

Thursday Afternoon, November 1, 2012

Electron Transport at the Nanoscale Focus Topic

Room: 16 - Session ET+SS+GR+SP-ThA

Electron Transport at the Nanoscale: Molecules and Defects

Moderator: S. Allen, The University of Nottingham, UK, J. Wendelken, Oak Ridge National Laboratory

2:00pm **ET+SS+GR+SP-ThA1 Molecule Substrate Interactions Probed by Scanning Tunneling Microscopy, H.-J. Gao**, Chinese Academy of Sciences **INVITED**

Molecule substrate interactions play an important role in constructing nanostructures of functionalities and controlling of the physical properties and thus have stimulated a great interest in the past decades. One of the challenges in this top is to make a single molecule or small quantum systems stably connected to a single metal atom on metal surfaces, and further to make the nanostructure create electric energy and optical/electro radiation. In the talk, I will present that by using Au adatoms of the Au(111) surface we have successfully formed a single molecule rotor array, isolated tetra-*tert*-butyl Zinc Phthalocyanine ((*t*-Bu)₄-ZnPc) molecules sticking to the Au adatoms of the Au(111) and rotating on the surface at 78 K. This kind of single molecular rotor was also found to be controlled by the different sites of the Au(111) surface using low temperature scanning tunneling microscopy (STM). Furthermore, by changing the molecular structure the same molecular family of the Pc, ZnPc and FePc can also modulate the rotation behavior of the molecular rotors. Given that the lateral structure of a molecule/substrate interface can be modified by the attachment of ligands, our results will be helpful for opening up the possibility to tailor physical properties of a single molecule or complex aggregates to the desired specifications.

2:40pm **ET+SS+GR+SP-ThA3 Electron Localization in Single Mixed-Valence Molecules, R.C. Quardokus, N.A. Wasio, Y. Lu, S.A. Kandel**, University of Notre Dame

Scanning tunneling microscopy (STM) is used to study two dinuclear organometallic molecules, meta-Fe₂ and para-Fe₂. These molecules share identical molecular formulas but differ in their positions of connectivity to the central phenyl ring. STM images of neutral meta-Fe₂ and para-Fe₂ show symmetrical distribution of electron density across the two metal centers. Chemical oxidation of these molecules leads to mixed-valence species. STM images of mixed-valence meta-Fe₂ show an asymmetric distribution of the electron density between the two metal centers. Despite the greater distance between the two metal centers, the electron density remains symmetric in mixed-valence para-Fe₂. Comparison with constrained density functional (CDFT) calculations leads to the conclusion that through-bond coupling of the two metal centers is more prevalent than through-space coupling. Further investigation of mixed-valence dinuclear organometallic molecules with asymmetric electron state density may open up the possibility for their use in molecularly based electronic devices.

3:00pm **ET+SS+GR+SP-ThA4 Rectification by a Single Molecular Diode, L. Adamska**, University of South Florida, *M. Kozhushner*, Institute of Chemical Physics, Russian Academy of Sciences, *I.I. Oleynik*, University of South Florida

Single-molecule rectification has been recently observed using the STM modulated break-junction technique in non-symmetric diblock dipyrimidinyl-diphenyl molecule covalently bound to metallic electrodes. To provide an insight to the nature of the rectification, first-principles calculations of atomic, electronic and transport properties of gold/molecule/gold junctions have been performed for both symmetrical tetraphenyl and asymmetrical dipyrimidinyl-diphenyl diblock molecules. The charge transport was found to occur by hole resonant tunneling mechanism via positively-charged hole states of the molecule, which are very susceptible to the external electric field and dispersive interactions with the metallic electrodes. It was found that the rectification effect in chemically-asymmetric dipyrimidinyl-diphenyl molecule is due to strong localization of the hole wave function at one end of the diblock under applied electric field. Such behavior is contrasted by symmetric I-V curves exhibited by symmetric tetraphenyl molecule.

