. Blomquist*, Lund University, Sweden

We have studied the exchange between surface and bulk molecules on amorphous solid ice using infrared vibrational spectroscopy. Intact molecules are grown in a layer by layer fashion, on Cu(100), allowing the formation of isotopically uniform layers at 84 K. A bulk layer consisting of

3-5 bilayers of ice of isotope A was exposed to 0.15 monolayers of isotope B. Three different water isotopes were used in this study, $H_2{}^{16}O$, $D_2{}^{16}O$ and $H_2{}^{18}O$. By studying the free O-H(D) stretch, present only at the ice surface, all isotopes could be spectroscopically identified. In particular, the decrease of isotope B could be monitored, along with the concomitant increase of isotope A, as a function of temperature. It is observed that mixing between surface and bulk water starts already at 100K. There are also a clear difference between the different isotopes. H/D exchange is observed and will be discussed. The vibrational data is interpreted with the aid of DFT cluster calculations.

4:40pm **SS1+NC-ThA9 The Adsorption of Water on Cu_2O and Al_2O_3Thin Films**, ***X. Deng***, *T. Herranz*, *C. Weis*, *H. Bluhm*, *M. Salmeron*, Lawrence Berkeley National Laboratory

The initial stages of water condensation, approximately 6 molecular layers, on two oxide surfaces, Cu2O and Al2O3, have been investigated using ambient pressure x-ray photoelectron spectroscopy at relative humidity values (RH) from 0 to > 90%. Water adsorbs first dissociatively on oxygen vacancies producing adsorbed hydroxyl groups in a stoichiometric reaction: Olattic + Vacancies + H2O = 2OH. The reaction is completed at ~ 1% RH and is followed by adsorption of molecular water. The thickness of the water film grows with increasing RH. The first monolayer is completed at ~ 15% RH on both oxides and is followed by a second layer at 35-40% RH. At 90% RH, about 6 layers of H2O film have been formed on Al2O3. The wetting process and the essential role of OH on oxide surfaces will also be discussed.

5:00pm **SS1+NC-ThA10 The Reactive Uptake of Water and CO_2 on MgO(100) Monitored by Ambient Pressure XPS**, ***J.T. Newberg***, *D.E. Starr*, Lawrence Berkeley National Lab., *S. Yamamoto*, *S. Kaya*, *H. Ogasawara*, Stanford Synchrotron Radiation Lab., *T. Kendelewicz*, Stanford University, *M. Salmeron*, Lawrence Berkeley National Lab., *G.E. Brown*, Stanford University, *A.R. Nilsson*, Stanford Synchrotron Radiation Lab., *H. Bluhm*, Lawrence Berkeley National Lab.

The MgO(100) substrate is one of the most widely studied surfaces for water adsorption.[1] However, fundamental questions about whether water adsorbs molecularly or dissociatively under ambient conditions remains unanswered. This has been due in part to the lack of an in situ, chemically specific, surface sensitive technique. CO_2 is an important greenhouse gas, and the carbonation of MgO in mineral deposits has been suggested as a potential medium for CO_2 sequestration.[2] Here we present results from the investigation of the interaction of water with MgO(100)/Ag(100) films using ambient pressure XPS (AP XPS). With AP XPS we can quantitatively probe the water film thickness along with the chemical speciation of the solid substrate, while in equilibrium with water vapor. We have characterized the uptake of water on MgO at water pressures from 10^{-9} to 1 Torr, up to a maximum of 25% relative humidity (RH). In addition, we monitored the interaction of CO_2 with the metal-oxide surface. At room temperature, both MgO hydroxylation and molecular water adsorption were observed at < 10^{-6} Torr. At ~0.1% RH about 0.3 ML of molecular water was observed (1 ML = 0.31 nm). However, at this RH the surface of MgO was completely passivated with an overlayer of hydroxide that has a thickness similar to that of brucite ($Mg(OH)_2$, 1 ML = 0.48nm). As the RH was increased to 25% RH, the Mg-hydroxide overlayer thickness remained at ~1 ML, while the molecular water film increased to ~1.5 ML. Preliminary results for CO_2 showed some dependency of RH on the reactivity towards the metal-oxide surface. The formation of a brucite-like overlayer is consistent with a favorable Gibbs free energy for the bulk reaction of liquid and gas phase water with MgO (-27 and -36 kJ/mol, respectively). A similar phenomenon was observed with AP XPS for water on hematite (Fe_2O_3).[3] These results indicate that even under the lowest ambient RH values in the environment, metal-oxides that have thermodynamically stable hydroxides are chemically transformed at the surface due to thin film water. Thus, the presence of thin film water can have implications for how mineral surfaces interact with organic, biological and inorganic species in the environment.

[1] M.A. Henderson 2002 Surf. Sci Rep. 46 1.

[2] T. Koljonen et al. 2004 Energy 29 1521.

[3] S. Yamamoto et al. publication in preparation.

5:20pm **SS1+NC-ThA11 Water-Stabilized Reconstructions on Polar Surfaces of Rocksalt Oxides**, ***J. Ciston***, *L.D. Marks*, Northwestern University

We have investigated the stabilizing effect of water on the $\sqrt{3}$x$\sqrt{3}$-R30^{o} and 2x2 reconstructions of the MgO(111) and NiO(111) surfaces using a combination of x-ray photoelecton spectroscopy (XPS) and transmission electron diffraction (TED). Combined experimental analysis has confirmed that the MgO(111)-$\sqrt{3}$x$\sqrt{3}$-R30^{o} is stable only in the presence of hydroxyl groups on the surface, which is contrary to previously published structures. Experimental refinements of the valence charge density at these surfaces will also be discussed. Our experimental studies have been coupled with full-potential, all-electron density functional theory calculations to estimate surface energies and perform structural relaxations. The NiO system is particularly difficult to calculate due to highly localized and correlated 3d electrons. This has necessitated the use of a hybrid exchange-correlation functional in which the generalized gradient approximation is augmented with a 25% mixing of Hartree-Fock exact exchange for the 3d shell. This methodology substantially improves the accuracy of DFT-calculated surface energies, sometimes by several eV.

Surface Science
Room: 208 - Session SS2-ThA

Novel Reactive Surfaces
Moderator: S. Chiang, University of California Davis

2:00pm **SS2-ThA1 The Photochemistry of Acetaldehyde on TiO_2(110)**, ***R.T. Zehr***, *M.A. Henderson*, Pacific Northwest National Laboratory

The ultraviolet (UV) photon induced decomposition of acetaldehyde adsorbed on the oxidized rutile TiO_2(110) surface was studied with photon stimulated desorption (PSD) and thermal programmed desorption (TPD). Saturation coverage of acetaldehyde adsorbed on a reduced TiO_2(110) surface with 15 % oxygen vacancies exhibited a molecular desorption peak at 235 K along with a higher temperature shoulder at > 260 K that accounts for 1/3rd of the monolayer. Butene desorbing at 530 K was observed as a minor decomposition channel accounting for 1-2% of the adsorbed acetaldehyde. Saturation coverage of acetaldehyde adsorbed on oxidized TiO_2 (110) desorbs molecularly at 240 K with a minor decomposition channel (7%) forming adsorbed acetate. Surface bound acetate decomposes to form gas phase ketene in a broad desorption peak centered at 700 K. Acetaldehyde adsorbed on oxidized TiO_2 (110) undergoes a facile thermal reaction (E_a = 8 kJ/mol) to form a photoactive acetaldehyde-oxygen complex. Acetaldehyde adsorbed on reduced TiO_2 (110) was photo-inactive. UV excitation of substrate charge carriers initiated photofragmentation of the acetaldehyde-oxygen complex resulting in the ejection of methyl radical into gas phase and conversion of the surface bound fragment to formate. The identity of methyl radical was confirmed using isotopically labeled acetaldehyde. The presence of surface bound formate was confirmed by desorption of formate thermal decomposition product, CO, at 550 K. Ejection of reactive organic radical species in TiO_2 photoxidation of organics can potentially lead to alternate reaction pathways occurring away from the catalyst surface.

2:20pm **SS2-ThA2 Cesium Promotion in Styrene Epoxidation on Silver Catalysts**, ***L. Zhou***, *R.J. Madix*, Harvard University

The promotion roles of cesium in styrene epoxidation on silver catalysts have been studied by means of temperature-program reaction spectroscopy (TPRS), X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). The TPRS data have shown that the addition of 0.1 ML cesium can inhibit the secondary oxidation of styrene on Ag(111), and more significantly, switch the partial oxidation pathway from the production of phenylacetaldehyde and phenylketene to the production of styrene oxide on Ag(110). The XPS studies have revealed the formation of selective oxametallacycle intermediate and the reduced transformation of this intermediate to a combustion intermediate in the reaction on 0.1 ML cesium-covered silver surface, comparing with the reaction on the clean silver surface. No significant change of the C 1s and O 1s binding energies for certain intermediates was observed, suggesting that cesium does not play obvious electronic effect on the bonding of the intermediates. The STM studies have disclosed an interesting (1x2) reconstruction of the Ag(110) surface induced by cesium and a (3x5) surface oxide structure on the cesium-reconstructed Ag(110) surface. This (3x5)-ordered surface oxide is superimposed on the highly corrugated Ag(111) micro-facets. Our studies provide the insight into the microscopic origins of the structural effects of cesium in styrene epoxidation on silver catalysts.

2:40pm **SS2-ThA3 Selectivity and Enantioselectivity on Metal Surfaces**, ***A.J. Gellman***, Carnegie Mellon University **INVITED**

One of the key contributions of surface science to the discipline of catalysis has been the understanding of selectivity in catalytic surface chemistry. The key feature of surface science methodologies that leads to this contribution is the ability to isolate and study elementary chemical reaction steps occurring on single crystal surfaces. These are two independently important attribute of the surface science method. The ability to isolate and then study the kinetics of elementary steps, decouples their kinetics from those of the overall mechanism of which they are part. The use of single crystal surfaces provides homogeneous environments in which the kinetics are not masked by the influence of surface structure. The impact of these aspects of surface chemistry will be illustrated by three examples: study of transition states to elementary catalytic reaction steps, the study of conformational effects in the desorption of large molecules from surfaces and the observations of enantioselectivity in reactions of chiral molecules with chiral surfaces.

3:20pm **SS2-ThA5 Tuning the Reactivity and Selectivity of Chiral Kink Sites on Surfaces through Alloying**, ***A.D. Jewell***, Tufts University, *J.W. Han*, Georgia Tech, *D.O. Bellisario, A.E. Baber, H.L. Tierney*, Tufts University, *D.S. Sholl*, Georgia Tech, *E.C.H. Sykes*, Tufts University

While chiral Cu surfaces have been shown to be enantioselective for certain dehalogenation reactions,[1,2] we seek to develop a surface with a much more general enantiospecific reactivity. To this end, Cu surfaces have been alloyed with a range of more reactive atoms. Simulations of the segregation of different metals to the step edges of Cu(322) has shown that Pd and Ag are promising candidates for segregation to the chiral kink sites of a Cu surface. Depositing reactive atoms selectively at the kink sites will allow us to increase the reactivity while preserving the chiral nature of the kink and thus tune the surface’s enantiospecificity. Low-temperature scanning tunneling microscopy has been used to follow the preferred adsorption site of Pd and Ag atoms deposited at step edges on a Cu{111} surface at a variety of temperatures. The Cu{111} is an ideal test bed for this study as it contains large terraces, step edges and equal numbers of R and S kink sites. Alloyed kink sites composed of both Cu and Ag or Pd atoms will have both structural and chemical asymmetry and thus one can expect their enantioselectivity to be enhanced.

