SYMPOSIUM T
Molecular Electronics
April 13 - 15, 2004

Chairs

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* Invited paper
This talk will present our latest research in carbon nanotube electronics and devices. The content will include ohmic contact, ballistic electron transport in both metallic and semiconducting nanotubes, pushing the performance limit of nanotube field effect transistors, and the scaling properties of both metallic and semiconducting nanotubes.

I will present results of transport and spectroscopic experiments and theoretical calculations to address such issues as the nature of the switching in nanotube transistors, the nanotube-metal electrode interaction, the resulting charge transfer and the role of the ambient environment on the transport properties. I will also discuss how these findings can be utilized to control the characteristics of nanotube field-effect transistors. Carbon nanotubes are direct gap materials and their one-dimensional structure has important implications for their electro-optical properties. I will show that an ambipolar nanotube field-effect transistor device can act as a single molecule electrically-driven light source. I will present photoluminescence spectra, polarization data, quantum yields and the dependence of light intensity on drain and gate bias that prove that the light is generated through radiative recombination of electrons and holes in the nanotube. The reverse process of current generation through IR laser irradiation of a single nanotube FETs will also be demonstrated. Resonant photoconductivity spectra from individual nanotubes will be compared with experimental absorption spectra and theoretical calculations on nanotube excitation states.

Junctions play a major role in determining the conductive properties of a circuit consisting of nanotubes and metal electrodes. The band structure of the nanotubes and the metal electrodes, coupled with the environment result in the unique current voltage characteristics. We have made use of conductive tip atomic force microscopy to study individual nanotube circuits. Through combination of scanning potential and current spectroscopy, and using the principle of transmission line model, we have isolated the contributions to the resistivity along the nanotube from that of the junctions. The contact potential between the nanotubes and the metal electrodes are found to depend on the specific metal used, and the environment. Atmospheric gases, chemical treatment, and substrate characteristics on which the circuit is fabricated strongly affect the resistance of these junctions. We believe that the adsorbents perturb the work function difference between the nanotube and metal causing these changes. This phenomenon can be used to tune the contact resistance, making it possible to identify recipes for different modes of current injection into the nanotubes. We can also consider the variations as a possible chemical sensor. Multiple nanotubes on a substrate form a complex network, with many junctions. Charge transport through the interface between molecules is expected to be associated with a very high resistance. We have found that appreciable current can be made to flow from one nanotube to another, which is in physical contact. The associated resistance is comparable to that of metal junctions, and can be analyzed similarly. The nanotube to nanotube junction properties can be varied with electrostatic fields set up using a back gate contact to the conductive substrate, and by altering the chemical environment.

A model is proposed for the lower Schottky barrier for hole transport in air than in vacuum at a metallic electrode - semiconducting carbon nanotube (CNT) junction observed in the experiment [R. Martel et al., Phys. Rev. Lett. 87, 256805 (2001)]. We consider the electrostatics of a transition region between the electrode and the CNT in the presence (air) or absence (vacuum) of oxygen molecules, where an appreciable potential can drop. The oxygen molecules are negatively charged because of their large electronegativity, and counter positive charges appear in both the electrode and the CNT to shield the oxygen charge under a closed circuit condition. The oxygen charge increases the potential drop in the transition region and tends to a lower Schottky barrier for hole transport. The Schottky barrier difference in air and in vacuum is large when a CNT depletion mode is involved, while the difference is negligible when only a CNT accumulation mode is involved. The mechanism prevails in both p- and n-CNTs, and the model consistently explains the key experimental findings. The model can be extended to the Schottky barrier modulation due to other gases.
a bottom metallic electrode functionalized with molecules. Using this technique, we will show how switches based on CNT can be prepared, the characteristics of which depend on the arrangement. In addition first measurements on molecules will be shown.

11:30 AM T1A

Large-scale fabrication of carbon nanotube-based circuit structures via self-assembly strategy, Seunghun Hong1, Salem Rae2 and Ling Huang2; 1Physics, Seoul National University, Seoul, South Korea; 2Physics, Florida State University, Tallahassee, Florida.

Carbon nanotube-based nanoelectronic devices, such as transistors and sensors, can be much smaller and more versatile than conventional microelectronic chips, but a lack of mass assembly method of such devices has been hindering their practical application. Inspired by biomolecular self-assembly processes, we have created chemically functionalized patterns on a surface, to which pre-grown nanotubes in solution can align themselves in huge numbers [1]. This method allows wafer-scale fabrication of millions of carbon-nanotube circuits with single-nanotube precision, and may enable massive production of nanotube-based devices. [1] Nature 425, 36 (2003).

11:45 AM T1B

Atomic-scale Topographic and Electronic Characterization of Single-walled Carbon Nanotubes on Silicon Surfaces, Peter Michael Albrecht and Joseph W. Lyding, Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

An ultrahigh-vacuum scanning tunneling microscope (UHV-STM) is used to elucidate the electrical and mechanical properties of individual single-walled carbon nanotubes (SWNTs) and to ascertain their atomic interactions with silicon surfaces. Atomically-resolved topographic imaging, combined with local density of states (LDOS) information inferred from spatially-selective dI/dV tunneling spectroscopy, make the UHV-STM an ideal instrument for correlating SWNT physical features with the associated electronic signatures. We employ a novel in situ dry deposition technique to generate an atomically pristine interface between SWNTs and silicon [1]. This solid-phase deposition process, whereby HiPco SWNTs are transferred to the substrate in UHV by direct mechanical contact, circumvents several undesirable consequences often encountered with solution-based schemes, including unintentional doping of SWNTs by charged species and residual substrate contamination by nonvolatile adsorbates. Results to be presented include UHV-STM topographic and current images showing simultaneous atomic resolution of SWNTs and the proximal H-passivated Si(100). Furthermore, tunneling spectroscopy reveals specific electronic features unique to semiconducting and metallic SWNTs, respectively. The theoretically-predicted constant tunneling conductance (I/V) about the Fermi level for an isolated armchair metallic SWNT is measured to be invariant to the presence of a supporting substrate with a semiconducting gap > 1 eV. All of our experiments to date suggest that the UHV-STM results in the transfer of a predominately isolated SWNTs, rather than cumbumsen SWNT ropes or catalyst particles, to the silicon surface. This fortuitous outcome sets the stage for sensitive electronic measurements that are unimpeded by tube-tube interactions arising within a bundle. We will also demonstrate how the STM tip can be implemented to cut and manipulate SWNTs. A H-terminated Si(100) surface lends itself to ligigraphic patterning via the controlled deposition of H by the STM tip [2]. One can exploit the chemical contrast between the highly reactive Si dangling bonds and the relatively inert H-passivated substrate to engineer the local environment at an arbitrary position along the SWNT. Lastly, the dry transfer technique is generalizable to the deposition of sensitive and/or nonvolatile molecules and nanoparticles onto a wide range of surfaces that are incompatible with ambient exposure [3]. The ultimate goal of our experimental effort is the nanofabrication of hybrid SWNT-Si devices and circuits leveraging these two unique electronic materials synergistically. [1] P. M. Albrecht and J. W. Lyding, Appl. Phys. Lett. (in press). [2] J. W. Lyding et al., Appl. Phys. Lett. 64, 1010 (1994). [3] L. B. Ruppalt, W. Ye, P. M. Albrecht, and J. W. Lyding (unpublished).

SESSION T2: Molecular Self-Assemblies
Chair: Marcelle May, Tuesday Afternoon, April 13, 2004 Room 3008 (Moscone West)

1:30 PM T2A


This presentation will explore methods to design, synthesize, and nanofabricate electronic materials on molecular length-scales. One of the new chemical systems that is to be presented self-organizes into one-dimensional assemblies that are only a single molecule wide but microns in length. Efforts are aimed at devising methods to measure the electrical transport and electroactive properties of these systems. A second chemical system presented forms self-assembled monolayers whose constituent molecules orient their path of conjugation perpendicular to the metallic surface. From these monolayerscence, scanned probe microscopy and nanofabrication fabrication are being used in concert with further chemical assembly to create molecular electronic test structures.

2:00 PM T2B

Self-Assemblies with Nanoscale Ordering for Molecular Electronics, Alex K.-Y. Jen, Hong Ma, Kyoung-Soo Kim, Mun-Sik Kang, Seok-Ho Kang, Melvin T. Zin, Hadi Zarifeh and Mehmet Sarikaya; Materials Science and Engineering, University of Washington, Seattle, Washington.

It is ideal to obtain highly-ordered and stable self-assembled monolayers (SAMs) with nanoscale features for exploring the charge injection/transport mechanisms in molecular electronics. Recently, several series of fused-ring aromatic self-assembling molecules have been designed and synthesized to have a variable molecular geometry through different molecular architectures, α-functional groups and hydrogen bonding moieties. We have found controlled self-assemblies of these molecules as crystalline arrays on gold substrates at room temperature. The size, shape, orientation and ordered assemblies of molecular wires can be engineered through a delicate interplay of the intermolecular π-π stacking and chemisorptive substrate-linker interactions. In particular, the molecule based on a fused-aromatic, aryne-cyclohexene or pyrene, forms an ordered two-dimensional array. Through scanning tunneling spectroscopy, we demonstrate changes in electronic behavior of single molecules that form into superlattices. We have also designed and synthesized a novel functional hybrid molecule by taking advantage of the excellent physical and chemical properties of C60 and nanoscale ordering of anthrily-based SAMs. The SAM of this molecule exhibits stable and highly ordered two-dimensional arrays that form an oblique lattice at room temperature. The self-assemblies have also shown both reversible electrochemical peaks and very interesting electronic properties such as a potential negative differential resistance (NDR) effect.

2:15 PM T2C

α,ω-Bis(thioacyl)oligothiophenevinylene Chromophores From Thiouanisol Precursors, Dwight S. Seferos1, David A. Banach2, Norma A. Alcantara3, Jacob N. Israelachvili3, James G. Kushmerick5 and Guillermo C. Bazan1,2,4; 1Department of Chemistry and Biochemistry, UCSB, Santa Barbara, California; 2Department of Materials, UCSB, Santa Barbara, California; 3Department of Chemical Engineering, USF, Tampa, Florida; 4Center for Bio/Molecular Science, NREL, Washington, DC; 5Department of Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Dithiol conjugated oligomers are important surface modifying reagents, and provide a platform for assembling molecular-scale junctions and devices. In this work we demonstrate the selective covalent cleavage of arylmethythioether is tolerant of Wittig and Heck-type reactions for the synthesis of all-E isomers of α,ω-bis(thioacyl)oligothiophenevinylene molecules (OPVs). The arylnlethioether is tolerant of Wittig and Heck-type reactions for forming OPV structures and can be converted to the S-acyl group by treatment with sodium thiomethoxide and acetyl chloride. The thermal conditions of this deprotection/reprotection step concurrently isomerize the conjugated chromophore to the all-E isomer, regardless of the stereochemistry of the starting olefinus. This synthetically approach is demonstrated for a variety of linear and [2.2]paracyclophane containing OPVs, which have been characterized by both electrochemical and spectroscopic techniques. Additionally, the self-assembly of these S-acyl terminated OPVs on gold surfaces is demonstrated. Monolayers containing these molecules were characterized by water contact angle measurements, ellipsometry, and X-ray photoelectron spectroscopy. The molecular structure of the [2.2]paracyclophane containing chromophores can serve to study how a well-defined through-space delocalized unit influences electronic communication between a pair of electroactive organic moieties. To examine this unique property we take advantage of the S-acyl group incorporated within the molecular structure, and its ability to self-assemble on gold surfaces, to fabricate and test molecular junctions in a cross-wire test bed.