3:40pm **ET+SS+GR+SP-ThA6 Electron Transport Study of Graphene Grain Boundaries Using Scanning Tunneling Potentiometry, K. Clark, X.-G. Zhang, I. Vlasiouk, A.-P. Li**, Oak Ridge National Laboratory

Graphene, due to its unique electronic structures, has quickly become one of the most notable "super-materials" poised to transform the electronics and nanotechnology landscape. The symmetry of the graphene honeycomb lattice is a key element for determining many of graphene's unique electronic properties, such as the linear energy-momentum dispersion and the reduced backscattering (i.e., high carrier mobility). However, topological lattice defects, such as grain boundaries and step edges, break the sublattice symmetry and can affect the electronic properties, especially in transport of graphene in unexpected ways. To utilize the full potential of graphene a complete understanding of the physical and electronic properties of defects in this system is needed. By using a scanning tunneling potentiometry method with a low temperature four-probe scanning tunneling microscope, two-dimensional maps of electrochemical potentials have been measured across individual grain boundaries on the graphene films grown on copper foil and transferred to SiO₂. An Atomic Force Microscope (AFM) is implemented to image the grain boundary that forms between individual graphene flakes that grow on the surface. The AFM imaging along with scanning tunneling potentiometry characterize the grain boundaries formed between coalesced grains on the SiO₂ surface. Results of the influence of the grain boundary on the electronic transport across this potentially revolutionary new electronic system will be presented. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

4:00pm **ET+SS+GR+SP-ThA7 Static and Dynamic Conductance in Topological Defects in Ferroelectrics, S.V. Kalinin**, Oak Ridge National Laboratory **INVITED**

Topological defects in ferroic materials are attracting much attention both as a playground of unique transport, magnetic, and ferroic phenomena and due potential applications in reconfigurable electronic devices. In this presentation, I will summarize recent studies of transport phenomena in 2D (domain walls) and 1D (vortexes and antivortexes) in ferroelectric materials by combination of piezoresponse force microscopy, phase-field modelling, and density functional theory. In particular, the observations such as memory effects and hysteresis in domain wall conductance, metallic conductivity of ferroelectric walls, and conductivity in vortex cores will be discussed. For domain walls, these observations are consistent with carrier accumulation due to presence of charged wall segments. We further demonstrate that a continuum of non-volatile metallic states across decades of conductance can be encoded in the size of ferroelectric nanodomains using electric field. For vortexes, modelling predicts that the core structure can undergo a reversible transformation into a metastable twist structure, extending charged domain walls segments through the film thickness. The vortex core is therefore a dynamic conductor controlled by the coupled response of polarization and electron/mobile vacancy subsystems with external bias. This controlled creation of conductive 1D channels opens a pathway for design and implementation of integrated oxide electronic devices based on domain patterning. Finally, recent insight on domain walls structure from combination of aberration corrected scanning transmission electron microscopy and phase-field theory will be discussed. Research supported (SVK) by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division and partially performed at the Center for Nanophase Materials Sciences, a DOE-BES user facility.

4:40pm **ET+SS+GR+SP-ThA9 Transport and Mechanical Properties of Molecular Junctions formed by Acetophenon Deposited on Si (100) Surface, M. Setvin, Z. Majzik, O. Krejci, P. Hapala, P. Jelinek**, Institute of Physics of ASCR, Czech Republic

One of the main challenges of Molecular electronics is to understand and control charge transfer through a reproducible single molecule contact between electrodes. Most investigations of electron transport through molecules have been performed in "blind" junction experiments, where the molecular conformation and contact geometry cannot be probed. Therefore large gaps in our knowledge remains since in molecular electronics the atomic-scale structure of the entire junction including the leads is important for its conductance properties.

