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 precursormediated 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 precursormediated 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 beamsurface scattering studies, the methane molecules in an industrial steamreforming 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 roomtemperature 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 CO₂ 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 CO₂ 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 CO2. The translational energy distributions and angular distributions of photodesorbing CO2 are compared to those of CO2 product from the photoreaction between coadsorbed CO and molecular O2. The similarities of the desorbing CO₂ distributions argue for similar exit channel dynamics following access to configurations near the transition state for CO₂ dissociation/CO oxidation (i.e., configurations at chemisorptive distances from the surface). Consequently, the initially physisorbed CO2 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 CO2.

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 CFCl₃ on Ag(111) have been investigated by timeresolved 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

^{*} 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-dithioanthracene¹ 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.

¹Kwon, K.Y., et al., Unidirectional adsorbate motion on a high-symmetry surface: "Walking" molecules can stay the course. Physical Review Letters, 2005. 95(16).
²Wong, 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 Ldimer). The signs of the scattering potentials by the impurity dimers were obtained by analyzing phase shift of the standing waves. The Si and Sn Ldimer, 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 dimers² 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.

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