[1] Rampulla, D. M.; Gellman, A. J., Surf. Sci. 2006, 600, 2823-2829.

[2] Rampulla, D. M.; Francis, A. J.; Knight, K. S.; Gellman, A. J., J. Phys. Chem. B 2006, 110, 10411-10420.

4:00pm **SS2-ThA7 STM Investigation of the Conversion of Ethylene to Carbon Clusters and Graphite on Pt(111)**, ***A.B. De La Ree***, University of California, Irvine, *V. Johánek*, University of Virginia, *J.C. Hemminger*, University of California, Irvine

New insight has been obtained on the conversion of ethylene to carbon clusters by thermal dehydrogenation on Pt(111). Previous experiments have shown that thermal dehydrogenation following saturation exposure of ethylene to Pt(111) results in the formation of well defined carbon clusters. This occurs through a process of aggregation during the dehydrogenation process in the temperature range from 400K to 700K. Previous experiments have shown that heating an ethylene covered Pt(111) surface to temperatures above 800K leads to the formation of large sheets of monolayer graphite (graphene). The aggregation to form carbon clusters leaves open Pt areas available for additional adsorption. It had not been previously determined whether the adsorption and dehydrogenation of additional ethylene would lead to the growth of the initial clusters or to the nucleation of more clusters of the same size. We have utilized UHV-Variable temperature scanning tunneling microscopy (VT-STM) to address this question. In our experiments, a saturation coverage of ethylene is adsorbed on the Pt(111) surface at room temperature forming a layer of the well known ethylidyne dehydrogenation intermediate. The surface was then heated to 700K leading to further dehydrogenation and formation of carbon clusters that are easily observed by VT-STM. Our STM images show that these carbon clusters are 15±2 Å in diameter and containing an average number of 34±9 carbon atoms per cluster. The surface was then exposed to additional ethylene at room temperature and again heated to 700K. This process was repeated in a number of cycles until the dehydrogenation activity of the Pt(111) surface was completely suppressed. Repeated dosing of ethylene onto the surface followed by annealing led to an increase in the number of carbon clusters without an increase in the size of previously produced clusters. The Pt(111) dehydrogenation activity was completely suppressed after 4 such cycles. The only growth in cluster size that was observed was due to agglomeration of clusters once the surface was covered with a high density of clusters. Continued cycles, such as were utilized in these experiments, leads to the formation of a graphite adlayer on the platinum (presumably via agglomeration of the clusters at high cluster density). This was observed at temperatures well below the onset of long range graphene formation in single ethylene dose experiments.

4:20pm **SS2-ThA8 Catalytic Activity and Morphology of Pt Clusters on the Graphite Surface**, ***T. Kondo***, *K. Watahiki, J.P. Oh, K. Izumi, Y. Iwasaki, D. Sekiba, H. Kudo, J. Nakamura*, University of Tsukuba, Japan

Catalytic activity and surface morphology of Pt vapor-deposited on highly oriented pyrolytic graphite (HOPG) have been investigated by hydrogen-deuterium exchange reaction, scanning tunneling microscopy (STM), temperature programmed desorption (TPD) of CO and in-situ measurement of helium atom scattering (HAS). Based on the STM observation, Pt particles deposited on HOPG with sub-monolayer coverage at room temperature are found to form mostly monolayer clusters on a graphite surface with the reduction in the nearest-neighbor atomic distance of the platinum atoms by as much as 13 % compared to that of the single crystal platinum. Turn over frequency of the hydrogen-deuterium exchange reaction at 24 Torr and 340 K is found to be one order magnitude higher for the monolayer Pt cluster than three-dimensional Pt cluster at 340 K, indicating the smaller adsorption energy of hydrogen on the Pt monolayer cluster. Based on the TPD experiment of CO from Pt/HOPG, the similar catalytic property is found for the monolayer Pt cluster: lower binding energy of CO with Pt compare to the case on the single crystal platinum. These specific catalytic activities are however found to be lost by the slight annealing of Pt/HOPG above 350 K. The change in the catalytic activity is attributed to the change in the morphology of the Pt cluster from monolayer to three-dimensional phase based on the HAS and STM measurements. The higher specific catalytic activity for the Pt monolayer cluster will be discussed in terms of the interface interaction between Pt atoms and the graphite surface.

4:40pm **SS2-ThA9 Surface Structures and Alloy Formation for Ge Deposition on Pt**, *B.E. Koel*, ***G. Liu***, Lehigh University

We have investigated surface structures formed by Ge deposition on Pt(111) and (100) single-crystal substrates by using STM, LEED, ALISS, and XPD. This combination of techniques provides an atomic level description of the surface structures necessary to understand the “site-directed” chemistry of these surfaces and can be used to distinguish formation of adlayers and surface alloys. We find large apparent differences between the behavior of Ge on Pt(100) compared to Pt(111) substrates. An ordered p(√19x√19)R23.4°-Ge/Pt(111) surface alloy was formed on Pt(111) by annealing at 900 K. This structure substitutionally incorporates 4%-ML Ge atoms into the Pt surface layer located very close to substitutional Pt atomic positions, without any corrugation or “buckling”. In contrast, and despite extensive bulk solubility of Ge in Pt, it was found that Ge remains on top of the Pt(100) surface as adatoms even after annealing to 1200 K. Furthermore, Pt adatoms produced by lifting of the Pt(100)-hex reconstruction in the vicinity of adsorbed Ge do not intermix with the Ge but rather segregate to form pure-Pt islands with Ge adsorbed on top. We interpret the c(2x2) Ge overlayer that is produced by 0.5 ML Ge deposition and annealing at 600 K as formation of a unique surface alloy or “layer compound”. The Pt(100) substrate thus is covered by a surface alloy film with the structure of a body-centered tetragonal Pt_2Ge layer compound. TPD shows that both CO and NO adsorb more weakly on the Pt-Ge bimetallic surfaces than on the clean Pt surfaces.

5:00pm **SS2-ThA10 Revisiting the Oxidation Kinetics of Plutonium Surfaces**, ***H.G. García Flores***, University of Nebraska-Lincoln and Los Alamos National Laboratory, *D.P. Moore, J.P. Baiardo, D.L. Pugmire*, Los Alamos National Laboratory

The oxidation of metal surfaces is an important application of kinetic modeling because it allows for the study of the influence of transport processes in a gas-solid reaction. Understanding the oxidation kinetics of plutonium is desired because this process can have an impact in the storage and handling of this radioactive element. The goal of this presentation is to investigate the early stages of the corrosion of plutonium in an attempt to elucidate the oxidation kinetics, in particular at the initial rapid stage of the oxidation. The data presented here will be evaluated with an inverse-logarithmic kinetic rate law, which has not previously been used to describe the oxidation kinetics of plutonium. The paralinear and parabolic models generally employed to describe oxide film growth of plutonium do not explain this rapid initial stage of oxide film growth of plutonium. To this aim, ellipsometry, x-ray photoelectron spectroscopy (XPS) & Auger electron spectroscopy (AES) data recently collected at Los Alamos and the ellipsometry data presented by Larson & Cash in the Journal of Physical Chemistry[1] will be used to perform a comparison of the kinetic models for oxygen corrosion of plutonium.

[1] D.T. Larson, D.L. Cash, J. Phys. Chem., 73 (1969) 2814.

5:20pm **SS2-ThA11 Kinetics of Hydride Front in Zircaloy 2 and H Release from a Fractional Hydrided Surface**, *M. Diaz*, Instituto de Ciencia de Materiales de Madrid, Spanish National Research Council, Spain, *B. Remartinez, S. Perez*, Iberdrola, S. A., Spain, ***J.L. Sacedon***, Instituto de Ciencia de Materiales de Madrid, Spanish National Research Council

In these Zirconium based materials, when the H_2 dissociation at a surface is enough efficient, a continuous and compact hydride layer is formed, increasing in thickness with time. Using a UHV equipment and method, specifically developed to compare the resistance to hydriding of tubular nuclear fuel claddings,[1] the propagation kinetics of the Hydride/metal interface through the cladding thickness is obtained. It results in a hydride thickness vs time dependence $th = K\ t^a$, where a is close to 1/2 and a rate dependence on the thickness $dth/dt = C\ th^b$ where b is close to -1. They are near to the expected values from an H ideal diffusion through the Hydride layer, and differ from the linear kinetics (a =1) and other fractional a exponents obtained from thermo-gravimetric methods. At difference, in our method the sample is directly heated in an UHV environment, which allows a fast control of the local temperature where the hydriding reaction takes place. At the same time, pure H_2flows inside the tube, starting the hydriding from the inner tube surface. The method allows determining the formation enthalpy of $ZrH_{1.5}$ (Zircaloy2) H=-117±8 kJ/mol at 295.5 K, giving the second determination of this value in the literature.[2] Being the Hydride composition determinate by X ray diffraction methods, mass spectrometry allows to follow the H_2 desorption produced by the surface reaction $H_s+H_s = H_2$[3] at the external surface of the tube, opposite to surface where the hydriding begins. A kinetic model and expression that explain the H_2 desorption curves is presented. In this model the H desorption rate, is proportional to a fractional surface Hydride coverage. This coverage increase in time by the excess of H precipitated from the H oversaturated metal. The Hydride/ metal interface acts as a very weak H source feeding the metal over saturation. The ratio between the of H flux precipitated at the external metal surface to that precipitated at the Hydride / metal interface is determinate to be $\leq 10^{-6}$.

[1] J. L. Sacedón, M. Díaz, J.S. Moya, B. Remartínez and J. Izquierdo, Journal of Nuclear Materials. 327 (2004) 11.

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Thursday Afternoon Poster Sessions

Surface Science
Room: Hall D - Session SS-ThP

Poster Session

SS-ThP1 Adsorption, Photo-Fragmentation, and Ion-Desorption Pathways of Organic Molecules at Semiconductor Surfaces using Synchrotron Radiation Techniques, ***T. Sekiguchi,*** Japan Atomic Energy Agency (JAEA), *H. Ikeura-Sekiguchi,* National Institute of Advanced Industrial Science and Technology (AIST), Japan, *Y. Baba*, Japan Atomic Energy Agency (JAEA)

The chemistry of organic molecules on semiconductor surfaces has attracted much attention due to the perspective of the molecular wires, self-assembled monomolecular layer (SAM), and semiconductor-organic hybrid formation such as SiC. We have investigated the adsorption interaction, photo-dissociation, and ion-desorption of multifunctional organic molecules such as acetone [(CH3)2C=O] adsorbed on Si substrates. We used synchrotron radiation techniques including polarization-angular dependences of near-edge x-ray absorption fine structure (NEXAFS) and photon-stimulated ion-desorption (PSID). We measured photon-energy dependences of ion yields for a variety of fragments in the carbon 1s excitation region, along with the NEXAFS. We compare results for the following three systems: (1) dissociatively adsorbed monolayered molecules prepared at a room temperature (RT), (2) molecularly adsorbed monolayered molecules prepared by heating condensed molecules very slowly from liquid-N2 low temperatures (LT) to RT, and (3) multilayered molecules prepared at LT. The results showed that mass-patterns and excitation spectra of PSID depend dramatically on the chemical states of adsorbed systems. We conclude that PSID and NEXAFS techniques are useful tools to investigate chemical states such as configuration, orientation, and charge-transfer interaction of adsorbed molecules at surfaces.