Our goal is to study electrical transport through well-defined molecular junction on semiconductor surfaces. Formation of molecular junctions using organic molecules on semiconductor surfaces might lead to interesting phenomena. For example, the presence of the band gap in electrodes can

lead to the negative differential resistance observed in transport through molecules bonded to dangling-bond sites[1].

In this contribution, we investigate formation of molecular junction consisting of a single acetophenone molecule deposited on Si(100) surface in upright position by means of simultaneous AFM/STM measurements and DFT calculations. We used a modified UHV VT STM/AFM Omicron machine allowing simultaneous acquisition of the current and forces with atomic resolution using a tuning fork sensor[2]. The simultaneous acquisition of the tunneling current and force during tip approach allows precise control of contact formation and its consequence on the charge transport through molecular junction[3]. On other hand, DFT simulations provide more insight into interaction mechanism between probe and molecule. It also helps to understand induced structural and electronic relaxations during tip approach.

References

- [1] T. Rakshit et al. Nanoletters 4, 1803–1807 (2004).
- [2] Z. Majzik et al, Beilstein J. Of Nanotech. 3, 249 (2012).
- [3] N. Fournier et al Phys. Rev. B 84, 035435 (2011).

5:00pm **ET+SS+GR+SP-ThA10 Experimental Determination of the Charge Neutrality Level (CNL) of Conjugated Polymers, W. Wang, R. Schlaf, University of South Florida**

The charge neutrality levels (CNL) of poly-(3-hexylthiophene) (P3HT) and poly-[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) were determined. This was achieved by investigating a number of interfaces between these conjugated polymers and metals with varying work function. The interfaces were fabricated using the electrospray deposition technique, which allows the direct deposition of polymers from solution into vacuum environment without interference of significant surface contamination. This enabled the measurement of the charge injection barriers at clean polymer interfaces without contamination interlayer with photoemission spectroscopy. The results of these measurements enabled the establishment of the correlation between barrier heights and substrate. The results indicate that conjugated polymer interfaces form in a similar fashion as small molecular materials interfaces to metals as described by the 'induced density of states' (IDIS) model. In contrast, the presented results also suggest that the 'integer charge transfer' (ICT) model, which was developed for polymer/metal interfaces, only describes interfaces prepared under atmosphere or inert environment, where the presence of contamination weakens the interaction between the materials in contact.

5:20pm **ET+SS+GR+SP-ThA11 Investigation on the Electronic Structure of Arylthio (ArS)-functionalized CdSe Nanoparticle Hybrid Materials, Z. Li, University of South Florida, K. Mazzi, University of Washington, S. Gutmann, University of South Florida, C.K. Luscombe, University of Washington, R. Schlaf, University of South Florida**

CdSe nanoparticles are a promising material for 3D heterojunction solar cells due to their tunable electronic and optical properties through size control. By covalently bonding these nanoparticles to organic ligands, a novel light absorption, charge separation and transportation system can be formed. This presentation will discuss efforts to measure the hybrid-internal orbital line-up at the nanoparticle/ligand junction. Photoemission spectroscopy was used to characterize a prototypical arylthio (ArS)-functionalized CdSe molecule nanoparticle/ligand hybrid. Generally, in such hybrid molecules, the highest occupied molecular orbital (HOMO) emission is a superposition of the emissions of the nanoparticles and that of the organic ligands. This superposition makes the direct study of the orbital line-up through PES measurements impossible. Hence, a new technique needed to be developed to delineate the orbital line-up at such inner-molecular contacts. This was achieved through the additional investigation of the isolated components, which yielded detailed information of their electronic structure. Combination of this data with measurements on the assembled hybrid molecules enabled the determination of the orbital line-up at the interface. The influence of the covalent bond on the orbital line-up was investigated by comparing the hybrid line-up with the electronic structure of a physisorbed interface formed between the hybrid components. This interface was prepared through in-vacuum electrospray deposition of a thin film sandwich of CdSe and ArSH films, while measuring the transition from the CdSe to the ArSH electronic structure.

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