Tuesday Afternoon, November 3, 1998

Surface Science Division Room 309 - Session SS2-TuA

Morton M. Traum Student Award Session

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

2:00pm SS2-TuA1 Hot Ethene Desorption by Dissociative Electron Attachment of Adsorbed Halocarbons, A.S.Y. Chan¹, R.G. Jones, University of Nottingham, United Kingdom

The electron stimulated reactions of adsorbed 1,2-dihalocarbons have been studied by measuring the time-of-flight (TOF) velocity distributions of the ethene product ejected from the surface. Both 1,2-dichloroethane (DCE) and 1-bromo-2-chloroethane (BCE) have been found to undergo dissociative electron attachment from secondary electrons generated by a pulsed 2 keV electron beam impinging on the Cu(111) surface, leaving chemisorbed halogens and ethene desorbing in the gas phase. The TOF distributions of the ethene product from both adsorbate molecules are quite similar; both exhibit a bimodal distribution with a hyperthermal channel of ~ 1200 K and a slow channel of ~ 200 K. When the distributions obtained from identical coverages of DCE and BCE are compared, a consistently smaller intensity of the slow channel is observed from the latter molecule. This slow component appears to grow with increasing number of adsorbed layers, indicating that it is most likely due to ethene molecules that have thermalised by interactions with the adsorbate. By comparing the possible dissociation dynamics of the two molecules, we discuss the possibility that a direct dissociation of the adsorbed molecule after electron capture, rather that a surface-mediated energy transfer mechanism, may be responsible for the high translational energy of the hyperthermal ethene.

2:20pm SS2-TuA2 Combined Experimental and Quantum Chemistry Study of the Disproportionation of Dimethylalane on Aluminum Surfaces, B.G. Willis², K.F. Jensen, Massachusetts Institute of Technology

A combined experimental/theoretical approach has been employed to study the decomposition reactions of trimethylaluminum and dimethylalane on aluminum surfaces. Together with UHV surface science experiments, plane wave pseudopotential density functional theory calculations have been implemented to augment the experimentally derived reaction mechanism. The plane wave surface calculations provide additional details of the surface reactions not easily probed with experiments, and where the two approaches overlap, comparisons are made. Dimethylalane is found experimentally to decompose on aluminum via a disproportionation reaction to produce trimethylaluminum. Trimethylaluminum follows the same reaction pathways on aluminum, but due to the difference in stoichiometry there is no net growth, and a dynamic equilibrium exists between the gas phase and surface at low temperatures. Based on the experimentally observed mechanism, the calculations are employed to generate thermodynamic heats of reaction for each elementary reaction step, and a complete mechanism is presented for the surface reactions. Results suggest exothermic steps for breaking down the dimethylalane and trimethylaluminum monomers to surface monomethylaluminum fragments. Further decomposition of these fragments, the desorption of hydrogen, and additional recombination reactions are found to be endothermic. The overall heat of reaction is calculated to be approximately -16 kcal if written in terms of monomeric gas phase units. If it is considered that trimethylaluminum and dimethylalane may exist as dimer gas phase units, the reaction is endothermic by approximately 16 kcal. At high temperatures both dimethylalane and trimethylaluminum share a strongly activated pathway for methyl dehydrogenation which produces a carbon contaminated surface. The experimental barrier is found to lie near 40 kcal for the methyl decomposition reaction. Theoretical calculations of this impurity incorporation pathway predict a methyl decomposition activation barrier near 40 kcal, in good agreement with experiments. The full ab initio model includes elementary reactions leading to growth, surface diffusion of the active methyl groups, methyl decomposition reactions to produce surface carbon, and the alternative (not experimentally observed) surface reaction pathway to form methane. Comparisons are made where both theory and experiment overlap and agreement is found to be good (within approximately ±5 kcal).

2:40pm SS2-TuA3 Low-Symmetry DFT Diffusion Barriers and Dimer Dynamics in Homoepitaxial Growth of Al(111), *A. Bogicevic*³, *J. Strömquist*, *P. Hyldgaard, G. Wahnström, B.I. Lundqvist*, Chalmers Univ. of Tech. and Göteborg Univ., Sweden