SS-ThP2 AFM Studies of poly-L-lysine Mediated Adsorption of Alginate to Hydrophilic and Hydrophobic Surfaces, ***C. Franqui***, *H. Applebaum, K.T. Queeney*, Smith College

The poly-L-lysine (PLL)-mediated adsorption of alginate to hydrophobic and hydrophilic substrates is a useful model system for understanding the initial stages of biofilm formation. Work in our lab using a variety of techniques has shown that film continuity and morphology are strongly influenced by the underlying substrate. The current work uses atomic force microscopy (AFM) to examine differences in film morphology as a function both of substrate surface chemistry and of adsorption conditions. On a hydrophobic, electrically neutral alkylsilane monolayer, PLL films adsorbed from pH 11 buffer and air dried exhibit morphologies that are suggestive of polymer shrinking as water is removed from the film, with networks of PLL surrounding regularly-spaced patches of bare surface. The proportion of surface covered by PLL decreases with increasing PLL molecular weight, which suggests stronger PLL-surface interactions for the lower MW polymers. Since adsorption under these conditions is thought to be driven by a transition from alpha helix in solution to random coil for adsorbed PLL, these results may indicated a lesser amount of uncoiling for the larger MW PLL. The role of drying in determining film morphologies is explored by comparing subsequently-adsorbed alginate films on both pre-dried and undried PLL overlayers. On hydrophilic silica PLL adsorbed at neutral pH forms much more uniform films, consistent with strong electrostatic interactions between the positively charged PLL and the negatively charged surface. As ionic strength increases, PLL begins to aggregate on the surface to form a much more discontinuous film, consistent with competition for binding sites between PLL and cations in solution. Alginate adsorption to these PLL overlayers results in more complex morphologies indicative more of isolated molecular adsorption than of true film formation.

SS-ThP3 Experimental Aspects of Measuring Dissociative Sticking Coefficients of Hydrocarbons on Solid Surfaces with Independently Variable Gas and Surface Temperatures, ***V. Johánek***, *L. Valadez, G.W. Cushing, I. Harrison*, University of Virginia

The thermal activation of alkanes on transition metals can be studied by a technique of effusive dosing of gases onto the metal surfaces where both gas and surface temperatures are independently variable. Dissociative sticking coefficients, $S(T_g, T_s)$, are measured by monitoring the deposited amount of surface carbon. This relatively simple method allows measurement of dissociative reaction rates of alkanes or other hydrocarbons with about 9 orders of magnitude dynamic range, however, a careful implementation is required to assure good accuracy and relevance. In particular, effects not related to the direct well-defined gas beam or to the surface under study have to be either eliminated or separated which brings several experimental challenges. Ultimately, such $S(T_g, T_s)$ experiments can be used to define reaction rates and transition states for activated dissociative chemisorption reactions that are otherwise difficult to study under ultrahigh vacuum, surface science conditions.

SS-ThP4 Low Energy Electron Microscopy Study of Adsorbed C on Pt(111), ***G.W. Cushing***, *V. Johánek, I. Harrison*, University of Virginia

Methane reforming rates on supported transition metal nanocatalysts at temperatures near 1000 K are apparently limited, in part, by the build-up and dynamics of adsorbed C.[1] We report on the use of a SPECS low energy electron microscope (LEEM) to examine the dynamics and reactivity of adsorbed C on Pt(111) at reforming temperatures. The adsorbed C coverage can be controlled by dosing hydrocarbons and/or oxygen at pressures as high as ~5 x 10^{-8} Torr whilst imaging with LEEM.

[1] H. L. Abbott and I. Harrison, "Methane dissociative chemisorption on Ru(0001) and comparison to metal nanocatalysts", J. Catal. 254, 27-38 (2008).

SS-ThP5 Interaction of Water with BaF_2(111) at Ambient Conditions, ***S. Kaya***, *S. Yamamoto,* Stanford Synchrotron Radiation Laboratory, *J.T. Newberg, H. Bluhm,* Lawrence Berkeley National Laboratory, *A.R. Nilsson*, Stanford Synchrotron Radiation Laboratory

Aggregation of water and ice nucleation on ionic surfaces have been a topic of interest for many years due to their importance in atmospheric and environmental chemistry. However, the fundamental questions such as the structure and chemical composition of thin film water on surfaces in equilibrium with ambient pressure water vapor are still largely unanswered. BaF_2(111) is one of the promising model substrates at which two dimensional hexagonal ice growth can be expected due to their matching lattice parameters. By using ambient pressure photoemission spectroscopy (APPES) and O K-edge near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, we have studied the interaction of water with the BaF_2(111) surface at water partial pressures up to 1.5 Torr. Water uptake curves indicate that monolayer coverage is achieved at relative humidities lower than 10 %. O K-edge NEXAFS findings reveal that the structure of submonolayer water on the BaF_2(111) surface is similar to the topmost surface of hexagonal ice which is lacking two dimensional long range order. Additional water layers obtained at higher relative humidities have slightly different hydrogen bonding structures. In addition, lateral hydrogen bonding network becomes more apparent with increasing water coverage.

SS-ThP6 LER Reduction by Means of a Grazing Incidence Ion Beam, ***C. Struck***, *D.N. Ruzic,* University of Illinois, *R.L. Bristol*, Intel Corp.

As lithographic feature sizes continue to increase, the phenomena of line edge roughness (LER) becomes more pronounced. While many efforts are underway to decrease LER from the photoresist, post-develop smoothing techniques may be required to achieve acceptable results. We report on one such technique employing the use of an ion beam at grazing incidence unidirectional with the features. One key potential advantage of this approach over many other smoothing techniques is the ability to smooth LER at relatively long spatial length scales over large sections of, or whole wafers. LER reduction numbers are reported at both short and long spatial wavelengths using Ne, He, and Ar beams. The angle of incidence is varied, as well as ion energy, and process time. LER measurements are taken from top-down analytical SEM measurements and Hitachi image analysis software. Line profile data are taken with the SEM in cross-section mode. Tests have achieved a reduction in LER from 9.8±0.67nm to 5.5±0.86nm for 45nm CDs using an Ar beam at 500eV for 6s at an 85° angle of incidence. A reduction from 10.1±1.07 nm to 6±1.02 nm was shown using an Ar beam at 1000eV for 4s at a 60° angle of incidence.

SS-ThP7 Modification of PMMA Thin Films with Atomic Oxygen and Ultra-violet Light, ***H. Yuan***, *D.R. Killelea, S. Tepavcevic, S.J. Sibener*, University of Chicago

The degradation and modification of polymeric surfaces by irradiation, oxygen plasmas and other reactive species have dramatic effect on their physical and chemical behavior. A molecular-level understanding of reactions at the polymer surface is necessary to guide further development of polymers in a wide range of fields, from microelectronics to aerospace. Here, we present the results of a study of photodegradation and oxidation of a model polymeric film. We exposed a poly(methyl methacrylate) (PMMA) film to vacuum ultraviolet (VUV) radiation and a collimated supersonic beam of $O(^3P)$ oxygen atoms. In separate experiments, we directly measured the mass loss of the film with a quartz-crystal microbalance (QCM) and identify the chemical changes in the PMMA film using in situ infrared spectroscopy. Previous work was limited by the necessity of removing the sample from vacuum for IR analysis; our new in situ IR system lifts this limitation and permits much greater time-resolution in our studies of the polymer modification process. Our analysis has determined the kinetics of the reactions of PMMA with VUV and atomic oxygen, and we have investigated how exposing PMMA films to both atomic oxygen and VUV light alters the polymer properties. We have also found that exposure of the polymer to these two reagents simultaneously results in kinetics that differ from the two individual effects.

SS-ThP8 State-Resolved Measurements of CH_4 Activation on Ni(111) Without Laser Excitation

N. Chen, Tufts University*, R.R. Smith,* Independent Consultant*, D.R. Killelea,* University of Chicago*, V.L. Campbell, D.F. Del Sesto, A.L. Utz*, Tufts University

We describe experimental work that yields vibrational-state-resolved reaction probabilities for a polyatomic molecule without the need for selective laser excitation of the target state. The method relies on a detailed knowledge of the vibrational structure of the molecule under study, its vibrational cooling dynamics in a supersonic expansion, and an understanding of how individual vibrational states contribute to the state-averaged reactivity measured in the experiment. The reagents in beam-surface scattering measurements of surface reactivity typically have a well-defined translational energy and a narrow distribution of rotational states, but the vibrational state distribution of the reagents remains nearly thermalized at the nozzle source temperature. As nozzle temperatures are raised to access higher incident kinetic energies, the thermal population of excited vibrational states grows. The high vibrational state density of polyatomic molecules can result in hundreds, or even thousands of vibrational states contributing to the measured reactivity. In addition to yielding reaction probabilities averaged over many internal states, the state or group of states that dominate reactivity may vary as a function of incident kinetic energy, even at a fixed nozzle source temperature. Recent results from state-resolved measurements of methane activation on Ni(111) allow us to model vibrational-state-averaged beam-surface data to gain insight into how reactivity scales with increasing vibrational excitation. We use this approach to extract a state-resolved reaction probability for the v=0 vibrational ground state of methane dissociating on a Ni(111) surface. At intermediate nozzle temperatures, only the v=0, ν_2, and ν_4 vibrations have sufficient population to impact reactivity. Non-equilibrium vibrational cooling in the expansion relaxes ν_2 to ν_4. Knowledge of S_0 for the v=0 state allows us to extract S_0 for the ν_4 vibrational fundamental of the "umbrella" bending vibration.

SS-ThP9 Interfacial Dynamics of Amorphous and Crystalline Thin Polymer Films

J.S. Becker, University of Chicago*, M.A. Freedman,* University of Colorado, Boulder*, S.J. Sibener*, University of Chicago

The surfaces of thin polymer films are a complex and dynamic macromolecular interface that have attracted significant attention. Presently, there is poor understanding regarding the modification of dynamics and crystallization at the free polymer surface by dimensional confinement of the polymer into a supported thin film. Helium atom scattering is a uniquely surface sensitive and non-destructive probe of vibrational motion and structure at complex interfaces. Elastic helium scattering reveals surface stiffening of amorphous poly(methyl methacrylate) (PMMA) in molecularly thin films as a function of diminishing film thickness. Furthermore, collisional energy transfer characteristics measured from amorphous PMMA, polystyrene, and polybutadiene films show remarkably similar lineshapes and temperature induced intensity decays, owing largely to the common methylene groups presented at the surface. Additionally, helium scattering provides exquisite sensitivity to surface order and crystallinity. Surface crystallization is presently being measured in thin films comprised of poly(ethylene terephthalate) and compared with related data obtained from glancing-angle Fourier-Transform Infrared Spectroscopy measurements acquired in an ultra high vacuum environment.

SS-ThP10 Interaction of Water with Pure and Mixed Monolayers of Hydrophobic and Hydrophilic Terminated Alkanethiols on Au(111),

N.M. Barrentine*, R.L. Grimm, J.C. Hemminger*, University of California, Irvine

The interaction of water adsorbed on self-assembled monolayers (SAMs) with moieties that are either hydrophobic, hydrophilic, or mixtures of both were characterized by temperature programmed desorption (TPD). The SAMs were fabricated on Au(111) from dilute ethanolic solutions of alkanethiols terminated with either a methyl group (hydrophobic) or a polar group (hydrophilic). The goal of our experiments is to understand the interaction of water with localized regions of hydrophilic character on an organic surface as a function of the spatial extent of the hydrophilic region (in the 10's of nanometer size regime). TPD experiments of water desorption from pure hydrophobic surfaces show first order desorption kinetics at low coverage with an activation of energy of ~34 kJ mol^{-1}. The peak temperatures seen in the pure hydrophilic TPD spectra are 10-60 K higher than that of the pure hydrophobic case, indicative of a stronger interaction with water. Surfaces functionalized with a mixture of the hydrophobic and hydrophilic terminated alkanethiols display different properties from either of the pure cases and are not well described by simple weighted addition of the two limiting cases. The aim of this work is to develop a well characterized model system that mimics the surfaces of organic-coated aerosols found in the troposphere. These aerosol surfaces are typically hydrophobic when the aerosol is first formed and are thought to become more hydrophilic as the aerosol undergoes varying degrees of oxidation due to reactions with atmospheric oxidizing species such as O_3 and OH radicals. We will discuss how our results can be useful in understanding water interactions with atmospheric aerosols.