2:30 PM T2D


[1-2]paracyclophane containing chromophores can serve to study how a well-defined through-space delocalized unit influences electronic communication between a pair of electroactive organic moieties. To examine this unique property we take advantage of the S-acyl group incorporated within the molecular structure, and its ability to self-assemble on gold surfaces, to fabricate and test molecular junctions in a cross-wire test bed.
the Liquid/Metal Interface. Denis Fichou1,2, Alexander Marchenko1,3, and Nathalie Katsonis1,3. 1DSM/DRECAM/SPCSI, CEA-Saclay, Gif-sur-Yvette, France; 2UMR 7611 CNRS-UPMC, Paris 6 University, Paris, France.

Molecular self-assemblies on atomically flat surfaces (gold, graphite, etc.) are governed by molecular interactions, and can be tailored by external stimuli. The strong influence of the immediate environment on molecular electronic properties and transport is demonstrated. In one case, a scanning tunneling microscopy (STM) was used to study the conductance of single C60 molecules in isolation and in monolayers adsorbed on an ultrathin alumina film grown on a NA1[110] surface. The differential conductance (dI/dV) spectroscopy displayed energy gaps of equally spaced features, attributed to the vibronic states of the molecules. The details of the spectra show the influence of molecular orientation and environment on the differential conductance. The local density of states of states of this structure was visualized by spatially resolved electronic spectroscopy and tuned by varying the number of metal atoms in the bridge by STM tip manipulation. This artificial bridge elucidates the nature of the contacts between the molecule and the metal in this junction. These experiments serve to highlight the role of the local environment in the spatially resolved conductance of molecules and provide the basic understanding that may play a significant role in the emerging field of molecular electronics.

4:45 PM T2.9
Self Assembly and Tunnelling Spectroscopy of Self Assembled Monolayers. Gascha R. Dittrich1,2, Robert Zeches1,2, and M. Meyyappan; Center for Nanotechnology, ELORET/NASA Ames Research Center, Moffett Field, California.

Self assembled monolayers of organic molecules are of potential interest for molecular electronic devices. We study the self assembly and electronic transport of different types of SAMs by scanning tunneling microscopy and spectroscopy. It is important to understand the transport mechanisms through these monolayers, and currently there are only a few temperature dependent transport studies. Whether the nature of electronic transport through the SAMs is by tunneling or by activated transport depends on the both the magnitude of the HOMO-LUMO gap and the length of gaps in the molecule. We perform temperature dependent scanning tunneling spectroscopic
current rectification is obviously associated with some form of symmetry breaking. This talk will focus on three scenarios of current rectification by molecular junctions. First, the asymmetric response of the electrostatic potential along a biased molecule in structurally asymmetric junctions; second, electron pumping by an external time-periodic potential interacting with an asymmetric molecular chain; and third, the asymmetric conduction of heat by non-linear molecular oscillators. The nanostructure-based single-electrode devices, the transfer of single electron is achieved by co-tunneling and quantum-size effects may further complicate the characteristics of the devices are calculated by the non-equilibrium Green’s function (NEGF) method and compared in a consistent manner. We demonstrate the variety of transport characteristics that can obtained through “engineering” of the metal-molecule interaction. We also consider the possibility of incorporating mechanical degree of freedom into such molecular-assembled single-electron devices through mechanical modulation of one of the tunnel junctions. It is known that the silicon surface is spontaneously defective. Normally flat surfaces contain re-entrant steps and some rows of non-stoichiometric steps which act as preferential sink for dopants, surfactants and chemical etchants. The purpose of this study is to get insight into the interactions of steps on the Si(100) surface with organic molecules of the simplest composition. The study is divided into two parts. The first part illustrates preferred adsorption sites and the step-molecule bonding. The possibility of a functionalization of a surface containing steps is also analyzed. This study is performed using a molecular orbital method with a semiempirical orbital method. In the second part the thermal and electrical conductivity of the systems studied in the first part is analyzed using the Kubo theory.

11:30 AM T3.8
10 nm Channel Length Pentacene and Oligothiophene Organic Thin-Film Transistors. Josephine Ben Lee1, Paul C. Chang2, Amanda R Murphy3, Jean M J Frechet3, J Alexander Liddell2 and Vivek Subramanian1, 1Department of Electrical Engineering and Computer Science, University of California, Berkeley, California; 2Center for X-Ray Optics, Lawrence Berkeley National Laboratory, Berkeley, California; 3Department of Chemistry, University of California, Berkeley, California.

Currently, there is great interest in scaling organic thin film transistors (OTFTs) to nanoscale channel lengths in order to probe the intrinsic behavior of organic materials and as part of the drive towards high performance organic devices. With certain organic semiconductors exhibiting thin film charge mobilities at or exceeding those of the best inorganic semiconductors, the technical motivation to extend OTFT scaling beyond 30 nm is less immediate than with inorganic semiconductors. However, the benefits of continued scaling include the ability to produce new transport regimes with enhanced charge mobility. However, attempts to scale OTFTs channel lengths below 100 nm have been met with a number of difficulties. Here, we report on the scaling of OTFTs to 10 nm channel lengths and discuss the issues that become significant at these dimensions, such as contact resistance and limits posed by electrostatics. We have fabricated 10 nm channel length organic thin-film transistors (OTFTs) from pentacene, dihexyl sexithiophene, and dihexyl tetradeca thiophene. These devices represent the smallest OTFTs reported to date. Gold electrodes were formed using e-beam lithography and lift-off techniques. Thin films of various organic semiconductors were then deposited by vacuum evaporation, spin coating, or dip coating to form bottom-contact, back-gated devices. As the channel length was scaled, short channel effects such as Vt-rolloff and increased off-state leakage were observed. The impact of contact resistance also became increasingly significant. Nanoscale devices consistently exhibited lower FET mobilities and worse on/off current ratios than identically processed micron-sized devices, likely due to the growth dynamics of the thin-film organic layer in the nanogaps. This study is a significant step towards optimization of the deeply scaled OTFT.

11:45 AM T3.9
From Electron Transfers to Electric Currents: Light-induced in-Plane Currents in Monomolecular Films. Vladimir Burtman1,2, Andrew Pakulev2 and Dimitry Zaslavsky2, 1Physics Dept., Univ. of Utah, SLC, Utah; 2Chemistry Department, University of Illinois at Urbana-Champaign, Urbana, Illinois.

The world of the in-plane currents in monomolecular films has been unexplored; having ultimately thin cross-sections, monolayers a priory did not seem to be prospective research avenue for the needs of electronics. However, we find that (i) monomolecular films of 1,4,5,8-naphthalene tetracarboxylic diimide (NTCDI) can be photo-chemically populated with positive charges via ejection of electrons into the semi-conducting base and (ii) these charges can travel within the films as far as several millimeters within microseconds. We show that this long-range charge migration requires a sufficiently dense packing of the film to permit electron transfer between the covalently immobilized molecules. Such density was achieved by chemo-sorption of the vaporized precursor and manifested itself as an additional broad asymmetric “aggregation” absorbency band. This in-plane “fluidity” of charge-carriers allows small-sized cathodes to harvest charges generated in remote areas and thus can be utilized in numerous applications.

SESSION T4: Transport in Molecular Junctions I
Chair: Marcel Mayor
Wednesday Afternoon, April 14, 2004
Room 3008 (Moscone West)

1:30 PM T4.1

We have studied electron transport properties of N-alkanedithiol chained and conjugated molecules and transistors. A single molecule junction is formed by repeatedly creating a large number of molecular junctions. For each molecule, a large variation in the conductance is observed from one junction to another, which reflects the difference in the molecular contact geometries. However, the conductance histograms obtained from thousands of measurements shows pronounced peaks at integer multiple of a fundamental conductance value, which is used to identify the conductance of a single molecule. The conductance of N-alkanedithiols can be described by G = e2/h and beta = 1.0 per carbon atom. When one of the C-C bonds in the chain is replaced with peptide bond, the conductance changes considerably. The dependence of the conductance of the conjugated molecules on the molecular length is much slower than that of alkanedithiol molecules. We have also studied electron transport by controlling the potential of the gold electrodes with respect to a reference electrode inserted in the electrolyte.

2:00 PM T4.2
Electrical Transport in Au-Alkanedithiol:GaAs. Jula W. P. Hua1, Ken W. West2, David V. Lang3, Matt D. Hallis3, Krishnan Bagnavarchi4 and Yael-Laa Loo4, 1Stanford National Laboratories, Albuquerque, New Mexico; 2Lucent Technologies, Murray Hill, New Jersey; 3Indiana University, Bloomington, Indiana; 4University of Texas - Austin, Austin, Texas.

Molecular junctions composed of alkanedithiol chemically bonded to Au and GaAs electrodes were made by nanotransfer printing. Electrical shorting between electrodes is minimized in these printed junctions. Furthermore, this new transport process ensures the current path through the entire length of the molecules. Current-voltage (I-V), capacitance-voltage (C-V) and internal photocurrent (IP) experiments were performed to study the transport properties of these junctions. Experimental results were compared with electronic structure calculations. C-V results indicate excess negative charges at the molecule-GaAs interface. This is in agreement with calculations in which more negative charges are localized on S when it is bonded to Ga than to Au. This contact asymmetry is the primary reason behind the I-V asymmetry at low bias. It is also consistent with the observation that the shape of I-V curves is the same for n type GaAs and p type GaAs. However, the current levels of the molecular junctions made on p-GaAs are many orders of magnitude higher, suggesting transport is predominating hole conduction through molecular occupied levels. Calculations also show the presence of occupied levels 1 eV below the Fermi energy which overlaps alkanedithiol and Au/GaAs electrodes. Furthermore, this is supported by the observed high yield in photocurrent measurements when the photon energy (E) is above the GaAs band gap. From E is below the GaAs band gap, we observe an exponential dependence. Exponential E dependence in IPE yield signifies exponential distribution of density of states, which could result from the presence of disordered materials or high fields. By varying the doping levels of GaAs, we separate out contributions due to the molecular junction from that of GaAs Franz-Keldysh effect. An exponential IPE yield with a characteristic energy of 70 meV can be attributed to the molecular layer. Band alignment across the molecule-semiconductor and molecule-metal interfaces will be discussed.

2:15 PM T4.3
High-Quality Alkanethiol Bilayer Molecular Junctions on Gold Substrates. John D. Le, Curtis C Mead and Richard A Kiehl; Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

The electrical characteristics of alkanethiol bilayer molecular junctions formed on gold substrates are reported over a wide range in thickness are consistent with tunneling over a ten order-of-magnitude gap. When E is below the GaAs band gap, we observed an exponential E dependence in IPE yield curves is the same for n type GaAs and p type GaAs. However, the current levels, as well as short molecules, which present localized on S when it is bonded to Ga than to Au. This contact asymmetry is the primary reason behind the I-V asymmetry at low bias. It is also consistent with the observation that the shape of I-V curves is the same for n type GaAs and p type GaAs. However, the current levels of the molecular junctions made on p-GaAs are many orders of magnitude higher, suggesting transport is predominating hole conduction through molecular occupied levels. Calculations also show the presence of occupied levels 1 eV below the Fermi energy which overlaps alkanedithiol and Au/GaAs electrodes. Furthermore, this is supported by the observed high yield in photocurrent measurements when the photon energy (E) is above the GaAs band gap. From E is below the GaAs band gap, we observe an exponential dependence. Exponential E dependence in IPE yield signifies exponential distribution of density of states, which could result from the presence of disordered materials or high fields. By varying the doping levels of GaAs, we separate out contributions due to the molecular junction from that of GaAs Franz-Keldysh effect. An exponential IPE yield with a characteristic energy of 70 meV can be attributed to the molecular layer. Band alignment across the molecule-semiconductor and molecule-metal interfaces will be discussed.
bipolarons on Au substrates. The breakdown voltage is found to exhibit a bias polarity dependence that decreases with molecular length. In general, the electrical characteristics for the metal-molecule-metal junctions presented here are greatly improved compared to previous results for similar bilayers on Au substrates and are comparable to the best results achieved for bilayers on Ag substrates. Possible explanations for the improved characteristics observed in this study are discussed.


