

Wednesday Afternoon, November 5, 2003

Surface Science

Room 328 - Session SS+NS-WeA

Perspectives and New Opportunities

Moderator: R.A. Bartynski, Rutgers University

2:00pm **SS+NS-WeA1 The Birth and Evolution of Surface Science: Key Role of AVS, C.B. Duke**, Xerox Wilson Center for R&T **INVITED**

This presentation consists of a description of the birth and evolution of surface science as an interdisciplinary research area. It provides an overview of the themes developed in the Surface Science section of the AVS 50th anniversary issue of The Journal of Vacuum Science and Technology (JVST). The history of Surface science can be traced in terms of four waves of innovation [see e.g., C. B. Duke, Proc. Nat. Acad. Sci. 100, 3858 (2003)]. It was born in the mid 1960s based on the combination of ultra high vacuum technology, the recognition that "low energy" (500 eV) electrons exhibit inelastic collision mean free paths of atomic dimensions, and the commercial availability of single-crystal samples. The founding in 1964 of JVST and Surface Science marks this event. During the 1970s through the turn of the century the evolution surface science was strongly influenced by the microelectronics revolution that in turn was profoundly impacted by the evolving surface analytical capabilities. In the 1980s scanning probe microscopy was invented. It blossomed in the 1990s, launching a new era of digital imaging in surface science. Today, the frontiers of surface science are increasingly in its applications to characterize complex systems, including solid-liquid interfaces and fragile biological systems. Descriptions of these are taken from C. B. Duke and E. Ward Plummer, eds. "Frontiers in Surface and Interface Science", Surf. Sci. 500 (2002). In this presentation I trace the evolution of surface science through these four eras of its evolution with emphasis on how AVS has been instrumental in shaping each era.

2:40pm **SS+NS-WeA3 STM Single Atom/Molecule Manipulation: A New Dimension for Nanoscience and Technology, S.-W. Hla**, Ohio University **INVITED**

The fascinating advances in single atom/molecule manipulations with the STM-tip allow scientists to fabricate artificial atomic scale structures, to study local quantum phenomena or to probe physical and chemical properties of matter at single atom and molecule level on crystal surfaces. The STM-tip is not only used as an imaging tool but also as a manipulating and even, as an engineering tool in these experiments. In this presentation, our recent results of single atom/molecule manipulation experiments conducted by using a low temperature UHV-STM on metallic surfaces will be presented. A variety of cutting-edge STM single atom/molecule manipulation procedures, in combination with complementary tunneling spectroscopy and imaging, are systematically used to develop robust and innovative experimental schemes. Using these schemes, we examine the mechanical stability, electronic properties and chemical reactivity of single molecules at the spatial limit. The presentation will include vibrational spectroscopy/microscopy of single semi-phenyl molecules, electronic spectroscopy examinations of single Ag atoms/vacancies and self-assembled molecular films. Determination of mechanical strengths and internal conformational changes of large single molecules using tip-molecule interaction forces will be shown. Detail single atom movement mechanisms during quantum corral constructions with the STM-tip will be demonstrated. The extraction of single atoms from the native substrate and construction of various atomic scale structures on an atom-by-atom basis using the STM-tip will be presented by showing STM movies. @FootnoteText@ @footnote 1@S.-W. Hla, K.-H. Rieder, Ann. Rev. Phys. Chem. 54, 307-330 (2003). @footnote 2@H.C. Manoharan, C.P. Lutz, D.M. Eigler, Nature 403, 512-515 (2000). @footnote 3@B.C. Stipe, M.A. Rezaei, W. Ho, Science 280, 1732-1735 (1998). @footnote 4@C. Joachim, K. Gimzewski, A. Aviram, Nature 408, 541-548 (2000).

