Tuesday Morning, October 26, 1999

Nanometer-scale Science and Technology Division Room 6C - Session NS2-TuM

Molecular Electronics

Moderator: R.J. Hamers, University of Wisconsin, Madison

8:20am NS2-TuM1 Single Molecule Engineering: Synthesis of Individual Biphenyl Molecules on Cu (111) with STM Tip, S.W. Hla, Freie Universitat Berlin, Germany; L. Bartels, Columbia University; G. Meyer, K.-H. Rieder, Freie Universitat Berlin, Germany

In 1904, Fritz Ullmann et al. discovered the way to produce biphenyl from iodobenzene by using Cu as a catalyst. Ever since this process is known as Ullmann reaction and becomes a basic Chemistry textbook case. Due to its varsatility to use different substituted benzenes allowing large number of products and high purity results, it is widely used in lab-style synthetic chemistry. Altogether three elementary steps involve in this reaction process; iodine dissociation from iodobenzene, migration to meet two phenyl radicals and their association to form biphenyl. Here we show that we can perform all elementary steps of Ullmann reaction over single molecules in controlled manner and can synthesize individual biphenyl molecules on the Cu(111) surface for the first time by utilising various single atom and molecule manipulation techniques with a low temperature scanning tunneling microscope (STM) at 20 K. The synthesis steps involve iodine dissociation from single iodobenzene molecules with tunneling electrons and the resulting phenyl radicals were put together by laterally moving them with STM tip. The association of two phenyl radicals to form a bi-phenyl molecule was realised by simultanuously exciting them with tunneling electrons. The threshold tunneling voltage to dissociate the iodobenzene and the energy range of phenyl oscillation on Cu(111) were determined by using I-V single molecule tunneling spectroscopy.

8:40am NS2-TuM2 Scanning Tunneling Microscopy of Conjugated Oligomers on Si(100), *B. Grandidier*, *J.P. Nys*, *D. Stievenard*, *C. Krzeminsky*, *C. Delerue*, IEMN CNRS, France; *J.M. Raimundo*, *P. Frere*, *J. Roncali*, IMMO, Universite d'Angers, France

Conjugated oligomers have attracted considerable interest as possible molecular wires. Investigation of the interaction of these molecules with the silicon (100) surface is therefore useful to gain insight into the way the oligomers could be connected to the silicon surface. The adsorption of different oligothiophenes on silicon (100) 2x1 have been studied by scanning tunneling microscopy in ultra high vacuum. The current constant images of the oligothiophenes are strongly bias dependent and allow the determination of the adsorption sites. The reaction involves the thiophene ring with a single Si atom of the Si=Si dimer. Ab initio calculations are performed to better characterize the chemical nature of the bonding.

9:00am NS2-TuM3 Initial Growth of 3,4,9,10-perylenetetracarboxylicdianhydride (PTCDA) on Au(111): A Scanning Tunneling Microscopy Study, *I. Chizhov, A. Kahn, G. Scoles,* Princeton University

and morphology 3,4,9,10-The structure of perylenetetracarboxylicdianhydride (PTCDA) films deposited on Au(111) surface in ultrahigh vacuum is studied via scanning tunneling microscopy (STM). In the first monolayer, PTCDA molecules form well-ordered domains with two distinct structural phases. The first phase is characterized by a "herring-bone" arrangement of PTCDA molecules similar to that of a bulk PTCDA molecular crystal. The second phase, which had not been reported so far, is characterized by a molecular arrangement in a square pattern that does not have a known bulk analog. This second phase is less dense than the first. Only the "herring-bone" phase is consistently observed in the second and subsequent layers. The crystallographic orientation of the PTCDA layers, with respect to the Au substrate as well as with respect to each other, is directly determined from the STM images. At coverages above 2 monolayers, the formation of PTCDA islands with good molecular order is observed. Transient effects related to STM-induced dynamic changes in the PTCDA molecular layer are also discussed.

9:20am NS2-TuM4 Isolating, Imaging, and Electrically Characterizing Individual Organic Molecules on the Si(100) Surface with the Scanning Tunneling Microscope, *M.C. Hersam*, *J.W. Lyding*, University of Illinois, Urbana-Champaign