SS-ThP11 Optimization of Hardness of Ultra Water Repellent Silica-Based Film by Tuning Surface Structure and Film Matrix,

H. Sakurai*, N. Saito, O. Takai*, Nagoya University, Japan

Ultra-water repellent film (UWR) has a water contact angle of more than 150°. The UWR property is governed by the hydrophobic groups and the geometrical structure of the surface. We have successfully fabricated UWR film by microwave plasma enhanced CVD (MPECVD) with trimethylmethoxysilane (TMMOS) as a raw material. However, the UWR film showed a poor mechanical property, because the film was composed of not a continuous film but aggregation of clusters. In order to improve the mechanical property of the UWR film, it is crucial to control the ratio of continuous film and aggregation of clusters in the film. The ratio is strongly related to the surface geometry accentuating the wettability. The large roughness makes the water repellency increase while the hardness of the structure decreases. In this study, we aimed to obtain UWR film with high hardness by tuning the surface structures and film matrix. The UWR film was deposited by MPECVD. A microwave generator (2.45GHz) was used at 250 W. Si wafer was used as substrate. TMMOS was used as a raw material, and Ar was introduced as excitation gas. The partial pressures of TMMOS and Ar were kept constant at 70Pa and 30Pa. And also, the distance between plasma and substrate was constant. The deposition time was changed 3 minutes to 30 minutes to change the surface roughness. Water contact angles on the resulting films were evaluated with a contact angle meter. Hardness of the films was measured by a nanoindentater as Vickers hardness. Surface structures of UWR films were observed by atomic force microscope (AFM). The surface roughness was evaluated by root mean square (RMS). The UWR films with smaller roughness were obtained. Even in the case, the relationship between water repellency and hardness depended on roughness. Smaller roughness would indicate the increase of continuous films. However, the Vickers hardness was not improved drastically. The film matrix was changed by the increase of oxygen and the addition of nitride and so on. The changes of film matrix have a great effect on the improvement of hardness.

SS-ThP12 Synchrotron Radiation-Induced Reactions of Astrochemical Interest*,

M.J. Abu Haija*, R.A. Rosenberg,* Argonne National Laboratory*, P.J. Ryan*, Ames Laboratory

In molecular cloud regions of the interstellar medium (ISM), astronomical observations have revealed a rich chemistry with the detection of over 130 different chemical species ranging from simple diatomic molecules to complex organic molecules such as polycyclic aromatic hydrocarbons (PAHs). These molecules may have been involved in the prebiotic chemistry that led to life's origin. Our approach for simulating such chemistry is to in-situ monitor the x-ray induced chemical reactions of model compounds adsorbed on well-characterized substrates. We are currently pursuing two areas of research in this field. The first one is to understand the source of chirality in prebiotic molecules, which is a subject of great interest to a wide group of researchers. We have recently demonstrated that low-energy spin-polarized secondary electrons, produced by irradiation of a magnetized permalloy substrate can induce chiral selective chemistry of adsorbed (R)- or (S)-2-butanol on permalloy.[1] Using x-ray photoelectron spectroscopy (XPS) to monitor the intensity of the C-O peak, the results showed an enhancement of ~10% in the rate of C-O bond cleavage that depends on the chirality of the molecule and the spin polarization of the substrate secondary electrons. In addition to the C1s XPS measurements used to determine the rate constants, O1s XPS and O1s near edge x-ray absorption fine structure (NEXAFS) as well as x-ray magnetic circular dichrosim (XMCD) measurements were performed. The second area of research is the investigation of x-ray induced chemical reactions of PAHs which are flat molecules based on rings of six carbon atoms. PAHs are of particular interest because they are often used as biomarkers that indicate life. A large variety of these molecules has been detected in meteorites after being delivered to Earth. We will present some preliminary results on the x-ray induced reactions of coronene ($C_{24}H_{12}$). The focus of this work will be to understand the kinetics and mechanisms of this system, as well as other PAHs. Experiments were performed under UHV conditions utilizing both XPS and x-ray excited optical luminescence (XEOL) to monitor the reactions.

*This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357.

[1] R.A. Rosenberg, M. Abu Haija and P.J. Ryan, to be published.

SS-ThP13 CCD for Ion Detection, *O. Hadjar*, ***G. Kibelka***, O.I. Analytical CMS Field Products

Photon imaging based on charged coupled devices (CCD) is a mature technology. Such detectors are used, for instance, in astrophysics instruments as well as in every day consumer products. As a consequence, the CCD underlying functionality is well understood and devices can easily be mass-produced. The common CCD is a fine-pitched, two-dimensional array detector, which can be operated in a vacuum as well as under high pressure. Replacement of the photosensitive layer of the CCD with a metal-oxide semiconductor (MOS) has proven to be a very successful and promising technique for ion imaging. Various instruments based on charge detection can benefit from such a device, particularly mass spectrometers (MS). Fusing the CCD with a miniaturized Matauch-Herzog type MS[1] results in a compact sector-field mass spectrometer with sufficient mass resolution and unmatched duty cycle. Using an electron-impact ion source, formed ions are m/z separated and detected by our CCD located at the focal plane of our instrument. The CCD response can be studied as a function of ion energies and incidence angles. Quantum efficiencies of singly and doubly charged rare gas ions are being investigated and results are compared with electron-impact ionization cross section found in literature.[2] These fundamental studies will increase the accuracy of quantifying abundances of ionic species and can be the base for future improvements.

[1] M. P. Sinha, M. Wadsworth. Rev. Sci. Ins. 76, 025103 (2005).

[2] A. Kobayashi, G. Fujiki, A. Okaji, T. Masuoko. J. Phys. B: At. Mol. Phys. 35 2087 (2002).

SS-ThP14 Atomistic Approaches to Fischer-Tropsch Model Catalysts, ***B. Wang***, *A. Purdie*, *M. Caffio*, *R. Schaub*, University of St Andrews, UK

Fischer-Tropsch synthesis, discovered in the 1920s, is one of the most researched topics within heterogeneous catalysis. Fe and Rh are two widely studied Fischer-Tropsch catalysts. The former strongly dissociates CO and catalyzes the preferential formation of methane and higher hydrocarbons, while the latter exhibits a unique catalytic activity on syngas reactions to form carbon-two oxygenates.[1] It has been demonstrated that additive Fe species to silica-supported Rh catalysts exert a significant promotion in CO hydrogenation by enhancing the yields and unexpectedly increasing the selectivities toward oxygen-containing products such as alcohols[2] In this work, we investigated the FeRh catalyst system within a surface science approach, aiming to get atomic level information on the structure, composition and chemical state of different bimetallic catalysts, and hence an understanding of the Fe promotional role. The nucleation and growth of Fe deposited at room temperature on single-crystalline Rh(111) surfaces (flat and stepped) was investigated as function of Fe coverage. Upon annealing at high temperatures (>600K), STM data confirm the formation of a near surface alloy. By a thorough and systematic comparison of STM images following CO exposure on Rh(111) and on Fe/Rh(111), we investigated the promotional role played by Fe (site specific versus local electronic structure alteration). In an attempt to address more realistic systems, we also performed STM measurements on Rh and Fe physically vapour deposited onto SiO_2 thin films. The morphology of the resulting nano-particles, their dispersion and sintering, were studied as function of the Fe:Rh molar ratio. We observed that the addition of Fe dramatically enhances the dispersion of the active Rh loading, concomitant with a significant decrease in average particles size. The implications of our findings are discussed in light of the selective catalysis reported for FeRh systems.

[1] M. Ichikawa, Polyhedron, 7 (1988) 2351.

[2] M. M. Bhasin, et al., Journal of Catalysis, 54 (1978) 120.

SS-ThP15 Wettability of Self-Assembled Monolayer Surfaces of Alkane Thiols on Au, ***N. Yoshida***, *T. Watanabe*, The University of Tokyo, Japan

Wettability of solid surface has attracted much attention in many fields, from basic surface science to practical uses. Up to now, numerous studies have sought to interpret the static hydrophobicity (contact angle of a droplet and surface energy/surface tention of soild surface) in terms of the interaction between liquid and solid surface. The static hydrophobicity has been well-clarified (controlled by surface energy and morphology), however, the dynamic hydrophobicity (sliding angle and velocity of a droplet), a measure of dynamic adhesive property against water, is still in controversy. Practically, dynamic hydrophobicity does not simply depend on static hydrophobicity. Thus far, no one could completely explain a fact that hydrophobic surfaces of similar water contact angles often show quite different adhesive property against water. In this study, we successfully prepared various hydrophobic surfaces on Au using alkane and fluoroalkane thiols with various adhesive properties against water in terms of solid-liquid interface engineering. We will demonstrate that the dynamic hydrophobicity, a measure of the adhesive property against water, depended on the surface morphology (even of the order of a few nanometers) and surface composition (small amount of polar groups on the surface) and that we could control it independent of static hydrophobicity.

SS-ThP16 Surface Characterization of Hydrophobic Thin Films Deposited by Various Plasma Polymerization Methods, ***Y.S. Kim***, *K.-J. Kim*, Korea University, *Y.H. Lee*, Korea Institute of Science and Technology

Plasma polymerization is a thin film deposition process and may be uniformly coated onto any substrate. Plasma polymers generally have different properties from those of conventional polymers due to their unique properties. Plasma polymer films have been used in a variety of applications including barrier coating, protective coating, anti-scratching coating, and dielectric layer in microelectronics. In this study, plasma-polymerized films fabricated by three different type plasma such as inductively coupled plasma (ICP), capacitively coupled plasma (CCP), and pulsed-plasma (PP). Different kinds of hydrocarbon gases and fluorine-containing gases were mixed to investigate their effect on the films. Also, process parameters for plasma polymerization such as gas ratio, gas pressure, plasma power, pulse width, and processing time were investigated. The physical properties of plasma-polymerized thin films made by three different methods were characterized using water contact angle measurement and mechanical test. The adhesion strength between plasma-polymerized thin film and substrate was measured by 90° peel test, and the mechanical properties of plasma-polymerized thin film surface were investigated by indentation. Surface analytical instruments such as Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), near-edge x-ray absorption fine structure (NEXAFS), and time-of-flight secondary ion mass spectrometry (TOF-SIMS) were also used to provide useful information about the chemical properties such as surface composition and functional groups.

SS-ThP18 Fabrication and Characterization of Well-Ordered Model Nanocatalysts using Anodic Aluminum Oxide (AAO) Template, ***Y.C. Chu***, *C.M. Kim*, Kyungpook National University, South Korea

Heterogeneous catalysts are usually composed of 1 ~ 20 nm metal clusters. It is generally observed that the catalytic activity is greatly affected by the size of metal clusters. It is crucial to control the size of metal clusters in the fundamental studies of catalytic reactions. We fabricated ordered arrays of nonostructures for the study of size-selective model catalysts using porous anodized aluminum oxide (AAO) templates. The AAO templates whose pore sizes were 5 ~ 50 nm were prepared. A silver electrode was sputter-deposited on one side of the templates and Ni, Au and Pt were electrodeposited to produce nanocatalysts with a uniform size. The model catalyst surfaces were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectoron spectroscopy and temperature-programmed desorption (TPD). Catalytic reaction of CO oxidation and propene epoxidation on these model catalyst surfaces will be presented.

