Friday Morning, October 19, 2007

Surface Science

Room: 608 - Session SS1-FrM

Surface Dynamics

Moderator: A.L. Utz, Tufts University

8:00am SS1-FrM1 Formation and Dynamics of Sputter Ripples on an Epitaxially Grown Au Surface, *K. Mitchell*, A. Yazdi, N. Ingle, T. Tiedje, University of British Columbia, Canada

Under bombardment by a rastered 30keV Ga^+ ion beam, a flat epitaxially grown Au surface is found to exhibit the well known sputter ripple instability as first observed by Bradley and Harper.[1] These ripples exhibit a characteristic lateral length scale on the order of 100nm and a short-range RMS saturation height on the order of 10nm after receiving a fluence of approximately 1500 ions/nm^2. The starting surface is grown under UHV at 350°C on a freshly cleaved mica substrate resulting in a 0.5μm film with flat areas up to 8μm^2 having an RMS roughness of 0.5nm. Accurate topography data are gathered using ex situ AFM on areas exposed to increasing ion fluence to track the increase in roughness associated with the pattern formation, while in situ SEM imaging is used to observe the dynamics before and after the ripples have formed. These experimental data are compared to 2D numerical solutions of a non-linear partial differential equation which captures the essential features of height saturation, characteristic length scale and parabolic ripple shape. A state of the art fourth-order "exponential time differencing" method as perfected by Kassam and Trefethen[2] is used to advance the solution in time while high accuracy spectral methods are used to compute spatial derivatives. The equation is similar to the chaotic Kuramoto-Sivashinsky equation, but with an additional higher order non-linear term as derived by Castro and Cuerno.[3] Like the Kuramoto-Sivashinsky equation, linear terms of competing stability set the initial characteristic length and growth rate, while the non-linear terms are responsible for the height saturation and surface shape. The additional non-linear term causes an increase in the characteristic time, length and height scales after saturation has occurred. By adjusting the strength of the new non-linear term, the solutions can be tuned to match the morphology of the experimentally observed surface. The resulting equation parameters are then able to give information about the physical constants involved in the experiment.

[1] Bradley, Harper, J. Vac. Sci. Technol. A 6,2390 (1988)
[2] Kassam, Trefethen, SIAM J. Sci. Comp. 26, 1214 (2006)
[3] Castro, Cuerno Phys. Rev. Lett. 94, 016102 (2005)

8:20am SS1-FrM2 Charge Transfer Dynamics in Alkanethiolate Self-Assembled Monomolecular Films, *M. Zharnikov*, Universität Heidelberg, Germany, *S. Neppl*, Technische Universität München, Germany, *A. Shaporenko*, Universität Heidelberg, Germany, *U. Bauer, D. Menzel*, Technische Universität München, Germany, *P. Kao, D. Allara*, Pennsylvania State University, *P. Feulner*, Technische Universität München, Germany

Whereas static conductance of molecules arranged in self-assembled monolayers (SAMs) has been extensively studied, less is known about the dynamics of the charge transfer in these systems. We show that the latter phenomena can be successfully addressed by resonant Auger electron spectroscopy, using the core hole clock (CHC) method. For the test system, nitrile-substituted alkanethiolate SAMs, we obtained clear, quantitative results on the characteristic transfer time of the resonantly excited electron along the molecular chain to the conductive substrate in good agreement with theory. As compared to previous studies, the charge transfer pathway in our experiment was unambiguously defined by resonant excitation of the nitrile tailgroup attached to the alkyl backbone. This particular tailgroup occurs to be a good candidate for such studies because of a suitable core hole lifetime (CLT) and the large contrast between resonant and non-resonant core decay spectra. The approach, used by us, avoids any contact and reproducibility problems and, by selection of suitable ligands with appropriate values of CLT and resonance position, spans a wide dynamic range. Extension to other functional groups is possible and promises to become a very valuable new source of information on charge dynamics in layers important for molecular electronics.