3:20pm **SS+NS-WeA5 Stark-Effect and Two-Electron Photon Emission in Scanning Tunnelling Spectroscopy, R. Berndt, G. Hoffmann, L. Limot, T. Maroutian**, University of Kiel, Germany; **P. Johansson**, University of Årrebro, Sweden; **J. Kroeger**, University of Kiel, Germany **INVITED**

We report a quantitative low-temperature scanning tunnelling spectroscopy (STS) study on the Ag(111) surface state over an unprecedented range of currents (50 pA to 6uA) through which we can tune the electric field in the tunnel junction of the microscope. We show that in STS a sizeable Stark effect causes a shift of the surface state binding

energy $E_{\text{sub S}}$, even at very low currents. Data taken are reproduced by a one-dimensional potential model calculation, and are found to yield a Stark-free energy $E_{\text{sub S}}$ in agreement with recent state-of-the-art photoemission spectroscopy measurements. Next, unusual emission of visible light is observed in scanning tunnelling microscopy of the quantum well system Na on Cu(111). Photons are emitted at energies exceeding the energy of the tunneling electrons. Model calculations of two-electron processes which lead to quantum well transitions reproduce the experimental fluorescence spectra, the quantum yield, and the power-law variation of the intensity with the excitation current.

4:00pm **SS+NS-WeA7 Electrostatic Potential Profile within a Biased Molecular Electronics Device: a Cavity QED Approach, J.W. Gadzuk**, National Institute of Standards and Technology

The fundamental principle behind a molecular electronics (MoleE) device is similar to that driving many resonant electron scattering or transmission processes; initial insertion of an electron into a resonance state, propagation in some manner (coherent, incoherent, or diffusive) that is a controllable characteristic of the resonance-supporting system, and final extraction of the selectively transmitted electron. The stages of a MoleE system responsible for the three-step conduction are often referred to as donor, bridge, and acceptor. The scattering or resonance properties depend amongst other things, upon the electrostatic potential profile along the bridge or molecular wire. Since the molecular wires are packed together within a self-assembled monolayer in real MoleE devices, the present study focuses on the electrostatics and dynamics of such structures, here formulated as a problem in cavity QED of a structured, polarizable continuum film of the bridge material inserted between parallel metallic plates rather than as one in conventional quantum chemistry. The plates (electrodes) and the molecular film are each characterized by their dielectric response functions and the donor/acceptor-electrode interactions by charge redistribution required to satisfy the appropriate electrodynamic boundary conditions. This approach provides fresh insights into the overall features of the electrostatic potential profile and select atomic-scale properties such as electrode-induced shifts in the resonance (aka HOMO and/or LUMO) energies within the molecules which in turn are crucial in determining the current-voltage characteristics of the MoleE device, as will be demonstrated.

4:20pm **SS+NS-WeA8 Quantum Size Effect Induced Modification of CO Chemisorption on Cu/fccFe/Cu(100), A.G. Danese, R.A. Bartynski**, Rutgers University

Nanoscale metal thin films can exhibit quantum size effects (QSE) whereby their electronic, structural, magnetic and chemical properties may differ greatly from those of the bulk. The quantum confinement of electrons due to high reflectivity scattering at the film's interfaces forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. We have studied the role of MQW states in the chemisorption of CO on n ML Cu/fccFe/Cu(100) where $\sim 2 < n < \sim 14$ using inverse photoemission (IPE) and temperature programmed desorption (TPD). IPE results show the unoccupied MQW states in the Cu overlayer increasing in energy as a function of increasing Cu thickness with MQW states crossing the Fermi energy ($E_{\text{sub F}}$) at 5 ML Cu and 11 ML Cu in both the bare and CO covered system. Accordingly the IPE intensity at $E_{\text{sub F}}$ oscillates as a function of Cu well thickness and temperature programmed desorption (TPD) performed on the CO covered Cu films exhibits modulations in the CO peak desorption temperature ($T_{\text{sub des}}$) which are correlated with these IPE modulations. The MQW states are quasi 2 dimensional (2-d) and we attribute this chemisorption QSE to the bottom of a 2-d subband that crosses $E_{\text{sub F}}$ every time a MQW is observed to cross $E_{\text{sub F}}$. This increases the density of states at $E_{\text{sub F}}$ available for the CO-Cu bond, thus strengthening the bond as observed by two $T_{\text{sub des}}$ maxima at 5 ML Cu and 11 ML Cu. Between these $E_{\text{sub F}}$ crossings, the DOS as measured by IPE intensity decreases and we observe that the two quantities oscillate together.