We have conducted conductance measurements with a self-assembled metal-molecule-metal junction [1] both at room temperature and low temperatures. The gap between the electrodes could be adapted in situ to the molecule’s length employing the mechanically controlled break junction technique. Part of our research is focusing on the correlation between molecular structure and electronic properties. As an example, molecules divided in two conjugated segments were designed and synthesized. By fluoriding one of the two segments, the functionality of a diode was targeted. Indeed the measurements result for test structures scaling sizes from small ensembles of tens to structural wells of varied dimensions. Using surfaces of Au(lll), we interrogate how factors such as metal-molecule coupling, molecular structural changes with the number of molecules contacted, and that the conductance of a molecular wire can be directly related to how well in-dielectric IV-characteristics with an on-off ratio of approx 5. Different mechanisms how asymmetries may arise are considered. Further attention is paid to the interaction of single-molecule junctions with light. [1] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, and H. v. Lohneysen, Phys. Rev. Lett. 88, 176804 (2002).

3:30 PM T4.5 Understanding Charge Transport in Metal-Molecule-Metal Junctions. James G. Kushmerick, Naval Research Laboratory, Washington, District of Columbia.

We use an experimentally simple crossed-wire tunnel junction to interrogate how factors such as metal-molecule coupling, molecular structure and the choice of metal electrode influence the current-voltage characteristics of a molecular junction. By tuning the coupling at the two metal-molecule interfaces through the use of different attachment chemistries and metal electrodes-are we able to control the amount of current rectification. Experimental measurements and theoretical calculations demonstrate that the conductance of a molecular wire can be directly related to how well it’s conjugated backbone mimics an ideal one-dimensional metal. Finally, we will show that the conductance of a molecular junction scales with the number of molecules contacted, and that the σ-systems of molecular wires in a self-assembled monolayer are not strongly coupled. Initial results demonstrating the utility of in situ vibrational spectroscopy to characterize molecular junctions will also be presented.

4:00 PM T4.6 Measuring Electrical Properties from Single Molecules to Molten Dots. Jayne Caroline Garno1, Christina A. Hacker2, Christopher D. Zangmeister 3, Carlos Gonzales4, Lee J. Richter l, 1Surface & Microanalytical Sciences Division, NIST, Gaithersburg, Maryland; 2Semiconductor Electronics Division, NIST, Gaithersburg, Maryland; 3Process Measurements Division, NIST, Gaithersburg, Maryland; 4Physical and Chemical Properties Division, NIST, Gaithersburg, Maryland.

Developing theoretical models to understand and predict electron transport in metal-molecule-metal junctions is a significant challenge, with direct potential benefits to technology. Advancement of molecular electronics-based systems requires the ability to achieve reliable and precise measurements of conductance and charge transport through metal-molecule-metal structures. A combination of modeling, spectroscopy, and scanned probe approaches are applied in a concerted effort to correlate theoretical studies with molecular level measurements of conduction, as well as measurements with device-level probe structures. All of the electrical characteristics are determined through the interfacial charge transfer and the corresponding formation of interfacial potentials. Using this framework, we present a unified theoretical model for studying charge transport in arbitrary molecular-scale devices, which combines Green’s function theory of quantum transport with atomicistic description of the interface electronic structure in the real space. We discuss the insights obtained from such atomistic modeling for understanding the interface effects in devices based on individual organic molecules, finite-size carbon nanotubes, and long carbon nanotubes in the limit of 1-D quantum wires. Both linear and nonlinear transport characteristics will be discussed.

4:30 PM T4.7 Charge transport in DNA probed by Conducting AFM and EFM. Dominique Vuillaume, Thomas Hein and Dominique Deresmes; CNRS-INM, Villeneuve d’Ascq, France.

We studied the electrical conductivity of DNA samples as function of the number of DNA molecules in the ropes. We performed a systematic study of the distance-dependent behavior of the CT in DNA versus the size of the DNA samples: from DNA polymers, bundles and ropes to few single molecules. In that latter case, the CT behavior was correlated with the flatted conformation of the DNA molecule as observed by topographic TM(tapping mode)-AFM. We showed that the insulating gap (no current at low voltage) increases from 1-2 nm for molecules and long ropes to 4-5 η for few DNA molecules. For the distance dependent variation of the current, a unique hopping distance of 3 nm is calculated (polaron-hopping model) independently of the number of DNA in the sample. The highly resistive behavior of the single DNA is correlated with its flatened conformation (measured by TM-AFM) on the surface (reduced thickness, 0.5-1.5 nm, compared to its nominal value, 2 nm). Contactless measurements were also used. We have injected charges locally in the DNA from the C-AFM tip. The charge distribution along the DNA molecule after injections at various voltages and time durations was investigated by EFM. We showed that on elongated DNA, the charges stay localized at their injection point; while charges are delocalized few micrometers along the DNA in non-elongated molecules. This long distance delocalization implies some conducting properties in that latter case. This results demonstrates possible long distance charge transfer in unordered and contactless DNA molecules.

4:45 PM T4.9 Implications of space charge limited transport for BEEM studies on metal-organic interfaces. Cedric Troadec, Linda Kunzard and Natarajan Chandrasekhar; Institute of Materials Research and Engineering, Singapore, Singapore.

Interfaces between metals and organics/semiconductors exhibit a Schottky barrier. Ballistic electron emission microscopy is a technique to determine the magnitude of this barrier, potentially with nanometer resolution. The carriers injected from a STM tip, travel ballistically through the top metal electrode and are collected at the bottom of the organic/semiconductor layer. Due to the large differences in mobilities of the carriers in the metal and the organic, transport of injected carriers is limited by space charge effects in the organic. In this work, we will discuss the implications for space charge limited transport on measurement of the Schottky barrier with engineered test arrays which consist of an alkanethiol matrix with candidate wire molecules such as oligo (phenylene-ethylene) oligomers (OPEs). We measure changes in electrical behavior induced by chemical modifications of OPEs. AFM and STM investigations of current-voltage measurements for a monofluorinated molecular wire SAM (F-OPE) show an increased rectifying behavior in comparison to the unsubstituted OPE. Studies of all OPEs and OPE SAMs are measuring and predicting the electrical response of molecules.
T5.1 Synthesis and Electrochemical Properties of Polyphenylene bearing nitroxide radicals as an Electrode Active Material.

Masahiro Suguro, Shigeyuki Iwasa, Jiro Irynya, Kentaro Nakahara, Yukiko Moroik and Masaharu Satoh; Environment and Material Research Laboratories, NEC Corporation, Kawasaki, Kanagawa, Japan.

Polycondensates are known to be oxidized and reduced electrochemically. We reported the redox processes would be suitable for a reaction of cathode active materials in rechargeable batteries. The use of organic materials as an active material in cathodes appears promising to design environmentally friendly, high-energy-density rechargeable batteries. We synthesized poly[1-(N-t-butyl nitroxyl)-3,5-phenylene](PBPN), which has the possibility of high energy-density. The ESR spectrum of PBPN consists of a single line. The g value is 2.010, which is characteristic of nitroxyl radicals. A coin-type cell fabricated with the polycondensate as cathode active material has demonstrated the reversibility and discharge curves. The voltage plateau of 3.6 V vs Li/Li+ for charge and 3.4 V vs Li/Li+ for discharge have been observed. These results indicate the possibility of PBPN for active materials of organic radical battery. Here we will present synthesis and fundamental properties of PBPN and the battery.

T5.2 Biomimetic Molecular Muscles, Yi Liu1,2, Amar H Flood1,2, Paul Bonvallet1,2, Tony J Huang3, Scott C Vignon1,2, Sergei Magonov4, Marko Baller1, Chih-Ming Ho5 and J Fraser Stoddart1,2; 1California NanoSystems Institute, Los Angeles, California; 2Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California; 3Mechanical and Aerospace Engineering, University of California, Los Angeles, Los Angeles, California; 4Veeco Metrology Group, Santa Barbara, California.

Switchable [2]rotaxanes have been likened to linear molecular motors.1 These compounds are composed of ring and dumbbell-shaped components that are interlocked with each other, in which the ring's linear mechanical movements along the dumbbell component can be precisely controlled. These mechanical movements have been utilized as the working electromechanical mechanism in rotaxane-based electronic devices.2 More recently, attention has been focused on harnessing the mechanical movements as the actuating mechanism in molecular electromechanical systems (NEMS). It is for this purpose that switchable artificial motor-molecules have been designed to perform extension and contraction movements, showing a unique form of two-way movement in molecular fibers. In this presentation, we outline (1) the design of a family of switchable artificial motor-molecules, (2) their modular synthesis, (3) the demonstration of controllable molecular movements in solution, (4) the self-assembled nanofiber devices, and (5) their potential application in a NEMS device. A variety of molecular muscle compounds have been designed and prepared. A linear [3]rotaxane, which has two rings encircling the dumbbell component, has been designed as a biomimetic molecular muscle capable of electrically-controlled contraction and extension. Disulfide tethers have been covalently attached to both of the ring components in the [3]rotaxane for the purposes of self-assembly onto a gold surface. A [2]daisy-chain construct, based on similar molecular recognition interactions, has been designed as an alternative biomimetic muscle motif. In addition, a smaller, self-complexing motor-molecule has been designed for self-assembly onto a gold surface for the purpose of producing a controllable functional surface. The chemical and electrochemical controllable machine-like movements of the two ring components in the [3]rotaxane are demonstrated by various techniques in solution. These results indicate a contraction and extension of the inter-ring distance to be a dramatic 3.5 nm, 44 percent of the overall molecular length. It has been shown subsequently that the [3]rotaxanes self-organize into large areas of regular superstructures on the surface of highly-ordered pyrolytic graphite (HOPG). Lastly, the surface-bound [3]rotaxane has been integrated into a NEMS device. The preliminary results indicate that the cooperative contraction and extension motion in the surface-bound muscle molecules can exert sufficient force to bend a cantilever beam that is much larger (μm) than the molecule's individual size. We thank DARPA biomolecular motor program for financial support. 1 Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. Angew. Chem. Int. Ed. 2000, 39, 3540. 2 Luo, Y.; Collier, C. P.; Jeppesen, J. O.; Nielsen, K. A.; Delomno, E.; Ho, G.; Perkins, J.; Twang, H. R.; Yamamoto, T.; Stoddart, J. F.; Heath, J. R. ChemPhysChem 2002, 3, 519.

T5.3 Degradation studies of blended polymer light emitting devices. Nicholas E Widdowson1, Michael C Petty2, Christopher Penman1, Changsheng Wang2 and Martin R Bryce2; 1Centre for Molecular and Nanoscale Electronics and School of Engineering, University of Durham, Durham, United Kingdom; 2Centre for Molecular and Nanoscale Electronics and Department of Chemistry, University of Durham, Durham, United Kingdom.