SS-ThP19 Synthesis of Nanostructured CoSb2O6 by a Co-Precipitation Method and its Potential Application as a Gas Sensor Material, *C.R. Michel*, *A.H. Martinez-Preciado*, ***H. Guillen-Bonilla***, *J. Rivera-Domíngez*, Universidad de Guadalajara, Mexico

Nanostructured powders of CoSb2O6 possessing the trirutile-type structure, were synthesized by a co-precipitation method, using antimony chloride and cobalt nitrate. During this process a precipitate was obtained when the reagents were mixed in ethanol, which was stirred for 24 h. Microwave radiation at low power was applied for the evaporation which produced a solid precursor. The thermal decomposition of the precursor, from room temperature to 700ºC in air, was made in order to investigate the crystal structure evolution while increasing the calcination temperature. To perform this characterization X-ray powder diffraction was used, resulting that the tetragonal CoSb2O6, with cell parameters a = 4.6544 Å and c = 9.2823 Å, and space group P42/nmn, can be obtain from 600ºC. The observation of the calcined materials by SEM shows that the main microstructure produced corresponds to a filamentary shape, with a length between 100 to 600 nm. The observation by TEM of these filaments revealed that are composed by an arrangement of nanoparticles with an average size of 20 nm. To test CoSb2O6 as a gas sensor material, the powder calcined at 700 ºC was deposited on alumina substrates using the screen-printing method. DC electrical characterization was performed in air, O2 and CO2, from room temperature to 600oC. The dynamic response of resistance was studied by supplying alternatively the gases while recording the electrical resistance; which increased in approximately 1000 ohms when detecting CO2, whereas for O2 the change was in the order of 100 ohms.

SS-ThP20 Ion Implantation and Microstructure - How Each Affects the Other in Tool Steel, ***L.A. Autry****, D.G. Goberman, H.M. Marcus, R.R. Ramprisad*, The University of Connecticut

Ion implantation has been a useful technique for advanced materials processing for many decades. The range of materials that have been ion beam modified covers most classes of materials and many of these classes in great detail. However, with advances in analytical techniques and new manufacturing techniques and objectives, interesting and new observations of ion beam affects are often just waiting to be found. This research has focused on the affect of various ion implanted species on the chemistry and microstructure of tool steel. The inherently heterogeneous microstructure of tool steels affects both the implantation depth and concentration of implanted ions within the steel. This leads to a near surface region where the ultimate affect of ion implantation is, itself, affected by the local microstructure. Small spot surface spectroscopic analysis will be presented which highlights the magnitude of the phenomenon and the implications of this will be discussed. In addition to the affect of heterogeneous microstructures on ion implanted tool steel, the intertwined affect of surface preparation will be discussed. Often surface oxides are removed prior to ion implantation either as a by-product of normal materials preparation or intentionally in order to simplify characterization. However, oxides can be quite adherent and are found on many tool steels in use today. An analysis of ion implanted oxidized steel will be presented and tied into the discussion of how local microstructure can affect ion implantation profiles within tool steel.

SS-ThP21 Temperature-Dependent Surface Structure and Fermi Level of InGaAs, *J. Shen,* ***W. Melitz****, A.C. Kummel*, University of California, San Diego

The Si based MOS field effect transistors (MOSFETs) technology is rapidly approaching its theoretical physical limits. III-V compound semiconductors are known as a potential additional technology platform to silicon. The key to fabricating a practical III-V MOSFET is forming an unpinned oxide-semiconductor interface with low fixed charge. The correlation between the atomic bonding structure and the electronic structure at oxide-semiconductor interfaces is critical to understanding how atomic scale changes in electronic structure can cause localization of electrons or holes at these interfaces. We have used atomically resolved scanning tunneling microscopy (STM) images and scanning tunneling spectra (STS) to determine the atomic and electronic structure of clean InGaAs surface structure and gate-oxide/InGaAs semiconductor interface. Using a low temperature preparation we can get an InGaAs(001)-(2×4) surface reconstruction that is mostly β2(2×4) with some α2(2×4) regions. However these surfaces are very oxygen sensitive and reconstruction is not pure. Then increasing preparation temperature, we can get mixed surface reconstruction structure of InGaAs(001)-(2×4) and (4×2). For even high temperature, we can get pure InGaAs(001)-(4×2) surface reconstruction. Then oxides are deposited on InGaAs surface and STS measurements are being performed to determine the electronic properties of the interface and whether Fermi level is pinning or unpinning.

SS-ThP22 XPS and Ellipsometry Analysis of Process Variations for Direct Current Plasma Enhanced Chemical Vapor Deposition of Trimethylsilane, ***P.R. Scott****, D.M. Wieliczka*, University of Missouri-Kansas City

Thin films were deposited onto Aluminum and Silicon substrates utilizing DC PECVD of Trimethylsilane. The process parameters of gas pressure, discharge voltage, discharge current and deposition time were varied. The films were analyzed using X-ray photoelectron spectroscopy in conjunction with argon ion etching to determine the chemical properties as a function of film thickness and to examine the film-substrate interaction. Spectroscopic ellipsometry was used to obtain the optical properties and film thickness. Results from the comparison and correlation of these film properties to the process parameters will be presented.

SS-ThP23 Cycloaddition and Cyclocondensation Processes on Silicon: Nitrosobenzene on Si(100)-2x1 and Nitrobenzene on Hydrogen-Terminated Si(100), ***K.A. Perrine****, T.R. Leftwich, C.R. Weiland, R.L. Opila, A.V. Teplyakov*, University of Delaware

Reactions of nitrogen-containing bifunctional molecules with silicon substrates can play an important role in such areas of science and engineering as molecular electronics, surface passivation, and building organic/inorganic interfaces. These nitrogen-containing bifunctional molecules can be attached to the silicon surface via the nitro or nitroso group. The other end of the bifunctional molecule, a phenyl ring, remains intact after the reaction allowing for the model studies of electron transfer processes or for further surface modification. Nitrosoadducts are obtained from two different bifunctional molecules and two different surfaces. Nitrosobenzene reacts initially through a [2+2] cycloaddition on a clean Si(100)-2x1 surface through the N=O group leaving the phenyl ring intact. The oxygen migrates subsurface leaving the phenylnitrene adduct the dominant product from the reaction leaving the minor presence of the nitrosoadduct on the surface. However, nitrosoadducts are the dominant products from the condensation reaction of nitrobenzene with hydrogen-terminated Si(100). All these products and their distribution on surfaces are verified using X-ray photoelectron spectroscopy (XPS), infrared spectroscopic measurements (FTIR), and density functional theory (DFT) calculations. Analysis of the surface reaction pathways and spectroscopic investigations draw parallels between the nitrobenzene reaction on clean Si(100)-2x1 and hydrogen-terminated Si(100) and nitrosobenzene on clean Si(100)-2x1.

SS-ThP24 Formation and Collapse of Au/n-Si Schottky-Barrier Contact at the SiO_2/Si Interface and Oxidation Kinetics in Au-Contaminated and Thermally Oxidized n-Si (001) Surfaces, ***S. Shimizu****, S. Shimada, N. Nagase, M. Muta, I. Ikeda*, Nihon University, Japan

We have investigated an anomalous profile of Au in SiO_2/Si region as a function of oxidation temperature and then clarified an oxidation mechanism utilizing ellipsometer, X-ray photoelectron spectroscopy (XPS) and alternating current surface photovoltage (AC SPV) methods. When n-type Si wafers having hydrophobic surface were rinsed in Au aqueous solution (the Au surface concentration = ~2 1015 atoms/cm2) and then thermally oxidized at between 550 and 750C, an Au cluster still resided both at the SiO_2/Si interface and the top area of SiO_2 film. Most of the Au at SiO_2/Si was identified to be detected as the Au cluster which did not make bonds with other elements such as O, H and Si. The Au at the SiO_2/Si interface formed Au/n-Si Schottky-barrier, causing depleted and/or inverted layer at the Si surface, thereby, giving rise to an occurrence of a frequency-dependent AC SPV. As the oxidation temperature and time increased, the frequency-dependent AC SPV decreased and disappeared, corresponding to the fact that the Au cluster at SiO_2/Si interface decreased and/or disappeared. At oxidation temperatures higher than at 750~800 C, the frequency-dependent AC SPV was not detected. The Au was found to diffuse deeper in both SiO_2 bulk and Si substrate as the oxidation advanced. Regarding oxidation kinetics at between 550 and 900C, Au caused a drastic SiO_2 growth enhancement for SiO_2 thickness less than ~10 nm. This result shows that Au acted as catalyst to promote the initial SiO_2 growth at the Si(001) surface. The behavior of the Au in SiO_2 layer explained the relationship between oxide thicknesses and oxidation time. Finally, the SiO_2 growth mechanism influenced by the addition of Au is proposed.

SS-ThP25 Oxidation of the PAH Coronene by Ozone and the Hydroxyl Radical, ***E.R. Mysak****, J.T. Newberg, J.D. Smith, K.R. Wilson, H. Bluhm*, Lawrence Berkeley National Laboratory

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants, consisting of two or more fused benzene rings, emitted directly into the atmosphere primarily through incomplete combustion processes and known to have allergenic, mutagenic, and carcinogenic effects. In the atmosphere, smaller PAHs are found primarily in gas-phase, whereas three or four-member ring compounds are partitioned between gas and particulate matter, and compounds with greater than five-member rings mostly reside in the particle phase. The atmospheric fate of these heavier PAHs is governed by heterogeneous reactions between the surface bound PAHs and gas-phase atmospheric oxidants such as ozone, the hydroxyl radical, and nitrates, however, these heterogeneous chemical reactions are relatively poorly understood and studied. In the current study, reactivity of the seven-member ring PAH coronene to oxidation sources ozone and hydroxyl radical is examined. To probe the extent of chemical reaction, product formation, and change in surface morphology as a function of reaction, we examine coronene adsorbed onto various substrates, from both a surface and bulk perspective, with ambient pressure photoemission spectroscopy (APPES) and aerosol mass spectrometry (AMS), respectively. In bulk on-line analysis, a 20nm thick layer of coronene adsorbed onto NaCl seed particles and reacted with either oxidant in a flow tube showed very little reactant conversion to product in the AMS. However, surface analysis by the APPES of the same reaction where coronene was adsorbed onto model substrates showed up to 90% conversion of the carbon species to volatilized or oxidized carbon. Data obtained with these two complimentary bulk and surface techniques provide evidence for a surface selective reaction. Using APPES, we are able observe the two oxidation reactions transforming on different timescales and through differing pathways, resulting in dissimilar final states.