Molecular electronics shows great potential as an approach for fabricating nanoelectronic devices and circuits. Despite this potential, many fundamental problems remain unsolved. This paper outlines a three pronged approach that addresses key molecular electronic issues for molecules supported on STM-patterned hydrogen passivated Si(100) surfaces. First, feedback controlled lithography (FCL) has been developed as a reliable technique for making templates of individual dangling bonds on the Si(100):H surface. FCL detects individual H desorption events while patterning, thereby compensating for variations in tip structure. When the surface is then exposed to a flux of molecules, they bind individually to the prepatterned sites. With this technique, norbornadiene and copper phthalocyanine molecules have been intentionally isolated into predefined patterns. STM images reveal intramolecular detail and suggest mechanical behavior such as molecular rotation. Secondly, using STM spectroscopy, molecules' electronic properties have been revealed. Filled states tunneling conductance maps of copper phthalocyanine molecules exhibit an enhanced density of electronic states. However, in empty states, a ring of reduced local density of states surrounds each copper phthalocyanine molecule. Further multi-bias images reveal a more complex intramolecular electronic structure that helps to differentiate among the possible binding configurations of the molecule. Finally, an all-UHV scheme for isolating and, ultimately, electrically contacting STM-patterned nanostructures has been developed that utilizes a pre-defined p-n junction on a Si(100) substrate. With STM potentiometry, the junction is easily located, allowing for efficient registration of nanostructures after intermediate processing steps. In addition, by STM patterning across the depletion region, the electrical properties of selectively deposited nanostructures can be directly evaluated when the p-n junction is biased.

9:40am NS2-TuM5 Molecular Wires and Molecular Junctions: Tunneling. Injection and Transport, M.A. Ratner, Northwestern University INVITED Molecular wires, molecular interconnect structures, molecular emission devices and, indeed, much of molecular electronics requires efficient control of charge transport processes at the molecule/electrode interface. Direct measurements on individual molecular transport junctions are beginning to appear, and will be featured in this symposium. Understanding the conductance properties of molecular junctions requires a computational model that deals effectively with both the continuum (electrode) and discrete (molecular) aspects of the issue. The problem is similar to that of chemisorption, and the Hamiltonian models discussed are also similar. Because of this discrete/continuum coupling, the molecular levels are shifted and broadened. This leads to self energies that describe the effective state densities for injection and transport. The use of Landauer type expressions then leads to specific predictions for voltage dependence conductance in the coherent regime: most measures of individual junctions reported to date indeed can be characterized in this way. For actual injection and dissipative charge transport, the Landauer model is no longer appropriate. Here considerations of typical molecular behavior arise, and at least five different charge transport mechanisms can be posited. We will discuss some aspects of these mechanisms, advantages and disadvantages for long range charge transport in molecular wires, aspects of the energy dissipation problem and the energetic control of transport by design both of the molecule itself and of the interface.

10:20am NS2-TuM7 Self-assembled Molecular Electronics: Is the Interface Conducting?, T. Vondrak, C.J. Cramer, X.-Y. Zhu, University of Minnesota

The use of a single molecule as a 'quantum dot' or 'quantum wire' in charge transport has attracted considerable attention due to its exciting potential in future electronic devices. A number of groups have studied the electron transport in single aromatic molecules using thiol self-assembled monolayers (SAMs) on gold surfaces. A critical issue in interpreting experimental current-voltage measurements and in designing selfassembled monolayer of molecular electronics is understanding the interfacial electronic structure. We present a systematic study to address the title question. We probe both occupied and unoccupied electronic states at the interface using laser two-photon photoemission spectroscopy, in conjunction with electronic structural calculations. We choose phenyl or fluorophenyl group tethered to the metal surface at various distance in self-assembled monolayers on Cu(111). We found that, for phenyl attached to Cu via the -S- linker, the molecular LUMO can be stabilized by as much as 3 eV. This large change cannot be accounted for exclusively by polarization effects. The majority of the stabilization energy must come from direct, strong electronic coupling between the substrate and the adsorbate. Ab initio calculations on model molecules confirms this conclusion. This kind of strong electronic coupling is absent when the molecule is located at a similar distance, but weakly coupled to the surface. Thus, we may view the -S-metal linker as a conducting contact in SAMs of molecular electronics. Our result also suggests the importance of sigma states for electron transport in short molecular wires.

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10:40am NS2-TuM8 Scanning Potentiometry Studies of Charge Transport in Sexithiophene-based FETs using Conducting Probe Atomic Force Microscopy (CP-AFM), K. Seshadri, T.W. Kelley, C.D. Frisbie, University of Minnesota

Investigation of charge transport mechanisms in organic semiconductors is of immense importance to development of devices such as thin film transistors and organic-based LEDs. Of particular interest is @alpha@sexithiophene (6T), with a hole mobility high enough for flexible, "all plastic" devices. Conducting Probe Atomic Force Microscopy (CP-AFM) has been used to measure electrical transport characteristics of 6T. The semiconductor was deposited as crystals, ranging from 1 to 6 molecules (2-14 nm) in thickness and from 1-2 µm in diameter by vacuum sublimation onto SiO2/p-Si substrates, with lithographically defined Au contacts. The semiconductor crystallite grows across the gap between two electrodes, with a capacitively coupled gate electrode, so as to achieve a field-effect transistor configuration (FET). A Au-coated conducting AFM probe is brought into contact with the electrically biased 6T crystallite, and the potential is measured as a function of position. This is a scanning potentiometry experiment, involving mapping the local potential over the surface of the organic semiconductor. Mesoscopic transport measurements, in combination with AFM imaging, are a useful strategy for elucidating charge transport across grain boundaries, charge trapping, and other structure-transport relationships in organic materials.

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