The degradation mechanisms in organic polymer electroluminescent devices in which the active layer is a blend of a polymer and an electron transport material have been studied. The polymer layer was poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene](MEH-PPV) while the electron transport material was 2,5-bis[3-(4-tetra-butylphenyl)-1,3,4-oxidazol-5-yl]pyridine (PDPyDP). The mixture (20:80 PDPyDP:MEH-PPV by weight) was deposited from solution by spin-coating. The anode and cathode consisted of indium tin oxide (ITO) and thermally evaporated aluminium, respectively. The light output of the as-deposited devices decayed rapidly to zero over a period of several hours. This was accompanied by a photodegradation of the polymer and delamination of the aluminium cathode. We suggest that this is the result of attack by water vapour and oxygen in the atmosphere. The effects of various encapsulation techniques, i.e. surrounding the devices in either nitrogen, dry air, vacuum or an epoxy resin, on the device performance and operating lifetime were investigated. Encapsulation in either dry nitrogen or in an epoxy resin considerably enhanced the operating lifetime and the devices could be operated continuously for several days. However, further degradation mechanism, associated with the ITO anode was also noted in these structures. This resulted in a significant increase in roughness of the ITO surfaces. It is suggested that this can produce localised short-circuits in the device. Although these can heal themselves, the active area of the device is reduced.

T5.4 Assessment of stability in polysilanes. Asha Sharma1, U. Lourderaj1, Deepak2, N. Satyanarthy2 and Monica Katiyar1; 1Materials and Metallurgical Engineering & Samtel Centre for Display Technology, Indian Institute of Technology, Kanpur, UP, India; 2Chemistry, Indian Institute of Technology, Kanpur, UP, India.

Polysilanes are Si-backbone polymers with organic substituents attached to the main chain. These are quasi one-dimensional materials with delocalized sigma electrons along the polymer chain, exhibiting photoluminescence in the UV or NUV region. They can be used as active sources for electroluminescent (EL) devices especially suitable for blue emission. We have examined four polysilanes, namely, polydi-n-butylsilane (PDBS), polydi-n-hexylsilane (PDHS), polymethylenephenylsilane (FMPS) and poly[bis([p-methylphenylsilane)](PBP)], which have been reported in [1]...
as active materials in LEDs. Among these, PBPS LEDs show the greatest durability of the device at room temperature and NUV-EL is observed over 12 hours in both. However, for PBPS LEDs, either room temperature EL is not observable or the device life time is very short. Understanding the factors influencing the stability of PBBS in comparison to other reported polyanilines would help design polymer LEDs. The four polyanilines mentioned above differ primarily in nature of the substituents attached to the main chain. Therefore, attempts have been made to determine the instability of PBDBS, PBDS and PMPS LEDs in comparison to the PBBS based LEDs. By comparing the effect of the substituents and the conformational changes in these polyanilines, it seems that the site state is stable for all electronic states. References: [1] Suzuki et al., IEEE Journal of Selected Topics in Quantum Electronics, Vol. 4, No.1, 1998, p. 129

T5.7 Efficient electroluminescence of europium complex based organic light emitting diodes, Tobias W. Czandrer and Junji Kidoh, Department of Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan.

The spectrally broad emission of most organic molecules makes it difficult to achieve high color purity as required for full color display applications. Lanthanide ions, however, exhibit narrow emission, due to the well shielded intra-atomic transitions within the 4f shell. Europium complexes, which exhibit a dominant photoluminescence peak at 612 nm, corresponding to the D_{0}→ F_{2} transition in Eu^{3+} ions, are hence promising materials for red EL devices. We use tris(dibenzonoylmethane)mono(4,7-diphenylphenanthrolime)europium(III) (Eu(DBM)_{3}BPhen) to fabricate red-light emitting devices. A simple two-layer device, consisting of N,N'-Diphenyl-N,N'-di(m-tolyl)-benzidine (TPD) as hole transport layer and Eu(DBM)_{3}BPhen as electron transport / emission layer, exhibits efficient emission at low currents. We attain peak external quantum and power efficiencies of 4% and 4mJ/W, respectively. By co-evaporation of the Eu complex with various host materials we achieve efficient electroluminescence also at higher currents. For high driving currents we observe slight changes in the emission spectrum by a relative increase of emission from the D_{1} state relative to the dominant D_{0} emission.

T5.8 Interface Formation in K doped poly(diallyl-vinylene) Light-Emitting Diodes, Hans Gommans 1, A W Denier van der Gon 1, G G Andersson 2, L J van IJzendoorn', R M T Pijper' and H H Brongersma'; 'Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; 2Departamento de Fisica de Teorias Clasicas, Universitat Leipzing, Leipzig, Germany.

AI / K / MDMO-PPV / ITO LED structures manufactured by physical vapor deposition of K onto the emitting polymer layer have been characterized by electroluminescence (EL) and ion spectroscopy. EL measurements clearly demonstrate a K-concentration dependent behavior: varying the deposited K area density in the sub-monolayer regime from 3.9x10^{12} to 1.2x10^{13} atoms cm^{-2} the external efficiency rises from 0.01 to 1.2 cd A^{-1}. The observed increase in built-in potential can at most partially account for this effect. Low Energy Ion Spectroscopy (LEIS) probes the elemental composition of the topmost atomic layer of the surface atoms determined from the analysis of the kinetic energy of elastically backscattered noble gas ions, while efficient neutralization of the ions ensures the surface sensitivity. In the set-up, the kinetic energy of ions scattered by 145 degrees was analyzed. When a 30 mm thick silicon ion toroidal analyzer and position sensitive detector and allowed for a detection limit of 100 ppm in the case of K. By measuring the time of flight (TOF) of the charged plus neutralized noble gas ions, we were able to study the composition in deeper layers with Neutral Impact Collision Scattering Spectroscopy (NICISS). A complete absence of K at the polymer outermost surface layer is observed. As the K deposition is clearly below the critical density that limits the charge transfer process typical for alkali / rr-conjugated systems, bulk diffusion is not impeded by cluster formation. Consequently, diffusion profiles were derived with a characteristic decay length as large as 62 Angstrom. These profiles were modeled using a Fickian diffusion model with an irreversible stepping reaction that indicates confinement of the electron at a conjugated segment. This demonstrates that evaporation of low work function metals onto organic systems should not be depicted as simple stacking process. We propose that in electroluminescence, the enhancement of the current with sub monolayer K deposition is attributed to the shift of the recombination zone away from the Au cathode, which is demonstrated to prevail over the known non-radiative exciton dissociation mechanism due to the formation of grain boundaries. This shift in the recombination zone can be either due to an improved balance in carrier density or the presence of radiative recombination centers in the interfacial layer.

T5.9 Organic Field Effect Transistors with PMMA/TA205 as Gate Dielectric, Anne-Laure Deman and Jacques P. Tardy; LEOM, ECL, France.

We report in this study on the fabrication of organic field effect transistors with a gate dielectric made of Ta205 covered with a thin PMMA film. In a MOSFET, the charge in the channel is proportional to the density of the dielectric constant of the gate dielectric and of the polymer, a gate dielectric consisting of Ta205 film covered with a PMMA film was reported in this study. Ta205 thin films were deposited on high quality single crystal silicon by electron beam evaporation in presence of an oxygen partial pressure on a substrate kept at near room temperature. After deposition, Ta205 is annealed in oxygen at temperature ranging between 120 and 600 C. Unannealed films were also checked. Films were characterized by ellipsometry and admittance spectrometry. Transistors have been processed with bare Ta205 either annealed or not. The semiconductor used was pentacene in a top contact geometry with gold source and drain electrode. For devices with interlayer, PMMA was spin coated to a thickness between 15 and 250 nm with the rest of the device being unchanged. Operating voltage as low as -1.5V were obtained with 120 nm thick Ta205. We point out the influence of annealing which leads to a better saturation characteristics and also to the decrease of gate leakage. The measured mobility is 0.02 cm^{2}/V.s. Upon deposition of PMMA overlay, the operating voltage increases (up to 20V for 250 nm PMMA) but the output characteristics do not exhibit any gate leakage. The mobility increases to 0.25 cm^{2}/V.s. on non purified pentacene and on devices characterized in room atmosphere. With annealed Ta205, the on/off ratio is 1. 105 and the voltage swing 1.2 V/decade. Work is in progress to evaluate other polymers onto Ta205, and comparative results will be presented.

T5.10 Small polarons in dry DNA, Helio Chacham1, Simone Silva Alexandre1, Jose Soler2 and Emilio Artacho3,1 Depamento de Fisica, Universidade Federal de Minas Gerais, Brazil; 2Department of Earth Sciences, University of Cambridge, Cambridge, United Kingdom; 3Depamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Madrid, Spain.

The phenomenon of charge transport in DNA has been attracting attention of both biologists and physicists. From the biological side, there are evidences that charge injection can be associated to damage, mutation, and repair processes in DNA. From the physical sciences side, recent developments in nanotechnology now allow the measurement of currents through single DNA molecules in dried samples, which depict semiconducting behavior. New models have been proposed for charge migration and transfer in DNA. In that respect, detailed electrical transport measurements through DNA molecules containing identical base pairs (poly(dA)-poly(dT) and poly(dG)-poly(dC)) have been recently reported by Yoo et al [1]. These results fit extremely well a model in which the conduction is due to small polaron motion. In particular, these results indicate that the L-V characteristic of dry poly(dG)-poly(dC) DNA above 200 K is consistent with a small polaron hopping regime with an activation energy of 0.12 eV. In this work [2] we investigate the polaron formation in dry DNA by applying ab initio calculations to both neutral and charged fragments of dry poly(dG)-poly(dC). Our calculations show that the hole polaron in dry poly(dG)-poly(dC) DNA is a clear case of small polaron. This is verified by four basic properties: (i) the small variation of the polaron binding energy as a function of the DNA fragment size, (ii) the smallness of the polaron, which is an indication of polaron localization; (iii) the fact that the width of
as the substrates of which surfaces forms step-terrace structures. Those morphologies are suitable to form uniform parallel steps with the height of 0.21 nm and terraces of low power consumption and high integration. C$_{60}$ substituents (3,3-dimethyl-1-butoxy and 9-methoxy-1,4,7-trioxanonyl) on substrates, the average height of the particles rose up by about 0.8 nm of its high symmetry, and its diameter is about 0.7 nm. C$_{60}$ molecules make strong bonds with metals rather than themselves. This characteristic is applied to prepare the C$_{60}$ monolayers only onto metals. Then C$_{60}$ molecules which didn’t adsorb to metals can be re-evaporated after deposition. In this work, we used MgO(110) and α-Al$_2$O$_3$(0001) as the substrates of which surfaces forms step-terrace structures. And we chose Au as metal layers of the specific sites of communication for solid-state devices. Paul R Frail T5.13

Recently, nanoscale electronic devices have attracted much attention from the points of low power consumption and high integration. C$_{60}$ is a hopeful candidate for the nanoscale devices fabricated by a bottom-up method. C$_{60}$ is available for a functional molecule because of its high symmetry, and its diameter is about 0.7 nm. C$_{60}$ molecules make strong bonds with metals rather than themselves. This characteristic is applied to prepare the C$_{60}$ monolayers only onto metals. Then C$_{60}$ molecules which didn’t adsorb to metals can be re-evaporated after deposition. In this work, we used MgO(110) and α-Al$_2$O$_3$(0001) as the substrates of which surfaces forms step-terrace structures. And we chose Au as metal layers of the specific sites of communication for solid-state devices. Paul R Frail T5.13

The Au films were evaporated on the substrates at 600°C from an Au source. In order to remove the reaction products of the surface, the substrates were heated at 60°C for 1 min from an effusion cell at 1300°C, and immediately annealed for 30 min at the temperature. The C$_{60}$ were deposited on the Au ultrathin films at 120°C for 10 min and then annealed at 350°C for 30 min. The films were evaluated by surface microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). From results of AFM measurements, the surfaces of annealed MgO(110) substrates formed one dimensional alignments of step-terrace structures with the terrace widths of 20-80 nm. This is due to the cleavage at (100) plane of MgO single crystals. The surfaces of annealed Al$_2$O$_3$(0001) substrates formed uniform parallel steps with the height of 0.2 nm and terraces with the width of 80 nm. The steps and terraces structures existed in the length larger than 2 nm. Those morphologies are suitable to prepare the one-dimensional nano-structures of C$_{60}$/Au. The AFM images insisted that Au particles aligned one dimensionally along the step-edges. After the deposition of C$_{60}$ onto the specific substrate, the average height of the particles rose up by about 0.8 nm than that of Au particles. This value is same as the C$_{60}$ diameter. Since the tail of XPS C$_{1s}$ peak extended to the higher binding energy side, this fact suggests that a C$_{60}$ molecule was transferred from Au. The results of AFM and XPS indicated that C$_{60}$ monolayers on Au nano-structures were realized by the re-evaporation method developed in this work.