Surface Science
Room: 207 - Session SS+AS+NC-FrM

Environmental Surfaces and Water Interaction with Oxide Surfaces
Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS+AS+NC-FrM1 Heterogeneous Reactivity of O_3 and OH Radical with Potassium Iodide**, ***M.A. Brown***, *T.M. McIntire, M.J. Krisch,* University of California, Irvine, *V. Johánek,* University of Virginia, *P.D. Ashby, Z. Liu,* Lawrence Berkeley National Laboratory, *A. Mehta,* Stanford Linear Accelerator Center, *D.F. Ogeltree, M. Salmeron,* Lawrence Berkeley National Laboratory, *J.C. Hemminger*, University of California, Irvine

Sea salt aerosols are known to undergo heterogeneous reactions with atmospheric oxidants, resulting in halide depletion as they travel through polluted regions of the environment. The subsequent photochemistry of halide compounds (including halogenated oxides) strongly influences the chemical composition of the atmosphere. The results from uptake measurements of O3 and OH radical on potassium iodide will be discussed. The reactivity of KI with O3 and OH radical are remarkably different and result in reaction products of KIO3 and KOH, respectively. We describe results from X-ray photoemission spectroscopy, X-ray diffraction, Atomic Force Microscopy and IR spectroscopy. In the case of O3, under conditions in which the KI surface is devoid of adsorbed water molecules the reaction is self-passivating, and results in a thin layer of KIO3 with an rms roughness of 3.6 nm. Subsequent exposure to water vapor mobilizes the KIO3 oxide layer, revealing additional KI substrate that is readily available for further oxidation. As such, under conditions of low relative humidity the uptake of O3 onto KI is not expected to be self-passivating. Under similar conditions, the reaction of OH radical with KI results in halide vacancies (iodide is released into the gas phase) created in the outermost surface lattice sites. The iodide vacancies are filled with OH- to generate a layer of KOH that is self-passivating following prolonged exposures. There is no spectroscopic evidence of stable oxidized iodide reaction products. AFM and IR results will also be discussed.

8:40am **SS+AS+NC-FrM2 Reactivity of Fe^0 Atoms, Clusters and Nanoparticles with CCl_4 Multilayers on FeO(111)**, ***G.S. Parkinson***, *Z. Dohnálek, R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

There is currently much interest in the development of Fe^0 nanoparticles as an agent for the destruction of chlorinated hydrocarbons in environmental remediation applications. However, the fundamental reaction pathways for the interaction of nano-Fe^0 with such target molecules is unknown, and this presents a major obstacle to the design of improved particles. Our work utilizes a novel "atom dropping" technique where Fe^0 atoms, clusters and nanoparticles are deposited into CCl_4 multilayers on FeO(111) at 30 K in ultra-high vacuum. A series of temperature programmed desorption and X-ray photoelectron spectroscopy experiments will be described which demonstrate an interesting size effect whereby isolated atoms and small clusters exhibit markedly different reactivity and product branching ratio to nanoparticles. The results will be discussed in the context of relevant theoretical calculations and the reaction pathways identified. The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

9:00am **SS+AS+NC-FrM3 New Paradigms for Environmental Surfaces: Structure and Reductive Transformation at α-Fe_2O_3/Water Interfaces**, ***K.M. Rosso***, *S.V. Yanina, S. Kerisit*, Pacific Northwest National Laboratory **INVITED**

The semiconducting properties of a wide range of minerals are often overlooked in the study of their interfacial chemical behavior. As a case study, reductive transformation of α-Fe_2O_3 (hematite) in aqueous solutions is a central part of the natural iron cycle in the environment. The transformation involves reduction of surface Fe(III) to Fe(II) by electron transfer, followed by Fe(II) solubilization and precipitation of new phases. It is a long-held perception that locations of Fe(III) reduction at the interface with aqueous solution correspond directly to sites of Fe(II) release. However, hematite is a semiconductor with a propensity for moderate electron diffusivity in the surface and bulk. Hematite surfaces are also reactive with water and ions leading to surface charging behavior that is closely dependent on the crystallographic termination. Our recent focus has been on understanding how these qualities create unique conditions for the interfacial electron transfer involved in reductive transformation. We show using atomic force microscopy and surface-specific potentiometry evidence that these qualities couple interfacial electron transfer reactions at hematite (001) surfaces with those occurring at crystallographic edge terminations such as (012) via current flow through the crystal bulk. At low pH, divergent charging behavior between (001) and (012) surfaces yield a surface potential bias across the crystal of several hundred millivolts capable of biasing diffusion of charge carriers. We examined this aspect in detail with atomistic simulations of electron diffusion in bulk hematite and at (001) and (012) surfaces using a small polaron hopping model. The model supports the experimentally evident reductive transformation process of net oxidative adsorption of Fe(II) at (001) surfaces coupled by bulk charge transport to net internal reductive dissolution of Fe(III) at edge surfaces. This new paradigm for hematite reductive transformation has important implications for our understanding of the natural iron cycle in the environment. More generally, the apparent importance of chemically induced bulk crystal conduction is likely to be generalizable to a host of naturally abundant semiconducting minerals playing varied key roles in soils, sediments, and the atmosphere.

9:40am **SS+AS+NC-FrM5 Molecular Beam Studies of Supercooled Mixtures of Methanol and Water**, ***J. Matthiesen***, *R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

Molecular beams, temperature programmed desorption, and infrared spectroscopy were used to study the diffusive intermixing of amorphous water and methanol nanoscale films. Composite films with initially separated layers were created by sequential dosing at 25 K in UHV. The films were then heated and the extent of intermixing was determined by the onset of desorption of the underlayer species and changes in the infrared spectra. Both linear ramp and isothermal experiments were conducted. In a series of experiments the layer thickness, film composition, and heating rate were varied to extract quantitative temperature dependent diffusivities. Isotopically labeled methanol was used to mimic tracer-type experiments. These results compare favorably to the results obtained from separated layer experiments. Numerical simulations of the diffusive intermixing were used to quantitatively model the experimental results. The details of the experiment and the interpretation of the results will be discussed in detail. The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

10:00am **SS+AS+NC-FrM6 DFT Study of Water Adsorption on $SrTiO_3$ (001) Bulk Termination and 2x1 Reconstruction**, ***A.E. Becerra-Toledo***, *L.D. Marks*, Northwestern University

Strontium titanate, $SrTiO_3$, has been studied extensively as a model perovskite system. Among other advances, its variety of cation oxidation states has provided critical insights into oxide surface reaction mechanisms. Understanding the reaction of ubiquitous water molecules with $SrTiO_3$ surfaces is of great importance to environmental science and catalysis. Density functional theory (DFT) calculations were performed to study the adsorption of water molecules on two different $SrTiO_3$ (001) surfaces. A repeated slab model was employed to study both a bulk-like TiO_2 surface termination and a 2x1 surface reconstruction. While similar studies have been carried out in the past, our treatment using a full-electron potential and a linear augmented plane wave plus local orbital (LAPW+lo) basis more accurately models the spatial character of single-particle wavefunctions. Two different exchange-correlation functionals were employed: the PBE[1] generalized gradient approximation (GGA) and the TPSS[2] meta-GGA. On the TiO_2-terminated surface, both molecular and dissociative adsorption of water were modeled. The results did not show a significant dependence on the choice of exchange-correlation functional. Most importantly, the adsorption energies for molecular and dissociative adsorption were more similar than has been previously reported,[3] and therefore favor the coexistence of hydroxyl groups and molecular water on the surface. On the 2x1 surface reconstruction, which was solved by Erdman et al.[4] and is typically formed under oxidizing conditions, dissociative adsorption was studied with several distinct stable structures considered. The most stable of these showed an adsorption energy (per H_2O molecule) much larger than that observed for the bulk TiO_2 termination. In all cases we observe the effect of hydrogen bonding between adsorbate and surface anions on the stabilization of the structures.

[1] Perdew, J.P. et al. Phys.Rev.Lett. 77, 3865 (1996).

[2] Tao, J. et al. Phys.Rev.Lett. 91, 146401 (2003).

[3] Evarestov, R.A. et al. Surf.Sci. 601, 1844 (2007).

[4] Erdman, N. et al. Nature 419, 55 (2002).

10:20am **SS+AS+NC-FrM7 Unraveling a Reaction on an Oxide Surface Step by Step: Formation of Water from Oxygen through Successive H Transfer Reactions on TiO_2(110)**, *F. Besenbacher, J. Matthiesen,* ***S. Wendt****, J.Ø. Hansen, E. Laegsgaard, B. Hammer*, University of Aarhus, Denmark

By means of high-resolution scanning tunneling microscopy(STM) measurements and density functional theory (DFT) calculations we studied the reaction between O_2 and H adatoms on reduced rutile TiO_2(110). We identified chemisorbed OH_O species as the initial intermediate that is produced by H transfer reactions to O_2 molecules, which concomitantly dissociate. Through further successive H transfer reactions, mediated by co-adsorbed water, the OH_O species are finally transformed into water dimers. Our data exemplify how time-lapsed STM imaging, in combination with DFT calculations, can be successfully used to unravel reactions on surfaces with a high number of intermediates.

10:40am **SS+AS+NC-FrM8 Water Dissociation on Single Crystalline Anatase TiO_2(001) Studied by Core Level Photoelectron Spectroscopy**, ***A. Sandell***, Uppsala University, Sweden, *J. Blomquist*, Lund University, Sweden, *L.E. Walle*, NTNU, Norway, *P. Uvdal*, Lund University, Sweden, *A. Borg*, NTNU, Norway

The interaction of water and TiO_2 surfaces has been intensely studied since the discovery of photoinduced splitting of water into hydrogen and oxygen on a rutile TiO_2 single crystal in 1972.[1] However, even though the anatase TiO_2 polymorph is more widely used as photocatalyst than rutile studies of the adsorption of water on well-defined anatase TiO_2 surfaces are scarce. So far, the efforts have mainly been theoretical. Based on calculations it has been proposed that molecular water adsorption is favored on the (101) surface, whereas water dissociation is favored on the (001) surface.[2,3] This implies that the (001) surface may be very important in spite of it being the minority surface termination of anatase crystallites. In this contribution, we present the first study on the coverage dependent adsorption of water on the anatase TiO_2(001)-(4x1) surface using core level photoemission spectroscopy. Data with high surface sensitivity were recorded at the MAX-lab synchrotron radiation source. Two types of anatase TiO_2(001)-(4x1) surfaces were prepared: One by MOCVD growth on a lattice matched substrate [$SrTiO_3$(001)] and one by cleaning of a natural single crystal. Our results confirm that water dissociate on the anatase TiO_2(001)-(4x1) surface. We can define two adsorption phases: Phase 1 consists only of dissociated water, observed as OH-groups. This phase is found at low coverage at low temperature (190 K) and is the only state of adsorbed water above ~230 K. The saturation coverage of phase 1 agrees with the number of four-fold coordinated Ti ridge atoms of the (4x1) surface reconstruction. Phase 2 is found at higher coverage, reached at low temperature. It consists of a mixture of dissociated and molecular water with a ratio of 1:1 at 170 K. The hydroxyl coverage of phase 2 is approximately two times that of phase 1.

[1] A. Fujishima and K. Honda, Nature (London) 238, 37 (1972).

[2] A. Vittadini, A. Selloni, F. P. Rotzinger, and M. Grätzel, Phys. Rev. Lett. 81, 2954 (1998).