From fractals to compact islands, epitaxial growth offers an exotic variety of surface morphologies that emanate from a handful of elementary atomic diffusion processes. Adsorption calculations have hitherto been limited to high-symmetry configurations, or to semi-quantitative methods. Using extensive density-functional calculations on parallel computers, we map out barriers for self-diffusion at steps, kinks, and corners on Al(111). The results include an unexpected exchange mechanism at kinks and a large barrier anisotropy at corners. Using transition state theory we are able to transform the barriers into a set of activation temperatures and hereby predict various growth modes as a function of temperature. New STM experiments confirm four of our main results in great detail, including the fractal-compact island transition and the transition to equilibrium shaped islands. The central role dimer stability and mobility plays during nucleation and in later stages of growth has motivated us to study Al dimer diffusion at 0 and 5% compressive strain. The smooth potential energy surface enables a long-ranged attraction between the dimer atoms, leading to a substantial temperature window in which dissociation is frozen and fascinating dimer dynamics takes place. Surface relaxations play a prominent role in the uncovering of unexpected ground states, which should be easy to verify with, e.g., STM measurements of dimer height or dimer direction. A new diffusion mechanism is found, where dimers migrate by concerted sliding. The effect of elastic strain on dimer diffusivity is addressed, and its impact on the epitaxial growth mode is discussed.

3:00pm SS2-TuA4 STM and LEIS Study of Oxygen-Induced Restructuring of Rutile TiO@sub 2@(110)(1x1) Surface, M. Li⁴, W. Hebenstreit, Tulane University; D.R. Jennison, Sandia National Laboratories; U. Diebold, Tulane University

The rutile TiO@sub 2@(110) surface is one of the most-popular substrate in the surface science of metal oxides. We show that the exact surface preparation conditions critically influence the surface structure and morphology of this material in a rather unexpected way. TiO@sub 2@(110) surfaces, prepared by sputtering and annealing at 850 K in UHV, exhibit a (1x1) surface termination and flat, several hundred Å wide terraces. After exposure to oxygen at elevated temperatures (onset ~470 K), the surfaces are covered with small (typically tens of Å wide) terraces with monoatomic step height and the same (1x1) structure. On top and in between these terraces appear patches of an irregular network consisting of interconnected rosettes (width ~ 7 Å) with pseudohexagonal symmetry. The positions of atoms within the network are consistent with an incomplete TiO@sub 2@(110) layer. Ab-initio LDA calculations support the stability of the proposed structural model. It contains undercoordinated atoms with an electronic structure that is distinctly different from (1x1) terminated surfaces. LEIS measurements of surfaces annealed in @super 18@O@sub 2@ clearly show that new TiO@sub 2@ layers are formed through outdiffusion of interstitial Ti cations from the reduced bulk to the surface where they react with ambient oxygen. The kinetics of this 'restructuring' mechanism as well as possible implications for the surface chemistry of TiO@sub 2@ are discussed.

3:20pm SS2-TuA5 A Study of the Relationship Between Si/SiO@sub 2@ Interface Charges and Roughness, *L. Lai*⁵, *K.J. Hebert, E.A. Irene,* University of North Carolina, Chapel Hill

This study examines the correlation between interface micro-roughness and charges. Atomic force microscopy (AFM) and a newly developed area roughness function, A(RMS,D@sub F@)@footnote 1@ which couples two roughness parameters, root mean square (RMS) and fractal dimension (D@sub F@), are used to reliably and accurately characterize surface micro-roughness. For the common surface area computation methods, this leads to large round-off errors. This new area roughness function obviates this problem, and it is not only a sensitive roughness parameter, but also a reliable area extracting tool for surfaces with micro-roughness. Microroughness has a small vertical magnitude relative to the large horizontal data sampling interval. Interface charges (D@sub it@ and Q@sub f@) are measured using high frequency and quasistatic capacitance-voltage methods. These charges are reported in per unit area, so in order to obtain reliable charges levels, one must know the area. This study is divided into

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three parts where smooth, purposely roughened, and purposely smoothened Si substrates are used to make MOS capacitors. For smooth samples, we found that interface charges decrease as the oxidation time increases. Purposely roughened substrates show that there is a correlation between interface roughness and charges. When the correct area, A(RMS,D@sub F@), is used, the excess interface charges due to roughness are accounted for. Roughened then smoothened substrates show that the rate of decrease of the corrected charges with respect to oxidation time become about the same as those from smooth substrates. We conclude that the increases of D@sub it@ and Q@sub f@ with Si roughness are due entirely to the area increase and orientation changes that result from roughness. @FootnoteText@ @footnote 1@ L. Lai and E. A. Irene, J. Vac. Sci. Technol. A. submitted (1998).