Two new series of soluble (porphinato)zinc oligomers that feature a highly conjugated meso-to-meso ethyne linkage topology have been synthesized: these materials exhibit excellent optical and excited state properties. One series of these conjugated oligomers possesses peripheral aryl groups at the macrocycle’s 10,20 positions; these aryl groups can exhibit excimer-like behavior, feature substituents (3,5-dimethyl-1-butoxy and 3-methoxy-4,4,4-trifluoronyl) that dramatically enhance solubility. The second series does not have macrocycle meso aryl substituents; solubilizing, sterically unencumbered the porphyrin planar, feature peripheral-phenyl-to-porphyrin interplanar contact distances. The electronic properties of these oligomers were investigated in solution and in the solid state. Comparison of key physical properties, as well as the magnitude and intermolecular electronic interactions, will be discussed.

Three-Dimensional Inhomogeneities In The Conductivity Of PEDOT/PSS. Martijn Kemerink1, Salvatore Timpanaro2, Margreet de Kok2, Eric Meulenkamp2, Fred Touwslager2 and Rene Janssen1,2; 1Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; 2Chemical Engineering, Eindhoven University of Technology, Eindhoven, Netherlands.

PEDOT-PSS (poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulfonic acid)) is a transparent and conductive dispersion that is widely used as anti-static and as electrode material in organic semiconductor devices like LEDs and photo-voltaic cells. One of its strengths is that smooth films can easily be spin-cast from water-solutions. However, for applications it is very important that also the electrical properties show little lateral variations within a film. So far, this issue has not been addressed. We have used scanning-tunneling microscopy and spectroscopy to study the conductive properties of a 1:1 PEDOT-PSS blend in all spatial dimensions. Extensive use is made of the fact that the metallic STM tip can penetrate the soft organic material without damage to the tip. In particular, I-V spectroscopy, in which the tip is kept under constant bias is measured as a function of depth, yields detailed information about the conductivity as a function of z. By taking I-z curves on a lateral grid, a three dimensional conductivity map is obtained. Despite the seemingly destructive nature of such experiments, reproducible conductivity images are obtained. In addition, z-V spectroscopy, in which the bias is ramped with the feedback system active, and conventional I-V spectroscopy are performed. Combination of the experimental results with a three-dimensional numerical model shows that these films are covered with a 5-20 nm thick layer of relatively low conductivity. The conductivity in this layer can be an order of magnitude higher than in the underlying bulk, which is used to estimate the reduced PEDOT content in the top layer. The latter assignment is in agreement with recent photo-emission experiments. Also deeper in the layer, considerable variations in conductivity occur as a function of depth. The former is identified as grains in topographic STM images and have a maximum size of 25-30 nm, which is in excellent agreement with the particle size in solution of 18-30 nm. The latter, long range variations, occur on a length scale of hundreds of nanometers and translate into conductivity variations of about one order of magnitude. Surprisingly, qualitative differences are found between PEDOT-PSS films gyenomenon different at different spots. Depending on position, either linear or quadratic curves are obtained. The former is what is expected for an ohmic medium, the latter is generally assumed to be indicative of space charge limited conduciton. This would indicate that either the PEDOT is inhomogeneously doped, or that the PSS is inhomogeneously distributed over the sample. When the tip is in contact with such a region, this domain limits the current, and thus determines the I-V curve.

Substitution And Preparation Effects On The Morphology Of PPV. Martijn Kemerink1,2, Erik Van Duren1,2, Alexander Van Zon1, Herman Schoo3 and Rene Janssen1,2; 1Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; 2Chemical Engineering, Eindhoven University of Technology, Eindhoven, Netherlands; 3TNO Industrial Technology, Eindhoven, Netherlands.

It is known that morphology plays a crucial role in determining the electrical and optical properties of conjugated polymers. In turn, the morphology can be influenced by numerous parameters. We present a systematic study to the morphology of spincoated films of poly(p-phenylene vinylene) derivatives as a function of substitution, concentration, annealing, and solvent. Using a recently developed method, we are able to resolve both individual molecules and aggregates at the surface of arbitrarily thick films by AFM. This ability allows monitoring subtle morphological changes, that are invisible by other means, including conventional AFM and STM. The most marked result is the difference between symmetric and asymmetric PPVs. The latter tends to self-aggregate into circular conformations with a 10-15 nm diameter. In contrast, the former tend to align the conjugated backbone of neighbouring chains, giving rise to relatively straight conformations and the formation of inter-chain aggregates. Inter-chain aggregation at the film surface is not observed for asymmetrical non-regio-regular (rr) PPVs. Strong aggregation was observed for an asymmetrical rr-PPV, proving the importance of considering traditional disorder in this methodology. Heating the films for about 1 hour at 170°C causes relatively small rearrangements in the molecular morphology. However, these rearrangements, occurring on a length scale of at most tens of nm, have profound effects on the (charge) transport, which is sensitive to changes in position and orientation on a sub-nm scale. In general, both inter-chain aggregation (for symmetric polymers) and intra-chain self-aggregation (for asymmetric polymers) are promoted by annealing. In contrast, chains based on indirect proof in literature, no strengthening of coiled-up chains is observed after annealing.
substrate bonding of the molecules. Carboxyl and amino terminated structure and chemical composition of the materials used as self-aggregation into circular conformations was observed for good solvents, but not for a relatively bad one, which yields a more extended network-like morphology. The larger inter-chain overlap in concentration from 1 to 5 mg/ml does not seem to give the component of the TFT and the assembled device. We will describe our T5.16

Characterization of Carboxyl Functionalized SAMs and Surface-Attached Interlocking Molecules Using NEXAFS. Trevor M Willey, Andrew L Vance 1, Tony van Buuren 1, C. Bostedt 1, B. R. Hart 1, R. W. Meulenberg 2, A. J. Nelson 1, L.J. Terminello 1 and C. S. Fadley 3, 2; 1Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; 2Physics, University of California, Davis, Davis, California, 3Materials Sciences, Lawrence Berkeley National Laboratory, Berkeley, California.

Self-Assembled Monolayers (SAMs) and other organo-thiol compounds on surfaces have been becoming an increasingly important to achieve surface attachment of complex molecules. In order to produce useful films, one needs to understand the orientation, order, and substrate bonding of the molecules. Carboxyl and amino terminated SAMs are useful for self-assembling surfaces for surface attachment and immobilization of proteins, DNA, viruses, as well as using the charged state of the endgroups in switchable surfaces. We are also using such functionalization in surface attached interlocking molecules to attempt to induce and measure orientation (switching) within interlocking molecules. However, functionalization often (adversely!) affects the synthesis, order, packing, and formation of these films. With proper synthetic protocol, many of these issues can be overcome. Here, Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) results probe the orientation of molecules while XPS is used to determine the attachment and chemical nature of the films. We present NEXAFS spectra to compare and contrast the ordering and between SAMs from mercaptohexadecanoic acid (HS(CH2)15COOH) a long-chain molecule with strong chain-chain interactions and thiocic acid (S2(CH2)22CH(CH2)2COOH) with a large base hindering strong interactions between its short chains. Stark conformational differences occur in these films of the endgroups with deprotonation (COO- vs. COOH). In addition, we will present preliminary results using functional groups in switching interlocking molecules on surfaces. This work is supported by the U.S. Department of Energy, BES contract W-7405-ENG-48, LLNL, also W-DE-AC03-76SF000008 at the ALS at LBNL, DE-AC03-76SF00515 at the SSRL at SLAC.

T5.17

Electronic processes and exciton decay dynamics at organic semiconductor donor-acceptor interfaces. Linus Lu, Ji-Seon Kim and Richard H Friend; Physics (Optoelectronics Group), University of Cambridge, Cambridge, United Kingdom.

We have studied different length-scale organic semiconductor heterojunctions based on blends and random copolymers of conjugated polyfluorene materials; poly(9,9-diocetyl-fluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB/Donor) and poly(9,9-diocetyl-fluorene-co-benzothiadiazole) (F8BT/Acceptor). In these materials, organic heterojunction starts with predominant micron-scale in the blends and ends with molecular-scale segregation in the copolymers. At these different length-scale organic heterojunction results are required to molecular-scale electronic processes such as charge-carrier injection, transport, recombination, and dissociation processes, through a combination of electrical, optical, and spectroscopic measurements at various device structures such as Light Emitting Diodes (LEDs) and Photovoltacs (PVs). Our results show that the molecular-scale electronic processes within these materials are quite different when these processes occur at the heterojunctions with different length-scales. For example, in the LEDs, the copolymer exhibits a much constant electroluminescence quantum efficiency through high electric field, whereas the blend shows initial high efficiency at low electric field but drastically decay as an electric field increases. In the PVs, the copolymer shows different short-circuit photocurrent action spectra compared to the blend, without changing the maximum peak external quantum efficiency of the short-circuit photocurrent. However, there is a very little difference in electron and hole mobility in copolymer and blend. In this report, we also present our spectroscopy study of exciton decay dynamics in these systems, based on the observations we made from time-correlated single-photon counting (TCSPC) experiments on both films and diluted solutions. We will discuss the role and implication of organic semiconductor heterojunctions, especially across the donor-acceptor interface in the copolymer, for organic semiconductor devices. We have initially identified a new intra-chain state/species found in this copolymer system previously absent in samples of both the homopolymers and the blend. This intra-chain exciton has a unique and distinctive decay dynamics and contribute to efficient electron-hole capture in light-emitting diodes and charge dissociation in photovoltaics (PVs) incorporating the copolymer as the active material.