8:40am SS1-FrM3 Dynamics of Analyte Binding onto a Metallophthalocyanine: NO/FePc, *S.R. Bishop*, N.L. Tran, G.C. Poon, A.C. Kummel, University of California, San Diego

The investigation of the gas-surface reaction dynamics of NO with an iron phthalocyanine (FePc) monolayer utilizing King and Wells sticking measurements is reported. The initial sticking probability is determined to be a function of both incident molecular beam energy (0.09 - 0.4 eV) and surface temperature (100 - 300 K). NO adsorption onto FePc saturates at 3% of a monolayer (ML) 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. It is determined the NO molecule adsorbs to the FePc monolayer via a multiple pathway precursor-mediated chemisorption mechanism. The absorption mechanism of NO onto FePc was confirmed by control studies of NO sticking onto metal-free H_2Pc, inert Au(111), and reactive Al(111).

9:00am SS1-FrM4 Atomic Scattering as a Probe of Polymer Surface and Thin Film Dynamics, *M.A. Freedman**, S.J. Sibener, The University of Chicago

We have studied the vibrational dynamics of self-assembled monolayers (SAMs) and polymer thin films, two complex systems of great technological interest, using the highly surface-sensitive and non-perturbative technique of low-energy helium atom scattering. While this technique has traditionally been used for single crystals and simple adsorbates on crystals, recent work in our group and elsewhere has expanded these studies to ordered organic monolayers. We have further broadened the range of studies performed with helium atom scattering to determine how much information can be gleaned from soft, disordered systems. We have shown that this technique provides a novel means for studying surface vibrational dynamics at these complex interfaces. We explored the interaction between the alkanethiol chains of the SAMs and the Au(111) substrate by investigating the energy of single phonon modes as a function of chain length. The fact that the observed phonon mode is dispersionless and exhibits no dependence on chain length indicates that the interaction between the adsorbate and substrate in the sagittal plane is dominated by single-chain harmonic-oscillator-type interactions. The energy of the single-phonon mode of decanethiol is larger than other chain lengths because its commensurate structure to the reconstructed Au(111) surface leads to stronger binding. We investigated the polymer thin film interface to determine the effect of nanoconfinement and polymer species on the vibrational dynamics. We find that helium atom scattering is a sensitive probe of the effect of nanoconfinement on the surface dynamics of poly(methyl methacrylate) (PMMA). Specifically, a reduction in the mean-square displacement derived from the elastic scattering and the reduced propensity for annihilation events in inelastic spectra indicate that thinner films are stiffer, perhaps due to substrate interactions. The inelastic spectra of PMMA, polystyrene, and polybutadiene have similar rates of intensity decay and absolute values of full width half maximum with increasing surface temperature. Deviations from a semiclassical scattering model and the linear increase in full width half maximum with increasing surface temperature indicate changes in the vibrational dynamics. We have shown that helium atom scattering is a sensitive probe of complex systems and may indeed give insight on whether the onset of glassy dynamics in the bulk affects dynamics at the topmost interface.

9:20am SS1-FrM5 Local Electronic Properties of Molecular Assemblies at Surfaces, *J.I. Pascual*, Freie Universität Berlin, Germany **INVITED**

The electronic properties of inorganic functional materials can be understood and predicted from a conceptual knowledge of electron dynamics. However, when organic molecules are to be used in electronic devices an atomistic picture of molecular bonding is additionally required. Local phenomenology occurring at the nanoscopic scale related with molecular chemical bonding, and hence with electronic coupling, governs many of the mesoscopic properties of organic devices. On the one hand organic-inorganic bonding can be more relevant than the molecular functionality itself. On the other, intermolecular interactions play a key role in structural organization of the molecular layer, and eventually govern the

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three-dimensional growth of molecular thin-films, beyond the interface limit. Our research in Berlin aims to provide a molecular scale picture about interactions occurring at the inorganic/organic interface. Our approach to this goal follows a combination of low-temperature scanning tunnelling microscopy and spectroscopy measurements with density functional theory simulations. We characterise the electronic structure of single molecules on a surface with sub-nanometer resolution in order to resolve the influence of local parameters (molecular orientation, neighbourhood, conformation,…) on its properties. Non covalent intermolecular interactions are also relevant at the inorganic interface, and may lead to the construction of three-dimensional supramolecular nanostructures with interesting electronic properties. In this seminar I will present several of our recent results about the electronic configuration of model molecular systems like C60, fullerene-based nanostructures and charge-transfer complexes on metal and semiconductors surfaces. The electronic configuration of the molecular ensembles will be analyzed in terms of their local neighbourhood and the degree of electronic coupling with the metal suface.