3:40pm SS2-TuA6 The Chemistry and Formation of Ordered Organic Molecular Films on Silicon (001)-2x1 Surfaces, J.S. Hovis¹, R.J. Hamers, University of Wisconsin, Madison

We have recently developed a novel method for growing ordered organic films on the technologically important Si(001)-2x1 surface. The reaction involves the interaction of a surface Si=Si dimer with a C=C double bond from an unsaturated alkene, resulting in the formation of two new Si-C @sigma@ bonds. Due to the directional nature of @pi@ bonds the Si=Si dimer bond is able to act like a template, controlling the locations and rotational orientation of the individual adsorbed molecules. One unique aspect of this growth method is the fact that the molecules adsorb without dissociation, leading to a well defined interface between the silicon substrate and the organic film. We find that a number of molecules, including cyclopentene, 1,5-cyclooctadiene, and 1,3,5,7-cyclooctatetraene form films that exhibit in-plane optical anisotropies on the length scales of centimeters when adsorbed on 4°-miscut (single-domain) wafers. The molecules 1,5-cyclooctadiene and 1,3,5,7-cyclooctatetraene form monolayers that terminate with ordered arrays of C=C double bonds at the vacuum-surface interface and the ability to grow further layers will be discussed. We have also examined the adsorption of 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene on the Si(001) surface. These molecules can form two different products on the surface; one of which is more thermodynamically favorable. Our studies show that both possible products are formed, indicating that kinetics play a larger role in the adsorption probability than do thermodynamics. Experimental evidence using scanning tunneling microscopy (STM), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) will be shown as will the results of ab inito calculations.

4:00pm SS2-TuA7 ToF-SIMS Characterization of the Interaction Between Vapor-Deposited AI Atoms and an Ordered Array of Organic Functional Groups, *G.L. Fisher*², *A.E. Hooper*, The Pennsylvania State University; *R.L. Opila*, Bell Laboratories, Lucent Technologies; *D.L. Allara*, *N. Winograd*, The Pennsylvania State University

The room temperature vapor deposition of up to 4Å of Al metal onto monolayers of @omega@-functionalized alkanethiolate molecules, of structure HS-(CH@sub 2@)@sub n@-X, self-assembled on polycrystalline Au was studied using static ToF-SIMS, XPS and IRS. Deposited Al was found to be highly reactive with methylester organic functional groups (OFGs). The data indicate a titration of one Al atom per methylester OFG, and the ether bonds appear to be unperturbed. Thus, deposited Al reacts solely with carbonyl oxygen of the OFG forming a uniform dielectric with an Al-O-C bonding arrangement. Upon saturation of methylester OFGs with deposited Al, further deposition results in formation of metallic overlayers. Deposited AI was found to be unreactive with methyl OFGs. Instead, the deposited Al diffuses through the monolayer to the monolayer/Au interface via thermally activated transient defects. Here, the Al atoms are observed to disrupt the Au-S bonding to form stable Au-Al-S bonds that quench further transient defect formation. As the deposition progresses deposited AI is observed to form islands on top of the monolayer. Island formation in this case is a result of physisorbed Al; no chemical reaction is observed. Penetration of deposited Al through the methylester-terminated monolayer to the monolayer/Au interface was not observed. Reaction between deposited AI and the methylene backbone of methyl-terminated and methylester-terminated monolayers was not observed.

4:20pm SS2-TuA8 The Reactivity of Surface Defects on the MoS@sub 2@(0001) Basal Plane: Methanethiol and Thiophene Reactivity Studies, *C.G. Wiegenstein*³, *K.H. Schulz*, Michigan Technological University

Molybdenum disulfide based materials are important industrial catalysts for the removal of aromatic organosulfur compounds from petroleum feedstocks. The removal of sulfur compounds is important since sulfur is a known catalysts poison. Although there have been significant amounts of study on the structure of the industrial hydrodesulfurization catalysts, there is still a significant amount of uncertainity as to the surface chemistry and reactivity of the organosulfur compounds on the catalyst surface. Information on surface intermediates and adsorbate structures is hindered by the high pressures used in commercial HDS reactors. MoS@sub 2@ grows large sheets of sulfur terminated planes which are not catalytically active towards thiophene. Wiegenstein and Schulz@footnote 1@ attempted to prepare basal surfaces with large defect densities using deuterium adsorption, but were not successful. Although defects were produced by adsorption of deuterium atoms on sulfur anions which subsequently desorbed as deuterium sulfide, no significant changes were observed in the population of ethyl-thiolate surface species following repeated sample exposures to atomic deuterium. However, reactive MoS@sub 2@(0001) surfaces have been prepared using short ion bombardment times. Three different surface preparation treatments were used: a freshly cleaved surface; a 30 second ion-bombarded surface; and a 60 second ion-bombarded surface. An increase in the population of the higher temperature state was observed as ion-bombardment time was increased. AES results demonstrated that surface sulfur was preferentially removed via ion-bombardment, and thus, the higher temperature state has been identified as arising from methyl-thiolate adsorption at defect sites thought to be sulfur vacancies. This paper will give the details of these studies, and will report on present efforts examining thiophene decomposition on ion-bombarded MoS@sub 2@(0001) surfaces. Finally, the usefulness of the defective basal plane as a model HDS catalyst will be discussed. @FootnoteText@ @footnote 1@Wiegenstein and Schulz, Surface Science, 396 (1998) 284.