T5.18

Negative Capacitance Phenomenon in Organic and Polymeric Light-Emitting Diodes: a Recombination-Dependent Event. Fernando A. Castro 1, 2, Paulo R. Bueno 1, Lucas F. Santos 2, Roberto M. Farra 3, Libero Zippiriolo 3, Frank A. Nuesch 3 and Carlos F.O. Graselli 2; 1IFM - FCFLIP, Universidade de Sao Paulo, Ribeirao Preto, Sao Paulo, Brazil; 2DFCM - IFSC, Universidade de Sao Paulo, Sao Carlos, Sao Paulo, Brazil; 3LOMM, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Organic semiconductors either based on molecular or macromolecular materials have attracted much attention for their potential applications as active materials in electronic and optoelectronic devices. However, the basic physical mechanisms underlying carrier injection, transport and recombination in such kind of devices are not understood up to this moment, despite of the great progress achieved in the last decade. A good approach to study injection, transport and recombination features involved in PLEDs and OLEDs is to use impedance (admittance) spectroscopy (IS), taking advantage of the fact that it is a frequency-resolutive technique. Here we have used IS technique to discuss about the evidences that negative capacitance phenomenon arises in PLEDs and OLEDs just when the recombination process is present, so that they are related to each other. The negative capacitance is observed in a variety of conditions and systems, representing one of the less clearly understood dielectric phenomena. Accordingly, there are few reports on negative capacitance in pure electronic devices and the physical origin of this phenomenon is far from been understood. Our goal in this work is to demonstrate that this negative capacitance phenomenon is related to the recombination process in PLEDs and OLEDs. We report the appearance of negative capacitance in tris-8-hydroxyquinoline-aluminum (Alq3) and poly(2-metoxi-5-(2-ethil-hexiloxy)-1,4-phenylene vinylen) (MEH-PPV) based LEDs, depending on the conditions leading to recombination. In ITO/CaPc/NPD/Alq3/LiF/Al LED we observe a capacitance increase as we start increasing the forward bias. However for bias higher than 2 V (when recombination starts to take place), the capacitance starts a decrease and become negative. On reverse bias no negative capacitance is observed. Similar results are observed for MEH-PPV, although the first capacitance increase in forward bias is not seen. In hole-only and electron-only organic diodes based on these active materials we observe a capacitance negative phenomenon in observed.
T5.19 Fabrication of N-electrode nano-junctions for mono-molecular electronics interconnects [1]. Olivier Cacciottl, 1 Christian Joachim, 1 Jean-Paul Martinez, 1 Franck Carcenac 2 and Erik Dujardin 1 1 NanoScience Group, CNRS - CEMES UPR 8011, TOULOUSE, France; 2 LLAS, CNRS, Toulouse, France.

So far, the CMOS-based microelectronics technology has been able to keep up with the miniaturization and integration challenges thanks to numerous scientific and technological innovations. However, the foreseeable physical limitations of the semiconductor industry could be reached within the next decade. The idea that a few (or even one) molecules could be embedded between electrodes and perform basic functions of digital electronics was suggested in the 70s and has now been implemented in a number of different so-called hybrid-molecular devices. Nevertheless, the fabrication of complex circuits out of individual components remains challenging. A second approach is mono-molecular electronics, in which a single molecule integrates several elementary functions and the required interconnections. Computation is achieved by interfacing the molecules with N input/output [2]. Following this second approach, we will present a new e-beam nanolithography process developed to fabricate N-electrode nano-junctions for the electrical interconnection of a mono-molecular circuit having N input/output, N > 4. The fabricated electrodes of the junction have a width below 20 nm and are buried beneath the paper surface coplanar with the SiO2 surface. For N = 5 and N = 20, such electrodes can be positioned on a circle of a diameter below 40 nm and 200 nm respectively. An interconnection roadmap for molecular electronics will be discussed. The process is compatible with all current possible ways of interconnecting a mono-molecular circuit via atomic wires, nanotubes or metallic nanowires. [1] O. Cacciottl, C. Joachim, J.P. Martinez, F. Carcenac, in press. [2] C. Joachim, J. K. Gimzewski, A. Aviram, Nature, 2000, 409, 541-548.


We present a new technique for characterizing thermal properties of SAMs which are chemisorbed onto isolated gold nanoparticles as well as continuous gold planar layers on SiNx. The Au films are deposited on a SiNx substrate, the growth of SAMs is performed by immersing the substrate into an alkanethiol solution. The amount of material sampled (20 picomole) is typically below the sensitivity limits of conventional calorimetry. However, the nanocalorimetry technique (1.2) - which has recently been used to observe glass transition in 1.3 nm thick films of polymers (3) and melting in 0.2 nm thick films of metals (4) - has higher sensitivity (less than 1 nJ/K) and allows us to study the order/disorder phase transition and desorption of SAMs. We envision this technique to be useful in characterizing SAMs formed on both planar (2-D) and particle (3-D) surfaces in a systematic manner. [1] M.Yu. Efremov, E.A. Olson, M. Zhang, F. Schiettekatte, Z.S. Zhang and L.R. Allen, Phys. Rev. Lett. 91 (2003) p.085703. (2) E.A. Olson, M.Yu. Efremov, M. Zhang, Z.S. Zhang, and L.H. Allen, J. MEMS 12 (2003) p.353. (3) M.Yu. Efremov, E.A. Olson, M. Zhang, Z.S. Zhang, and L.H. Allen, Phys. Rev. Lett. 93 (2003) p.085703. (4) M.Yu. Efremov, F. Schiettekatte, M. Zhang, E.A. Olson, A.T. Kwan, R.S. Berry, and L.H. Allen, Phys. Rev. Lett. 85 (2000) p.3560.

T5.21 Nanoscale Patterning of Organic and Molecular Electron Devices through Radiation-induced Film Modification. Brian Alexander Matts, Yoon Jeong Kang, and Vivek Subramanian; Electrical Engineering, University of California, Berkeley, California.

Molecular electron devices have recently gained significant attention, with particular applications in ultra-dense memories and computational parallelism. As the date, all ultra-dense molecular circuits have used blanket organic layers, resulting in the potential for crosstalk between adjacent devices. Furthermore, such demonstrations have either used silicon-based addressing circuits, or hardwired off-chip addressing. Clean electrical isolation is a crucial need for ultra-dense molecular electronics. However, to increase device density to nanoscale dimensions, it has become essential to develop a patterning technology that can electrically isolate devices regions even further than at the nanoscale and is still obtainable via the shadow masking. Self-assembled monolayer. Here, the direct patterning of organic semiconducting films utilizing electron-beam lithography has proven to modify the molecular structures, resulting in drastic changes in the film's electrical characteristics. By testing the exposure of OTFT device channels, electron doses as low as 10eC/cm2 can reduce both mobility and current by at least 10% of their original values. These effects have also shown high contrast, as only slight changes in applied dosage can have a significant electrical impact, which is important when considering the inevitable beam-spreading and the resulting unintentional exposure occurring as electrons bombard the organic film surface. Current organic materials under investigation include poly(3-hexylthiophene) and pentacene, which are chosen for their high mobility and wide-spread usage in the research community. Both materials show excellent contrast and, in conjunction with this technology, allow for the fabrication of densely packed transistor arrays with extremely low inter-device currents. Such transistor arrays may be used to provide on-pitch addressing for molecular crosspoint array memories.

T5.22 A New Method of Fabricating Nano-sized Gap Electrodes, Chung-Park Park, Sung-Ouk Ryu, Sung-Hee Ko Park, Han Young Yu, Ung Hwan Pi and Sung-Yool Choi; Basic Research Laboratory, Electronics and Telecommunications Research Institute, Daejeon, South Korea.

We have fabricated a pair of metal electrodes with a nano-sized gap to characterize the electrical properties of a single molecule for the application in molecular electronic devices. A physical width of the nano-sized gap is crucial for characterization of molecules and has to be comparable to the length of a molecule. In the previous techniques of fabricating nano-gap electrodes, for example, the mechanical break-junction, electrochemical deposition, and electromigration methods, the overall process is complicated and the size, shape, and location of nano-gaps cannot be easily controlled in a reproducible manner. In this paper, a new method of forming nano-gap electrodes with a high quality of the metallic arc-sprayed thin electrode and the gap width of the gap can be easily controlled by adjusting the thickness of the sacrificial layer. Using atomic-layer-deposited films as sacrificial layers, we fabricated several Au/Pt electrode pairs with gaps of a few nm reproducibly.

T5.23 Conductance Measurements on Different Phases of Dodecanethiol Self-Assembled Monolayer. Ung Hwan Pi, Chan Woo Park, Sung-Ouk Ryu, Han Young Yu and Sung-Yool Choi, Basic Research Lab., ETRI, Daejeon, South Korea.

We report the effect of the order of molecules on the tunneling conductance through the molecular layers. A Self-assembled Monolayer (SAM) of dodecanethiol was deposited on Au(111)/mica substrate followed by annealing in UVH condition. Scanning tunneling microscope (STM) imaging reveals the formation of three different phases, a high density one with (sqrt(3)xsqrt(3))R30° structure, and two lower density phase, with well-ordered and disordered mixed one. Current-voltage characteristics were measured on each of different structures by using scanning tunneling spectroscopy. The current voltage curves measured at different phase were less reproducible than those measured on the well ordered phase. This shows that the ordering of the molecules is very important in stable measurement of the electrical properties of the molecular films.


The bamboo-shaped multiwalled carbon nanotubes (BS-MWNTs) have been reported in various forms, such as arc-discharge evaporation of graphite, catalytic pyrolysis of hydrocarbons at high temperature, chemical vapor deposition on catalytic film deposited substrates, and nitrogen-containing CNTs (CNX nanotubes). Their growth mechanism and properties of BS-MWNTs have been of great interest. In this work, we report the electrical properties of BS-MWNTs. The temperature-dependent resistivity measurements were carried out on BS-MWNTs vertically grown on cobalt catalys deposited Al2O3/Ti substrates and iron catalys deposited SiO2/Ti/TiO2/Ti substrate at 290 - 900 °C by thermal chemical vapor deposition. Besides, the electrical properties of individual BS-MWNTs with 2-µm size Ti/Au electrodes were measured. For the bulk BS-MWNTs, a heterogeneous model, comprising quasi 1-D metal term and the fluctuation-induced tunneling through thin barriers between metallic
regions, was introduced to explain the conduction mechanism of bulk sample. As a result, the intersheet conduction has been found to be a decisive factor of the conduction mechanism. The electrical properties of individual BS-MWNTs were investigated in relation to the compartment structure in the BS-MWNTs.

T5.25

Acidochromism of Fluorescent Distyrylbenzenes containing Pyridine Rings. Heiner Detert, Institut fuer Organische Chemie, Johannes Gutenberg-Universitaet, Mainz, Germany.

A series of C2-symmetrical azo-analogous 1,4-distyrylbenzenes has been synthesised via twofold PO-activated olefination or Heck reactions. Pyridine, pyrimidine and quinoline were used as terminal rings, forming the central benzene ring of the parent compound 1,4-distyrylbenzene. All compounds were freely soluble and strongly fluorescent. Whereas the electronic spectra of the pyridine and pyrimidine chromophores were very similar to those of the parent compound 1,4-distyrylbenzene, the spectra of the former were strongly altered in the presence of trifluoroacetic acid. Depending on the concentration of acid, protonation of the ground state and/or the excited state caused bathochromic shifts of the absorption and the emission spectra accompanied by reductions of the fluorescence efficiencies.

T5.26

Abstract Withdrawn

T5.27


Molecular electronics, a new technology based on molecules and molecular-scale components, is getting an interesting topic as the miniaturization of solid-state silicon circuitry is edging closer and closer to fundamental limits, especially for the circuit density and the cost of chip-manufacturing facilities. It has been proposed that molecular electronics may provide moderate computational power, high-density memory and logic devices in an extremely small, low-power format that will not require high cost fabrication facilities. For the realization of logic gates with diode array device, a stable molecular rectifier consisting of self-assembled monolayer (SAM) on the metal electrode has been required. Here, we report the synthesis and characterization of novel electron donor-sigma-acceptor-thioacetate molecule including reduction and oxidation potentials of CV data and the characterization for the formation of single monolayer by SAM. In addition, we also report molecular rectifying properties with CP-AFM and metal-molecule-metal (MMM)-type device. Finally, the array device fabrication and performance of molecular logic gates will be presented.