4:40pm **SS+NS-WeA9 Manipulating Single Metal Atoms with the Scanning Tunnelling Microscope, K.-F. Braun, K.H. Rieder**, Freie Universit@um a@t Berlin, Germany; **K. Flipse**, Eindhoven University of Technology, The Netherlands; **S.-W. Hla**, Ohio University

Scanning tunnelling microscopy has been used to manipulate single atoms, small molecules as well as larger molecules and parts of it. Lateral manipulation can be applied to position atoms for the construction of artificial assemblies on desired atomic sites. Although manipulation techniques have been used on a variety of systems only little is known about the interaction forces between microscope tip and adparticle. Here

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we present a detailed study of the lateral manipulation of Au and Ag atoms on Ag(111) and Ni(111) surfaces. We describe a complete picture of how single Ag atoms move on the various potential energy landscapes of a Ag(111) surface during a quantum corral construction by using an STM tip at 6 K. The threshold tunnelling resistance and tip-height to move the Ag atom across the surface are experimentally measured as $210 \pm 19 \text{ k}\Omega$ and $1.3 \pm 0.2 \text{ \AA}$... The experimental atom manipulation signals reveal remarkably detailed atom movement behaviour dependent on the surface crystallographic orientation and offer atomic-level tribology information. @footnote 1@ Manipulation experiments with Au atoms on the same Ag(111) surface show a voltage dependent threshold resistance above $\pm 100 \text{ mV}$. Possible current and field effects will be discussed. Measurements on Au atoms on a Ni(111) surface display even a long-ranged repulsive interaction for voltages below -300 mV . The influence of the electronic surface structure on the manipulation will be discussed. Electrons injected in the antibonding levels of the atom-surface system can weaken the bond to allow lateral manipulation at high voltages as well as desorb the atom. @footnote 2@ @FootnoteText@ @footnote 1@ S.W. Hla, K.-F. Braun, K.H. Rieder, Phys. Rev. B, Rapid Comm., accepted (2003). @footnote 2@ K.-F. Braun, K. Flipse, K.H. Rieder, in preparation (2003).

5:00pm **SS+NS-WeA10 Adsorption and Deprotonation of Dichlorothiophenol on Cu(111): STM-Based Hydrogen Abstraction and Thiolate Formation**, B.V. Rao, K.-Y. Kwon, J. Zhang, A. Liu, L. Bartels, University of California at Riverside

We present low-temperature scanning tunneling microscope (STM) measurements of the initial steps of the adsorption of di-chloro-thiophenol (DCTP), an aromatic thiol, on Cu(111). Upon adsorption of ultra-low coverages at 15 K individual molecules can be found on Cu(111) terraces which appear as large, flower-shaped protrusion in STM images. This is caused by the rotation of the molecule around the sulfur atom which rests at an on-top site of the substrate. Deprotonation to the thiolate may be caused by annealing to nitrogen temperatures or attachment/removal of electrons to/out of the molecule at a bias exceeding 300 mV. Following deprotonation, the sulfur atom shifts to a higher-coordinated substrate site and the molecules is fixed in place. STM-based vibrational spectroscopy reveals a pronounced S-H stretch mode at 320 meV before deprotonation, which is absent from spectra taken after deprotonation. The STM based hydrogen abstraction process can be accomplished reliably at -500 mV with a first-order dependence on the current. Perfect selectivity for the sulfur bound hydrogen is achieved even if the excitation current targets the benzene ring. Adsorption of 1 L of DCTP at nitrogen followed by annealing to ambient temperatures leads to the formation of an ordered structure comprised of pairs of DCTPs of opposite chirality in the adsorbed state. Further increasing the adsorbate coverage, more and more of the molecules do not lie flat on the surface but have the benzene ring pointing up.

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