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11:00am **SS+AS+NC-FrM9 Study of the Oxidation of Titanium and the Adsorption of Biomolecules on Titanium by Means of Electrochemical Quartz Crystal Microbalance with Dissipation Supported by X-ray Photoelectron Spectroscopy**, ***I. Van De Keere***, Vrije Univ. Brussel, Belgium, *S. Svedhem, A. Kunze*, Chalmers Univ. of Tech., Sweden, *J. Vereecken*, Vrije Univ. Brussel, Belgium, *B. Kasemo*, Chalmers Univ. of Tech., Sweden, *A. Hubin*, Vrije Univ. Brussel, Belgium

Titanium is frequently used as a biomaterial in orthopaedics and cardiovascular devices. The metal is covered with a native oxide layer of a few nm, which contributes to the high biocompatibility of Ti implants. One of the surface properties of a biomaterial, which plays an important role in the interaction with biomolecules is electrostatic interaction at the surface. By varying the potential of Ti, the surface charge of Ti changes, and electrostatic interactions are likely to be influenced. The goal of the present study is to investigate the influence of an electric field on the adsorption of biomolecules, such as proteins and lipids, onto Ti surfaces and their conformational changes with electrochemical quartz crystal microbalance with dissipation (ECQCMD). QCMD is a well-established technique for monitoring mass and film thickness (through the frequency shift) and to obtain information about the viscoelastic properties of the adsorbed layers (through the dissipation shift). It has recently become possible to carry out combined QCMD and electrochemical measurements using a specially designed flow cell. This combination is valuable for adsorption studies under the influence of external fields and/or where one wants to in situ change the oxide layer thickness. A difficulty arises upon using Ti compared to other model substrates as gold since the surface of Ti is always covered with a native oxide layer, which may grow upon application of an external potential to the Ti surface. Firstly, the oxidation of Ti in buffer under the influence of an electric field was investigated, because a stable oxide layer was desired before investigating the interaction of biomolecules with Ti under applied external potential. With ECQCMD, quantitative information on the growth behaviour and the thickness of the Ti oxide layer was obtained. The calculated thickness from ECQCMD was correlated with the depth profiles obtained from X-ray Photoelectron Spectroscopy (XPS). Secondly, the adsorption of biomolecules on Ti was studied. The influence of an external potential applied to the Ti-surface on the formation of supported lipid bilayers of DOEPC (positively charged phospholipid) is pronounced. The moment of vesicle rupture, which precedes the formation of bilayers, is delayed significantly upon application of a potential of 0 V vs SHE, compared to open circuit potential and 0.6 V vs SHE. For these two potentials, the rupture of vesicles occurs faster and at the same moment.

11:20am **SS+AS+NC-FrM10 Acidic Dissolution Mechanism, pH-dependent Stabilization and Adhesion of Single Molecules on Single Crystalline ZnO(0001)-Zn Model Surfaces Studied by in-situ AFM and DFT Simulations**, ***M. Valtiner***, Max-Planck-Institut für Eisenforschung, Germany, *G. Grundmeier*, University of Paderborn, Germany

The surface chemistry at oxide/water interfaces is a key issue in adhesion science and related areas such as corrosion science. De-adhesion processes as well as corrosion processes are often accompanied by a change of the pH at the interface. Hence an atomistic understanding of oxide dissolution promoting effects of H+, OH- and anions, as chlorides or sulfates, are an important aspect of de-/adhesion, metal corrosion and its inhibition. In this context, experimental results on single crystalline ZnO(0001)-Zn model surfaces and DFT-based ab-initio studies will be discussed. First, it will be shown that single crystalline ZnO(0001)-Zn model surfaces can be prepared easily and surprisingly clean under ambient conditions by introducing hydroxide stabilization via a wet chemical etching step. The prepared model surfaces will be discussed by AFM, LEED, angle resolved XPS, ToF-SIMS and Auger spectroscopy data.[1] Secondly, the stability of these ZnO(0001)-Zn surfaces in electrolyte solutions will be demonstrated by a combined approach of in-situ AFM imaging and ex-situ LEED investigations. It will be shown that ZnO(0001)-Zn surfaces are stable and single crystalline in aqueous solutions within a wide pH range due to hydroxide stabilization. An in-situ AFM study of the acidic dissolution allowed an imaging of the dissolution process and hence a mechanistic understanding of the dissolution process of ZnO can be supported.[2] Moreover, Single Molecule Adhesion studies - by means of single molecule de-sorption of polyelectrolyte molecules - on these surfaces at variation of the pH level will be presented. Finally, the potential of a synergistic combination of these approaches with ab-initio based simulation methods will be highlighted.

[1] M. Valtiner, S. Borodin, G. Grundmeier; Physical Chemistry Chemical Physics, 9(19), (2007) 2406-2412.

[2] M. Valtiner, S. Borodin, G. Grundmeier; Langmuir (2008), ASAP Article: 10.1021/la7037697.

11:40am **SS+AS+NC-FrM11 The Adsorption of Water on a PdO(101) Thin Film on Pd(111)**, ***H.H. Kan****, R.J. Colmyer, J.F. Weaver*, University of Florida

Palladium oxide (PdO) is an excellent catalyst for the oxidation of hydrocarbons and CO under oxygen-rich conditions. Unfortunately, however, many fundamental questions about the surface chemistry of PdO have remained unanswered since it has been challenging to prepare well-defined PdO surfaces for detailed experimental investigations. In this talk, I will discuss our recent experimental study of the adsorption of water on a PdO(101) thin film that was grown in ultrahigh vacuum by oxidizing Pd(111) using an oxygen atom beam. From temperature programmed desorption (TPD) measurements, we find that water can populate several adsorbed states on PdO(101). Physisorbed water molecules populate both monolayer and multilayer states on PdO(101), with desorption from these states yielding TPD peaks at 150 and 197 K, respectively. The desorption temperature from the physisorbed monolayer is about 35 K higher for PdO(101) compared with Pd(111), which suggests that hydrogen-bonding enhances the physisorption bond strength on the oxide. We also observe a relatively broad desorption feature of water from PdO(101) that appears to consist of two components centered at 320 K and 350 K. We present evidence that these components arise from distinct states of molecularly and dissociatively chemisorbed water, respectively, and that both forms of chemisorbed water bind to coordinatively unsaturated Pd cations that are prevalent on the PdO(101) surface. Finally, although the dissociative chemisorption of water presumably involves hydrogen transfer to an oxygen anion of the oxide, we observe only small amounts of oxygen exchange between water and the oxide in experiments with oxygen-labeled water. This finding suggests that water dissociation produces inequivalent hydroxyl groups on PdO(101).

Surface Science
Room: 208 - Session SS+EM+NC-FrM

Semiconductor Surfaces
Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am **SS+EM+NC-FrM1 From Nanochemistry to Active Nano-Objects at Semiconductor Surfaces**, ***P.G. Soukiassian***, Commissariat à l'Energie Atomique and Université de Paris-Sud/Orsay, France **INVITED**

Silicon carbide (SiC) surfaces/interfaces are studied by atom-resolved scanning tunneling microscopy and spectroscopy (STM/STS) using electrons and/or photons, synchrotron radiation-based photoelectron spectroscopies (XPS, UPS, µ-spot XPS) and/or diffraction, low energy electron microscopy (LEEM) experimental techniques and density functional theory. Such important issues as self-organized active metal nano-objects, defects and an amazing nanochemistry will be presented and discussed. It includes: The 1st example of H/D-induced clean/pre-oxidized semiconductor surface metallization, with an isotopic effect occurring using D; Selective formation of ultra-thin nitride layer at Si-SiC interface; Atomic crack defects developing at SiC surfaces; Anisotropic metal diffusion, metal atom pairs, chains and wires formation; Massively parallel active architecture based on metal/Si nanowires exhibiting a negative differential resistance behavior. These findings impact some important issues such as i) metallization of wide band-gap chemically passive semiconductor surfaces which is of particular interest in interfacing with biology, ii) selective SiC interface passivation especially useful in limiting dopant diffusion, iii) identifying and understanding some unusual defects most likely involved in the high density of interface states recurrent at SiC interfaces, and iv) achieving a massively parallel active architecture in the solid state.

9:00am **SS+EM+NC-FrM3 Chemistry of the Si-rich β-SiC(100) Surface Compared to the Si(100) Surface**, ***S.M. Casey***, *L.N. Adhikari*, University of Nevada, Reno

The chemistry of the Si-rich β-SiC(100) surface has been studied using density functional theory (DFT) computational methods and small clusters to model the surface reactivity. Results for the reactions of the cluster models of the silicon carbide surface with ammonia and small alcohols and amines will be presented and the energetics compared to the corresponding pathways on the Si(100) surface. The computational results generally show that the silicon-rich silicon carbide surface exhibits stronger interactions with these types of adsorbates by 5-10 kJ/mol relative to the clean silicon surface. The major difference is that the silicon carbide surface has no closely bordering reactive silicon surface dimers, and, thus, the "intrinsic" reactivity of the silicon surface dimer can be examined without complicating multi-dimer reactions. The computational results will also be compared to experimental thermal desorption studies on these surfaces. The thermal desorption results are in general agreement with the DFT results.

9:20am **SS+EM+NC-FrM4 Surface Band Bending in GaN**, *M. Ruchala, M. Foussekis, H. Morkoc, M.A. Reshchikov,* ***A.A. Baski***, Virginia Commonwealth University

In spite of tremendous progress in the development of nitride semiconductors, the detrimental effects of surfaces and interfaces on the electrical and optical properties of devices based on these semiconductors is often underestimated. We have investigated band bending at the surface of undoped GaN and its change caused by illumination (photovoltage) with scanning Kelvin probe microscopy (SKPM) in ambient and with a Kelvin probe attached to an optical cryostat in high vacuum. In the microscopy set-up, we charged the surface and increased band bending by several eV using conductive atomic force microscopy (CAFM), and then used SKPM to observe discharge transients of the surface band bending in dark from room temperature (RT) to 35 °C, as well as under sub-bandgap illumination. In the Kelvin probe set-up, we measured the photovoltage spectrum and its transients after UV illumination at temperatures from RT to 125 °C in vacuum and air ambient. These two complementary techniques provide independent information about surface band bending and its transient behavior after charge injection or illumination. The rate of restoration of the initial band bending in dark for both experiments (after CAFM charging or after flattening of band bending due to illumination) increased at higher temperatures and typically exhibited a quasi-logarithmic time dependence. The results indicate that the restoration of band bending disturbed from equilibrium occurs primarily by means of adsorption of some species from air, and not by thermionic emission of electrons over the surface potential barrier. Indeed, transients of the photovoltage (PV) caused by UV illumination in the Kelvin probe strongly depended on the ambient. In air ambient under illumination, the PV signal increased to its maximum of 0.65 V in a few seconds and then gradually decayed by 0.3 V over 3 h, whereas in vacuum the signal quickly increased to 0.55 V and then slowly increased by 0.1 V over 3 h. This behavior indicates the photo-induced adsorption of negatively charged species in ambient or the photo-induced desorption of such species in vacuum. With regard to temperature, the initial band bending increased by 0.2 V from RT to 125 °C due to more bulk electrons overcoming the surface barrier and becoming trapped at surface states. Experiments are now in progress in the Kelvin probe to investigate the band bending behavior as a function of introduced gas species such as oxygen or water vapor.

9:40am **SS+EM+NC-FrM5 An Accelerated Molecular Dynamics Study of Diffusion on the GaAs (001) β2(2x4) Reconstruction**, ***M.H. Mignogna***, *K.A. Fichthorn*, The Pennsylvania State University

The GaAs (001) β2(2x4) reconstruction is the most commonly used substrate for growth in GaAs homoepitaxy by molecular beam epitaxy. Kinetic Monte Carlo (KMC) simulations based on first-principles calculations[1] have illuminated the mechanisms for recovering this reconstruction during growth. However, the KMC simulations are based on rates of processes that occur on perfect β2(2x4) unit cells. In experimental studies with reflection high-energy electron diffraction and scanning-tunneling microscopy, the surface is observed to exhibit domains of perfect β2(2x4) unit cells, but long-range disorder persists and a possible origin is out-of-phase β2(2x4) domains.[2] To examine the atomic-scale processes that lead to long-range disorder, as well as to characterize diffusion and the early stages of homoepitaxy on this surface, we employ accelerated molecular dynamics (MD). Our simulations are based on a semi-empirical, Tersoff-type potential that exhibits good agreement with a variety of bulk and surface properties of GaAs. Using accelerated MD we can probe long time scales, extending into the microsecond range and beyond. On the bare surface, we observe breaking, re-forming, and shifting of As row and trench dimers, that promotes the formation of out-of-phase domains of β2(2x4) unit cells and leads to long-range disorder of the surface. The kinetic processes of the As dimers affect the surface diffusion of Ga adatoms, as well as the initial morphologies that occur during growth.