T5.28

Abstract Withdrawn

T5.29

Resistivity Anomaly Observed at Interfaces of C60 Derivatives Self-Assembly Monolayer /Ultrathin Au Films. Hiroshi Yamamoto, Nobuyuki Itawa and Yoshiaki Shimizu; College of Sci. & Technol., Nihon University, Funabashi, Chiba, Japan.

The exoctic electric conducting properties, for example a room temperature superconductivity have been expected at interfaces of organic molecule monolayer/contact ultrathin film. The purposes of this work are to prepare such the interface and to examine its conducting properties. Self-assembly monolayers of C60 derivatives, C60-O-C8SH, (C60-SAM) were accumulated on ultrathin Au films which were deposited on MgO (100) single crystal substrates. The surface morphology of the conductive monolayer observed and analyzed by AFM. Since the surfaces of pre-annealed MgO were atomically flat and revealed step-terrace structures, the ultrathin Au films were deposited along the edges of the steps with the length of a few micro-meters. As the result of the characteristic nano-structure of the Au films, the C60-SAM adsorbed on them showed also one-dimensional alignments with the width of few tens nm. When temperature dependences of the resistivity of the C60-SAM/Ultrathin Au Au film were measured by a four probe technique, the Au electrodes were simultaneously deposited during the preparation of the Au ultrathin films through the metal masks in which the distance between the holes is 0.15mm. Some of the specimens revealed the temperature dependences of resistivity differed from metal-doped C60 films by a few orders of magnitude with the dependence of resistivity at the temperature range of 150 - 250K.

T5.30

Fabrication and Conduction mechanism of the nanometer-SAM-metal contact. Hyoyoung Lee, Do-Hyun Kim, Eun-ju Lee and Taehyoung Zyung; ETRI, Taejon, South Korea; 2KRIST, Daejeon, South Korea; 3Dept. of Electrical & Electronics & Computer Eng, Dong-A Univ., Busan, South Korea.

As microelectronics devices approach their technological and physical limits, molecule electronics, i.e., the information technology at the molecular-scale, becomes more and more investigated and envisaged as a promising candidate for the nanoelectronics of the future. To this respect, synthesized molecules on solid substrates is a powerful ‘bottom-up’ approach (Langmuir-Blodgett(LB) and Self Assembly(SA) method) for the fabrication of devices for molecular-scale electronics. For the molecular devices it is the most difficult task to attach nano-size metal contacts on the active molecule. Several ways have been suggested. But, these methods are complicated and required expensive fabrication cost. In addition, to measure the electronic transport through an organic monolayer, we need a test device as simple as possible. In this presentation we fabricated an array of molecular devices with a single vertical metal-molecule-metal (MMM) junction. Especially, SiO2 or SiNx insulating layer was employed in order to prevent the electrical short circuit between bottom and top contacts. And to contain the molecules inside, the nanopores were formed in insulating layer by RIE. The molecular devices produced diode-like characteristics and they produced a good yield only with 4% of short circuits, reflecting a possible application to characterize unknown molecules and fabricate a molecular diode. Also, we report measurements on two-electron-bond metal-molecule-metal transport properties of phenylene ethined based molecule-metal junctions. Nanoscale metal-molecule-metal junctions with single monolayer of self-assembled phenylene ethined were fabricated with variable temperature conductance measurements to determine the dominant electronic transport mechanisms.

T5.31

Measuring and Engineering the Conductivities of tris-(8-hydroxyquinoline) Aluminum, S.K. So, S.C. Tse and H.H. Fong; Physics, Hong Kong Baptist University, Hong Kong, China.

The electron mobility of tris-(8-hydroxyquinoline) aluminum (Alq3) is intentionally altered by means of doping. Transient electroluminescence (EL) is then employed to measure the electron mobility of doped Alq3. The transient EL sample has a structure of ITO/TPD/undoped Alq3/doped Alq3/cathode. Intrinsic electron mobility of Alq3 can be evaluated for the thick film devices and the results are in excellent agreement with independent time-of-flight measurements on non-dispersive transient. Mobilities of C540, DCM, and Bphen doped-Alq3 are measured. The electron mobility is reduced by almost one order of magnitude after doping C540 while DCM doped-Alq3 exhibits much lower electron mobility. The decrease in mobility can be attributed to scattering or trapping of carriers as they traverse through the doped layer. However, the electron mobility is enhanced in Bphen doped-Alq3. It is expected that by combining Alq3 and Bphen at the right composition, the conductivity and the stability of the “alloy” will be optimized.

T5.32

Atomic Resolution STM Study of Single-Walled Carbon Nanotubes on GaAs(110). Laura Ruppert, Peter M. Albrecht and Joseph W. Lyding; Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Carbon nanotubes, because of their unique blend of robust electronic and material properties and inherent nanocable-dimensionality, could form the fundamental building block of the next generation of electronic devices. Additionally, reports of the photoconductivity [2] and -absorptive [3] properties of these structures raise the possibility of nanotube-based optoelectronic devices. However, before such devices can be fully realized and the materials properties of nanotubes fully explored, a thorough understanding of the properties of nanotubes and their interactions with technologically relevant substrates must be achieved. To that end, we have deposited and obtained atomic resolution scanning tunneling microscopy (STM) images of single walled carbon nanotubes on GaAs(110) surface in ultra-high vacuum (UVH). The cleaved III-V substrate is well suited to surface interaction studies due to the absence of surface states within the bandgap. Additionally, the conducting III-V materials form the basis of most current optoelectronic devices and may play an important role in the development of nanotube-based photonic devices. In our study, SWNT’s were deposited in situ via a dry-contact procedure previously demonstrated on the hydrogen passivated Si (110) surface. Subsequent STM images reveal evidence of the formation of single-walled carbon nanotubes on GaAs(110) surface.
of a fairly high density of nanotubes, similar to that seen on Si, with no indication of tube or substrate perturbation due to the deposition process. The energetic disorder in the as-deposited films was significant; the spin-scan contact deposition technique to more substrates, a step that would greatly facilitate further UV/STM investigations of nanotube interactions with surfaces not compatible with solution-based ex-situ deposition procedures. Both topographic and current images provide simultaneous atomic resolution of the SWNT's and the underlying substrate. Individual tube chirality can be identified and theoretical band gap predictions calculated. Spectroscopic data reveals nanotube bandgaps in the semiconducting range, with electronic features distinguishable within the GaAs substrate bandgap. Further studies of SWNT's on the cleaved GaAs surface and investigations of carbon nanotubes coupled to more complex III-V heterostructures will be reported. 1J. Appenzeller, R. Martel, V. Derycke, M. Radosavljevic, S. Wind, D. Neumayer, Ph. Avouris, Micro. Engin. 64, 301-97 (2002). 2M. Freitag, Y. Martin, J.A. Misewich, R. Martel, Ph. Avouris, NanoLetters 3 1607-71 (2003). 3H. Kataura, et. al., Jpn. J. Appl. Phys. 38, L555-58 (1999). 4F. Albrecht, R.M. Farrell, W.Y. Je, and J.W. Lyding, Conference Proceedings, Third IEEE Conference on Nanotechnology 2003, 327-30 (2003). T5.33 Ultrathin Polymer Film Capacitor Composed of Relaxor-Ferroelectric Fluoropolymer Langmuir-Blodgett Films. Cheng Huang 1, Q.D. Shen 2 and Q.M. Zhang 1. 1Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania; 2Department of Polymer Science and Engineering, Nanjing University, Nanjing, Jiangsu, China.

Polymer film capacitors are widely used in electronics. However, compared with ceramics, the dielectric constant of polymers is small and the polymer film capacitors have low dielectric strength and the dielectric constant and reducing the film thickness of capacitor have two points of merit, that is, large value of capacitance and smaller size of capacitor. Smaller size of capacitors is recently required for miniaturizing cellular phones and portable computers. Furthermore, molecular size capacitor will be need for nanotechnology. Recently we have developed processible and high-performance poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) based electroactive fluoropolymers which possess a relatively high room-temperature dielectric constant, one order of magnitude higher than that of current dielectric polymers. The high-dielectric-constant fluoropolymer ultrathin film might be a good candidate for an ultrathin polymer film capacitor. To achieve ultrathin film capacitor and molecular size capacitor, the Langmuir-Blodgett (LB) technique was carried out on the silicon wafer. In this paper, the capacitor properties of poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymer (PVDF-TFE-CFE), Langmuir-Blodgett films were investigated as a function of number of layers with dielectric and current-voltage measurements. The breakdown electric field of the LB films was also measured with the number of layers. The results gave us an idea for constructing molecular capacitor using the LB technique. Using the LB technique, thin film thickness can be precisely controlled. One of the advantages of the LB technique, thin film thickness can be precisely controlled by the number of deposited layers; thus, we can make an ultrathin polymer film capacitor at a molecular level.

T5.34 Effect of tertiary butyl substitution on the charge transport of aromatic hydrocarbon based organic semiconductors. H.R. Feng, K.L. Tong and S.K. So. Physics, Hong Kong Baptist University, Hong Kong, Hong Kong.

Aromatic hydrocarbon based organic compounds (e.g. anthracene, naphthalene, and pentacene) have demonstrated importance in organic electronic devices. However, the high bandgap gives rise to low efficiency and superior stability. In device application, tertiary butyl (t-butyl) substitution is practically used to prevent re-crystallization of organic transporting and fluorescence quenching of organic emitter. Therefore, it is worth to investigate the effect of t-butyl substitution on these hydrocarbon-based complexes. As a demonstration, the charge transport of rubrene (5,6,11,12-tetraphenylanthracene or RB), and the novel butyl-based t-butyl rubrene [2,8-di(t-butyl)-5,11,12-di(4-t-butyl)phenyl]-5,12-diphenyllanthracene or TBBR], were examined in form of amorphous films as functions of electric field and temperature by means of time-of-flight technique. It was found that both materials exhibited g-type conduction. By ab initio calculations, results suggest that the hole conduction is contributed by the central naphthalene moiety. At room temperature, the hole mobility $\mu_h$ for RB is $7.9 \times 10^{-7}$ cm$^2$ V$^{-1}$ s$^{-1}$ whereas $\mu_h$ for the more bulky TBBR is about 2.7 to 3 times larger. The microscopic conduction mechanism in both materials can be modeled by the Gaussian disorder model (GDM) in which hopping conduction occurs through a manifold of sites with energetic and positional disorder. The dielectric constant is about 78 meV in each case, and is mainly controlled by Van der Waals interaction. Indeed, the t-butyl groups in TBBR induce large fluctuations in the spatial separation among TBBR molecules and result in a decrease in the conduction and disorder factor, hence a reduction in the hole mobility. With sufficient high mobility in amorphous state, RB can be blended into the polycarbonate (PC) in order to engineer the mobility such that RB:PC is able to establish potential applications in organic transistors.
present our results using density functional theory (DFT) and complete active space self-consistent field (CASSCF) methods that strongly support the intriguing finding that even small (heptacene and higher) oligoacenes exhibit a significantly high biradical character and a constant non-zero semiconductor type HOMO-LUMO gap. We were somewhat curious to find that at the RB3LYP /6-31G(d) level of theory, the HOMO-LUMO gap of heptacene is 2.7 kcal/mol smaller than the open-shell singlet state and the spin contamination is small \((<0.2\text{ at }\text{RB3LYP})\). However, these values increased with respect to the number of benzenoid units. The relative energy of the triplet state (using the same level of theory) for heptacene is 4.7 kcal/mol lower than the closed-shell singlet state; however, it is still 5.8 kcal/mol higher than the open-shell singlet state. Similar results were obtained with BLYP, PW91 and B3PW91 functionals. Triplet structures are always higher in energy than open shell singlet structures, but the triplet is more stable than closed shell singlet for nonacene. Hence, our calculations predict that oligoacenes will maintain a ground state singlet even above heptacene-octacene. CASSCF calculations are in agreement with DFT results. The data presented here, in contrast to the literature, predict a non-zero HOMO-LUMO gap (1.8 eV), similar to that of hexacene, but the experimentally unknown oligoacenes are near the limit of the calculated HOMO-LUMO gap. Moreover, longer oligoacenes are expected to exhibit a biradical character. This might be a reason for their high reactivity and reported difficulty in isolation. Any design of electronic devices based on the higher oligoacenes will require that attention be paid to the theoretical results given above.