4:40pm SS2-TuA9 The Influence of Chlorine on the Dispersion of Cu Particles on Cu/ZnO(0001) Model Catalysts, A.W. Grant⁴, University of Washington; A. Jamieson, Massachusetts Institute of Technology; T. Evans, University of Manchester, United Kingdom, UK; G. Thornton, University of Manchester, United Kingdom; C.T. Campbell, University of Washington

Adsorbed chlorine is thought to affect the dispersion of metal catalysts on oxide supports. We have studied this by vapor depositing thin films of Cu onto Zn-terminated ZnO(0001), both with and without a pre-exposure of Cl@sub 2@. First, the adsorption of Cl@sub 2@ was studied on ZnO using XPS, LEIS, work function, and band-bending. A close-packed monolayer of Cl adatoms forms at saturation with 0.31 Cl adatoms per Zn site. The work function increase of 2.2 eV indicates anionic Cl@sub ad@. Without Cl@sub ad@, vapor-deposited Cu grows in two-dimensional islands that cover ~33% of the ZnO, after which these islands thicken (i.e., as 3D Cu particles) while the clean ZnO between these Cu islands gets covered with Cu only very slowly. The presence of Cl@sub ad@ decreases the fraction of the surface that is covered by Cu islands by ~3-fold, so Cl@sub ad@ either decreases the number of 2D Cu islands or their critical area before thickening. This is consistent with weaker binding of Cu to the Cl covered surface than to the clean ZnO. In addition, Cl@sub ad@ not only covers the surface of the ZnO, but also covers the surface of the Cu islands, as suggested by the constant CI-LEIS signal during Cu deposition. This was verified further by following the formate-derived TPD features from HCOOH adsorption, which are distinctly different for Cu and Zn sites on Clfree Cu/ZnO(0001). Pre-dosed Cl virtually eliminated the 575K Zn-formate peak. When Cu was vapor-deposited onto a Cl-precovered surface, neither the Zn- nor Cu- formate peaks were observed. Apparently, Cu displaces some of the Cl adatoms from Zn sites, and they subsequently cover the Cu islands.

5:00pm SS2-TuA10 Modeling Molybdenum Carbide-Based Hydrodesulfurization (HDS) Catalysts Using Carbon and Sulfur-Modified Mo(110) Surfaces, C.L. Roe⁵, K.H. Schulz, Michigan Technological University Mo@sub 2@C catalysts have shown potential for commercial use in hydrodesulfurization (HDS) processes. Although these molybdenum carbide catalysts look encouraging as replacements for MoS@sub 2@based catalysts, questions remain regarding the fundamental surface

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chemistry associated with the HDS of organosulfur molecules on carbided and sulfided molybdenum catalyst surfaces. Previous surface science studies examining HDS reactions have focused on using Mo(110) and Mo(100) surfaces as model catalysts, but have not been extended to include models of the newer Mo@sub 2@C-based materials. To further investigate the suitability of Mo@sub 2@C for HDS applications, the interaction of sulfur-containing molecules with molybdenum surfaces was examined by utilizing carbon and sulfur-modified Mo(110) single crystals as model catalysts. Specifically, the reactivity of ethanethiol, 1,2ethanedithiol, and thiirane were studied on the clean Mo(110) and p(4x4)-C/Mo(110) surfaces as a function of sulfur coverage. Ethanedithiol TPD experiments performed on the clean and carbon modified Mo(110) surfaces produced similar reaction products, although changes were observed in selectivity. On the clean Mo(110) surface, the major products observed during TPD experiments were acetylene, ethylene, vinyl thiol, and ethanethiol. However, the reaction of ethanedithiol on the p(4x4)-C/Mo(110) surface produced acetylene, ethylene, and ethanedithiol. Product molecules are thought to arise from two distinct types of surface intermediates: 1) a monodentate thiolate species and 2) a bidentate organosulfur metallocycle. We propose that vinyl thiol and ethanethiol are produced via C-S bond scission and subsequent hydride elimination of the thiolate intermediates, and that the surface metallocycles undergo C-S bond scission to yield acetylene and ethylene. On the carbon-modified surface, complete desulfurization of ethanedithiol occurs upon decomposition, yielding only hydrocarbon products. With increasing sulfur coverage, a decrease in reactivity and a shift in desorption features to lower temperatures is observed for ethanedithiol on the clean and carbonmodified surfaces. Additionally, experimental results on the reaction of ethanethiol and thiirane on the Mo(110) and p(4x4)-C/Mo(110) surfaces will be discussed.

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