10:00am SS1-FrM7 Reactions of Atomic Hydrogen with Self Assembled Monolayers, *J.M. Gorham*, *B. Smith, A. Stover, J.D. Wnuk, H. Fairbrother*, Johns Hopkins University

The interaction of atomic hydrogen with hydrocarbon and semi-fluorinated self assembled monolayers (SAM) has been studied in-situ using x-ray photoelectron spectroscopy (XPS) and ex-situ contact angle measurements. Results indicate that atomic hydrogen (AH) reactions with alkanethiolate SAMs are strongly dependent upon the hydrocarbon chain length. For short chained SAMs (ie. C_9 and C_{12}), AH permeates rapidly through the hydrocarbon film and reacts primarily with the native thiolate bond resulting in chain desorption, as evidenced by a simultaneous loss in both carbon and sulfur. Conversely, sulfur was removed preferentially from longer chained alkanethiolates (ie. C_{16} and C_{18}), followed by the AH mediated erosion of the hydrocarbon film. The different reaction pathways for the long and short chain SAMs are due to effect of chain length on the residence time of AH in the hydrocarbon overlayer. In contrast to the short chain SAMs, AH reactions within the hydrocarbon film become important due to the increased length of the alkyl chain. Reactions of AH with semi-fluorinated SAMs (e.g. Si-$(CH_2)_2(CF_2)_5(CF_3)$) were consistent with a kinetically controlled process initiated by H atom abstraction from C-H bonds within the SAM. Secondary reactions of the carbon-centered radicals formed in the organic film with AH leads to the desorption of fluorocarbon radicals (e.g. $CF_3(CF_2)_5$). As a result of this reaction mechanism, the rate of fluorocarbon loss from the film is proportional to the adsorbate coverage and the flux of AH. The decrease in contact angle that occurs as a result of AH exposure is directly proportional to the coverage of CF_3 and CF_2 groups, providing a convenient route to control the surface wettability and other interfacial properties. In comparison to low energy electron modification, reactions of AH with semi-fluorinated SAMs are found to be more effective in etching the organic film.

10:20am SS1-FrM8 Misfit-Dislocation-Mediated Migration of Cu Nanostructures on Ag(111), *A.W. Signor, J.H. Weaver*, University of Illinois at Urbana-Champaign

Experimental studies of island migration, an important process in crystal growth and nanostructure synthesis, have mostly been limited to homoepitaxial systems. In these systems, either diffusion or evaporation and condensation of adatoms at the island edge gives rise to motion of the entire structure, leading to size-independent barriers, and diffusivities that scale with radius according to $D \sim R^{-B}$, with B =1, 2, or 3 for the simplest cases. The present work with Cu-Ag(111), a lattice-mismatched system, provides compelling evidence for a collective mechanism involving glide of misfit dislocations. Here, the entire structure is moved by one Burger's vector b= 1/6 <211> as the dislocation nucleates and glides through the island. Scanning tunneling microscopy (STM) images show that islands with magic sizes have a propensity for defect nucleation and glide leading to enhanced mobility. Quantitative analysis of island trajectories from STM movies collected at 130-200 K yield energy barriers as low as 0.35 eV for this process, even for multilayer islands containing up to ~90 atoms. Significantly, the barriers are very sensitive to island size, and hence island diffusivities do not scale with size in the ways predicted for traditional atomistic mechanisms, greatly affecting the overall coarsening kinetics.