[1] P. Kratzer, E. Penev, M. Scheffler, Appl. Phys. A 75, 79 (2002)

[2] D.W. Pashley, J.H. Neave, B.A. Joyce, Surf. Sci., 582, 189 (2005).

10:00am **SS+EM+NC-FrM6 First Principles Investigation of Dimer Ordering on III-V Semiconductor Surfaces**, ***J.C. Thomas***, *J.E. Bickel, J.M. Millunchick, A. Van der Ven*, University of Michigan

Surface disorder can contribute significantly to optoelectronic, thermodynamic, kinetic and interfacial properties of epitaxial thin films, especially at the nano-scale. Surface reconstructions, which decrease surface free energy relative to bulk configurations via a reduction in unfavorable bonding and increase in configurational entropy, play a vital role in the determination of these properties. In this work, the effect of finite temperature on the free energy of surface reconstructions is investigated in order to determine the role of entropy in surface dimer concentration and ordering. As a model system, we consider the α2(2x4) and β2(2x4) reconstructions on the (001) surface of homoepitaxial InAs, as these reconstructions are not only well studied, but are also stable within a continuous interval of chemical potential. A first principles model Hamiltonian is developed within the cluster expansion formalism and applied to equilibrium Monte Carlo simulations to obtain accurate thermodynamic quantities, as well as configurational trends. For example, fitting to energies for seven different dimer configurations of these 2x4 reconstructions, calculated via density functional theory show that there is an energetic preference for third nearest neighbor pairing (along the diagonal), giving rise to a "zig-zag" ordering of dimers, referred to as the z(4x4). Evidence of this structure has been previously reported. Monte Carlo simulations show the α2(2x4) to be stable within an intermediate range of chemical potentials, giving way to the β2(2x4) at higher chemical potential. The transition between configurations shows a step-like behavior at low temperatures, smoothing out at higher temperatures. The fraction of the α2(2x4) that posseses the z(4x4) ordering was determined from averaged correlations. The coverage is about 60% at room temperature, and decreases to approximately 50% at typical growth temperatures, in reasonable agreement with published results. We show that size mismatch strain in ternary III-V alloys drives In surface segregation in GaAs and locks in a zig-zag ordering of As surface dimers.

10:20am **SS+EM+NC-FrM7 Hydroxyl Termination and Passivation of the Group III-rich (4x2)/c(8x2) Surfaces of InAs(001) and InGaAs(001) Surface Studied by STM, STS, and DFT**, ***J.B. Clemens***, *T. Song, A.C. Kummel*, University of California, San Diego

Atomic Layer Deposition requires the substrate to have a chemical passivation/termination layer consisting of reactive groups that initiate the ALD reaction. A suitable passivation/termination layer would have ligands that mimic the surface during growth, such as hydroxyl (OH$^-$).[1,2] Scanning tunneling microscopy was used to study the initial bonding configuration of hydroxyl onto the group III-rich InAs(001)-(4x2)/c(8x2) surface, which is almost identical to the InGaAs(001)-(4x2)/c(8x2) surface. These surfaces are more resistant to oxidation than group V-rich surfaces, which is true of many III-arsenide semiconductors, and therefore is a better starting template for ALD.[3] Aqueous (30%) hydrogen peroxide vapour is used as the OH source. After annealing, the surface reaction forms well-ordered interfaces that terminate at about one ML indicating that this process is self-limiting. Substrate lattice disruption is minimal following OH desorption after annealing at 350° C. If pure water vapour is used as a control dose, less surface reaction occurs and it centers at surface defect sites. Density functional theory was used to model the interaction of InGaAs(001)-(4x2) with OH, H, and H_2O. Energies and kinetics of adsorption and desorption of OH, H, and H_2O are presented, which compares the stability of the $HOOH/H_2O$ vs the H_2O only termination/passivation methods. DFT results show that the OH passivation method using HOOH is stable at high temperatures that are typically found under ALD growth conditions, while the passivation method using only water is not. The electronic structure was probed using scanning tunneling spectroscopy. On the clean as-prepared substrates, both n- and p-type InAs(001)-(4x2)/c(8x2) show n-type behavior, consistent with literature.[4,5] Upon OH termination, both surfaces exhibit n-type behavior, with the Fermi level about 0.1 eV below the CB minimum. This shows no evidence for midgap Fermi level pinning, suggesting that this method has potential for high-κ gate oxide ALD on III-V semiconductor surfaces.

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10:40am **SS+EM+NC-FrM8 Pit Nucleation in the Presence of (nx3) and β2(2x4) Surface Reconstructions on $In_{.81}Ga_{.19}As/InP$ Films**, ***L.E. Sears***, *A. Riposan*, *J.M. Millunchick*, University of Michigan - Ann Arbor

The growth of heteroepitaxial films with high misfit strains on the crystallographic surface such as InGaAs/GaAs usually occurs in the Stranski-Krastanov mode, whereby coherent islands form on a planar wetting layer as a way to relieve strain due to a lattice mismatch. Theory has shown that both islands and pits can relieve strain on high misfit, low temperature films,[1] but experimentally only islands are typically observed as the initial mechanism of strain relief. We have discovered a growth regime in which pits relieve strain rather than islands due to a decrease in surface energy with increasing indium content. Models have predicted that altering the growth conditions, such as growth rate and temperature, or materials properties, such as surface energy or lattice mismatch, can lead to the nucleation of pits initially on the surface instead of islands,[1,2] but little experimental data exists to support those claims. We examine the growth of $In_{0.27}Ga_{0.73}As/GaAs(001)$ and $In_{0.81}Ga_{0.19}As/InP(001)$, which both have the same lattice mismatch strain, and show that In composition is important in determining the type of 3D features that nucleate on the surface. As the critical thickness is exceeded, low indium composition films have a tendency to form 3D islands as the primary strain relief mechanism. On the other hand, pits are the preferred strain relief mechanism in high In composition films grown with the same growth conditions and lattice mismatch. Increasing the indium content results in a more metallic surface that has a lower surface energy (γ) and models have predicted that at sufficiently low γ pit nucleation is favored over islands as the initial strain relief mechanism.[2] Models have suggested that the presence of β2(2x4) reconstructions may also act as strain relief mechanism in $In_{0.81}Ga_{0.19}As/InP(001)$ films.[3] Analysis of the atomic surface structure of these films using scanning tunneling microscopy show that the reconstructions are also affected by the presence of pits, lending more evidence to surface reconstructions as a mechanism for strain relief.

[1] Lung MT, Lam CH, and Sander LM, Phys. Rev. Lett. 95 (086102) AUG 18 2005

[2] Bouville M, Millunchick JM, Falk ML, Phys. Rev. B 70 (235312) DEC 10 2004

[3] Riposan A, C. Pearson, and JM Millunchick, J. Vac. Sci. Technol. A 24 (2041) OCT 10 2006.

11:00am **SS+EM+NC-FrM9 In-situ ALD Studies of Al- and La-oxide on $In_{0.53}Ga_{0.47}As$**, ***M. Milojevic***, University of Texas at Dallas, *B. Brennan*, Dublin City University, Ireland, *H.C. Kim*, University of Texas at Dallas, *F.S. Aguirre-Tostado*, The University of Texas at Dallas, *J. Kim*, *R.M. Wallace*, University of Texas at Dallas, *G. Hughes*, Dublin City University, Ireland

The combination of high k dielectric materials on high mobility III-V semiconductors offers the potential for MOSFETs with larger transconductance at lower operating voltages than are currently achievable with silicon based devices. Arsenic and gallium oxidation states are suspected to be the cause of Fermi level pinning, and therefore the removal or minimization of such states is required in order to develop practical devices. This study investigates the atomic layer deposition (ALD) of aluminium and lanthanum oxide based high-k dielectrics on the ammonium sulphide $(NH_4)_2S$ and ammonium hydroxide NH_4OH treated $In_{0.53}Ga_{0.47}As$ surface grown by metal organic vapour phase epitaxy (MOVPE) on lattice matched InP substrates using in-situ surface chemical analysis. Monochromatic, in-situ X-ray photoelectron spectroscopy (XPS) and ex-situ atomic force microscopy (AFM) were used to determine optimal $(NH_4)_2S$ conditions based on varying the sulphur concentration, temperature and treatment time. The ALD of the high-k films carried out at 300°C consists of a metal precursor pulse followed by a water pulse with an high purity N_2 carrier gas and was sequentially examined with in-situ XPS after every half cycle of the deposition process to determine the initial interfacial oxide and substrate reactions taking place during the growth. A 'clean up' effect, whereby the ALD process reduces native oxides at the surface during high-k deposition, is well known for thin dielectric films. In the case of TMA/water based deposition of Al_2O_3, we have found that the first TMA pulse is responsible for the removal of virtually all of the arsenic oxide left on the surface after the pre-treatments, especially with $(NH_4)_2S$, to within the detection limits of XPS. Gallium oxide bonding is reduced to approximately a monolayer consistent with a Ga-O-Al bond at the interface. Similar results for La-based precursor reactions will also be presented. Capacitance-voltage measurements were also carried out on metal oxide semiconductor MOS devices formed after the high-k dielectric growth. Supported by MARCO MSD Focus Center, Science Foundation Ireland, and FUSION.

11:20am **SS+EM+NC-FrM10 Atomic Scale Investigation of Mn Impurities on the InAs(110) Surface**, ***Y.J. Song***, University of Maryland, College Park and NIST, *G.M. Rutter*, *P.N. First*, Georgia Institute of Technology, *N. Zhitenev*, *J.A. Stroscio*, National Institute of Standards and Technology

Increased interest in spin-based electronics as a replacement for charge-based electronics has led to significant scientific attention to dilute magnetic semiconductors (DMS). One of the main dilute magnetic semiconductors involves doping III-V semiconductors with Mn acceptors with the aim of achieving high Curie temperatures. In the present work, we studied Mn deposited on the InAs(110) surface with low temperature scanning tunneling microscopy and spectroscopy (STM/STS). Single Mn atoms were deposited onto a cleaved n-InAs(110) surface at cryogenic temperatures. The as-deposited Mn adatoms were found to be in two distinct configurations. About 10% of the Mn adatoms appear in the topographic images to be positively charged. The other 90% appear to be in a neutral configuration. Both types of adatoms can undergo an exchange process whereby the surface Mn atom substitutes for an In atom in the top surface layer. This process involves raising the sample tunneling voltage beyond a certain threshold voltage of approximately -0.6 eV for both types of Mn adatoms. This process is similar to that seen in the Mn/GaAs system.[1] And we also studied that in-situ deposition of Mn onto a cleaved n-doped InAs(110) substrate at low temperature produces an adsorbate-induced 2DEG at the InAs surface. Spatial properties of Landau level quantization[2] in high magnetic fields of both the 2D sub-bands and 3D conduction bands were studied in relation to the configuration of Mn atoms on the surface.

[1] D. Kitchen et al, Nature 442, 436 (2006)

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