10:40am SS1-FrM9 Subpicosecond Photodesorption and Photoreaction of CO on Pd(111), *P. Szymanski, A.L. Harris, N. Camillone III*, Brookhaven National Laboratory

We have examined the dynamics of the desorption and oxidation of CO on a Pd(111) surface following irradiation with ~110-fs pulses of 780-nm light. For a mixed layer of CO and atomic oxygen, both the desorption of CO and the production of CO_2 exhibit superlinear dependences on the absorbed laser fluence. The fluence dependence of CO desorption at saturation coverage is unaffected by the presence of coadsorbed atomic oxygen. For both CO/Pd(111) and (CO+O)/Pd(111) systems, the probability of CO desorption increases with the initial CO coverage due to population of lower-adsorption-energy sites. Two-pulse correlation (2PC) measurements of the photodesorption yield show rapid relaxation of the excited adsorbate-substrate complex and are well explained by an electron-mediated process. The photoinduced CO_2 production in the (CO+O) mixed layer, by contrast, involves mainly CO molecules with higher binding energies. The 2PC of the CO_2 product is five times broader than that of CO, suggesting that a different effective molecule-surface coupling is responsible for the reaction compared to the desorption. Our results are consistent with a picture where strong coupling between substrate electrons and adsorbed CO leads to high transient adsorbate temperatures, which can cause a subsequent reaction with oxygen if the barrier to direct CO desorption is sufficiently high.

11:00am SS1-FrM10 Grating-Coupled Excitation of Surface Plasmon Polariton Waves on Single Crystalline Cu(111) using Periodic Density Patterns of Rare Gas Monolayers for Adsorbate Surface Diffusion Study, *X.D. Zhu, Y.Y. Fei, X. Wang*, University of California at Davis

Using periodic density profiles of xenon (Xe) as thin as $1 \sim 5$ monolayers, we have excited and detected grating-coupled surface plasmon polariton waves (SPPW) on Cu(111) in ultrahigh vacuum. The periodic density profiles are formed by laser-induced thermal desorption with a pair of coherent laser pulses at vacuum wavelength of 0.532 microns. The periodicity of the profiles is 5.45 microns. By illuminating the xenon-density-grating-covered Cu(111) with a converging He-Ne laser covering a span of incidence angles from 66.4° to 74.4° and detecting the oblique-incidence reflectivity difference r_p/r_{p0} - r_s/r_{s0} vs. incidence angle with a multiple-element photodiode array, we observed the surface-plasmon resonance (SPR) peaked at the incidence angle of θ_{SPR} = 70.4° with a full-width at half-maximum of Δ_{SPR} = 0.29°. From the resonance angle θ_{SPR} and Δ_{SPR}, we have determined the optical dielectric constant of single crystalline Cu at 633 nm to be ε_{Cu} = -9.53 + i 0.142, markedly different from the literature values for evaporated Cu films. At elevated temperatures such that a xenon density grating on Cu(111) decays in contrast, the surface plasmon resonance as measured by r_p/r_{p0} - r_s/r_{s0} diminishes, reflecting the kinetic of surface diffusion of xenon on Cu(111).

11:20am SS1-FrM11 Dynamical Study of the Elastic Forces between Dislocations in a Strained Metal Film, *B. Diaconescu*, K. Pohl*, University of New Hampshire

Misfit dislocation networks can be used as natural templates for the growth of 2D large scale ordered arrays of clusters. The strain relaxation in metallic ultra thin films leads to the formation of large scale ordered arrays of dislocations, with unit cell sizes ranging from a few hundred to thousands of atoms. Understanding how the long-range stabilizing forces arrive from atomic interactions will provide a way of controlling the unit cell size and symmetry of the reconstructed surface. Here we show how, using atomically resolved scanning tunneling microscopy data, the dynamical evolution of vibrations of the 2D network of misfit dislocations of atomically thick Ag films on Ru(0001) can provide opportunities for measuring the long range elastic forces that stabilize the system. Fast-scanning STM data at rates of about 3 s/frame are providing a good temporal resolution of the process. In this way, an elastic constant of about 3 meV/Å^{-2} was obtained. The large size of the unit cell does not allow for full ab initio calculations, thus the experimentally determined long range stabilizing forces in such systems are related with first principles interaction parameters via 2D Frenkel-Kontorova models.

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