**T5.38**

Conjugated polymer wires for nano-scale field effect transistors.

Bazley, S.\(^1\), Lidzey, D.\(^1\), Woong Sang Jahng\(^2\), L. Jay Guo\(^3\) and M. David Curtis\(^1,2\).

\(^1\)Molecular Science and Engineering, University of Michigan, Ann Arbor, Michigan; \(^2\)Chemistry, University of Michigan, Ann Arbor, Michigan; \(^3\)Electrical engineering and computer science, University of Michigan, Ann Arbor, Michigan.

Organic semiconductors can be described as molecular assemblies in which conjugated molecules are held together by weak van der Waals force type. The weak intermolecular interactions lead to the potential limitation of the performance of organic field effect transistors because of substantial electron-phonon scattering at room temperature. One of two strategies for higher field effect mobility is to design organic semiconductors with strong intermolecular interactions among nearest neighbor molecules. The stronger interaction will result in stiffer crystalline structures, facilitating charge carrier transport. The other is to explore alternative conduction mechanisms and device structures. We have developed and employed a modified CASSCF methodology for studying conjugated polymers, the two ends of which are anchored by strong intermolecular interactions. The stronger interaction results in higher energy barriers between polymer segments, which can be utilized to make good contacts. Secondly, transistor channel length has to be reduced from micro size to nano size to fit the length of the single polymer chain. In this work, we designed and prepared polyphenylene ethynylene (PPEs) with thiocarbocic acid groups at the polymer chain ends, and fabricated nano-scale field effect transistor. The Heck-Cassar-Sonogashira-Hagihara reaction, the Pd-catalyzed coupling of aromatic allyl acetylene and aromatic iodides in tetrahydrofuran/ amine solvent, yielded multiple reactive terminal groups. Subsequent coupling reaction between the PPE and a compound containing the thiocarbocic acid groups produced the target polymer. The synthesized polymer was self assembled onto the devices with a nano channel which was prepared by E-beam lithography. We will present molecular design, synthesis, self-assembly and device properties.

**T5.39**

Monte Carlo modelling of charge transport in polymer photovoltaic materials.

Jenny Nelson\(^1\), Amanda J Chatt\(^2\), Stelios A Choulis\(^3\) and James R Durrant\(^4\).

\(^1\)Physics, Imperial College London, London, United Kingdom; \(^2\)Chemistry, Imperial College London; \(^3\)London, United Kingdom.

Understanding the mechanism of charge transport in single polymer materials and blends is critical to the development of improved organic solar cells and other molecular electronic devices. Transport in organic electronic materials is traditionally evaluated within frameworks such as the Gaussian Disorder Model and its variants \([1,2]\) which model field and temperature dependence of charge transport used to quantify the degree of energetic and configurational disorder in the charge transport matrix. Although useful for comparative studies, these models are unhelpful for identifying the microscopic transport mechanism or predicting the charge transport properties to the chemical or physical structure of the materials. Moreover, they have as yet been applied only to single component systems and do not allow for the impact of geometry on transport in a two-component polymer. Carlo models of polaron transport in organic films that allow for more than one component material, and for alternative microscopic models for the intermolecular hole transfer rate, as well as for correlations in the site energies, which may result from dipolar or torsional interactions \([2]\). We apply the models to simulate the results of time-of-flight mobility measurements in a range of homopolymers and blends. We show that geometric effects on transport in two component systems lead to characteristics typical of dispersive transport even using non-dispersive components. We find that a small-polaron hopping rate is more appropriate than the commonly used "symmetric" and Miller-Abrahams charge transfer expressions in the limit of ordered materials, and we argue that both polaronic effects and disorder must be incorporated to describe transport in the general case. A complementary probe of charge transport is provided by transient absorption spectroscopy, where the population of polaronic species is monitored optically following photoexcitation. Unlike time-of-flight mobility studies, transient absorption probes transport in the low-field diffusion-limited regime, and in certain conditions the dynamics are dominated by polaron diffusion in a single component \([2]\). We have previously shown that the rates of transport and recombination in the same material system, respectively measured by ToF and transient absorption, can be correlated experimentally \([4]\). In this paper we extend our Monte Carlo transport model to the low field regime and in order to explain the observed behaviour with a single transport model. \([1\) H.Baessler, Phys. Status Solidi (b) 175, 15 (1993); \(2\) S. V. Novikov et al., Phys. Rev. Lett. 81, 4472 (1998); \(3\) Z.G.Yu et al., Phys. Rev. Lett. 84, 721 (2000); \(4\) J.Nelson, Phys. Rev. B 67, 155209, (2003); \(5\) I.Montanari et al., Appl. Phys. Lett. 81, 3001 (2002); \(6\) S.A. Choulis et al., Phys. Lett. (in press)](299x322)
Alignment and Photopolymerization of Difunctional Liquid Crystal Monomers Consisting of Disk-like (Discotic) Liquid Crystalline Polymers (LCPs) and the Optical Simulation to Induce Optimal Compensation.

Nitrogen concentrations of 0.4% to 2.4% were obtained. According to the XPS measurements, increasing nitrogen concentration gave rise to an increase of the N-sp² C bonds as well as deterioration of the crystallinity of the BS-MWNTs. Besides, the N-sp² C bonds were found to prevail over the N-sp³ C bonds above 5% nitrogen concentration. At higher nitrogen concentration, the N-sp² C bonds blended in, indicating a decrease in the catalyst activity. The growth of BS-MWNTs was then, therefore, limited from its initial growth.

The electrical characteristics were measured by applying a DC voltage of 3.5 V and monitoring the source-drain current and channel resistance. The measurements were carried out under different gate voltages ranging from -5 V to 7 V. The results showed a significant improvement in the device yield with the increasing gate voltage. At a gate voltage of 7 V, the channel resistance dropped from 650 nA to 240 nA for a source-to-drain voltage of 4 V. The results indicated that the fabricated devices showed field-effect characteristics, with current-voltage characteristics that are typical of field-effect transistors. The results suggest that the incorporation of nitrogen-doped carbon nanotubes in the molecular electronics is a promising approach for achieving high yield in molecular electronics devices.
vacuum-deposited gold film. The admittance characteristics reveal the presence of interfacial states at the dielectric-semiconductor interface. We have performed a detailed analysis of these states based on equivalent circuits models and propose that they could be responsible for the recently reported instability problems in organic TFTs. We have also performed a study on the change in the electrical characteristics and has been biased for prolonged periods of time at different temperatures. Capacitance-voltage measurements show that instability problems occur not only in the accumulation regime but also in the depletion regime. We have found that light with band-gap wavelength rapidly restores the initial characteristics. Our results suggest that interfacial traps present at the dielectric-semiconductor interface and at the dielectric itself play an important role in the operation of organic semiconductor devices by trapping both majority and minority carriers and are responsible for the electrical instability found in TFTs.

T5.46
Electron transport in short macromolecular nanotubes.
Ali Javey and Hongjie Dai; Stanford, Stanford, California.

Electron transport and phonon scattering in metallic carbon nanotubes are explored as a function of length. The mean free paths for acoustic and optical phonon scatterings are estimated to be 300 and 13 nm respectively. Transport through short macromolecular (10 nm) nanotubes is therefore, found to be free of any significant scattering and thus essentially ballistic at both the low and high bias voltage limits. High currents of up to 120 μA can flow through an individual short nanotube.

T5.47
The memory effect of a quaterthiophene field effect transistor with a polarizable gate dielectric.
Narayanuni K.N., Jean-Michel Nunzi, Sylvie Dabos Seignon and Renni de Bettignies; Laboratory POMA, University d'Angers, Angers, Angers, France.

The nonvolatile transistor memory element is an interesting topic in organic electronics. In this case a memory cell consists of only one device where the stored information is written as a gate insulator polarization by a gate voltage pulse and read by the channel conductance control with channel voltage pulse without destruction of the stored information. Therefore such transistor could be the base of nonvolatile non destructively reachable computer memory of extremely high density. In the present work we have fabricated organic field effect transistors with quaterthiophene as the active material and poly(vinylidene fluoride-trifluoroethylene) as the gate insulator. The device exhibits memory effect because of the ferroelectric properties of the gate. The effect of using another insulating layer of lower dielectric constant as a buffer layer between the ferroelectric polymer and the semiconductor is also discussed.

SESSION T6: Transport in Molecular Junctions II
Chair: Cherie R. Kagan
Thursday Morning, April 15, 2004
Room 3008 (Moscone West)

8:30 AM *T6.3
Electrical Transport Properties of Nanoscale Molecular Junctions.
Theresa S Mayer1, Lintao Cai1, Yoram Selzer2, Marco Cabassi1, Thomas Malinowski2 and David Allara2; Department of Electrical Engineering, Penn State University, University Park, Pennsylvania; 2Department of Chemistry, Penn State University, University Park, Pennsylvania.

Designing molecular devices that exhibit desired electronic properties requires a fundamental understanding of conduction in molecular junctions. Progress toward this goal has been hindered by the complexity of fabricating robust and reliable metal-molecule junctions and in identifying the nature of the as-fabricated molecular junction. This presentation will compare temperature dependent electrical transport measurements and inelastic tunneling spectra collected from three different nanoscale molecular junction testbeds that incorporate dithiolated molecular wire molecules coupled to Au- or Pd-metal electrodes. The testbeds include individual molecules spanning planar nanogaps introduced by Au electromigration, and self-assembled monolayers inserted within or at the intersection of crossing 30-nm diameter Pd- or Au-metal nanowires. The results of these measurements is beginning to provide insight into the role of factors such as molecular structure, endgroup, contacts, and collective effects in metal-molecule junction transport properties.

9:00 AM *T6.2
Molecular features that govern resonant tunneling behaviors.
Christopher Gorman, Chemistry, North Carolina State University, Raleigh, North Carolina.

We will show how structurally simple, electroactive self-assembled monolayers can give rise to negative differential resistance. We will then show how chemical modifications can modify the characteristics of this behavior. These interactions include chemically well-defined lithographic patterning and reversible, non-covalent assembly, disassembly and modulation of the junction.

9:30 AM T6.3
Multilevel Molecular Memory. Chao Li, Wendy Fan and Chongwu Zhou; USC, LA, California.

Multilevel Molecular Memory Chao Li, Wendy Fan, Bo Lei, Daishun Zhan, Song Han, Tao Tang, Xiaolei Liu, Zugen Liu, Sylvain Assaro, M. Meyyapan, Je Hean, Chongwu Zhou; Abstract Multilevel molecular memory was proposed and demonstrated for nonvolatile data storage up to three bits (eight levels) per cell, in contrast to the standard one-bit-per-cell (two levels) technology. In the demonstration, charges were precisely placed at up to eight discrete levels in redox active molecules self-assembled on a single-crystal semiconducting nanowire field effect transistor. Gate voltage pulses and current sensing were used for writing and reading operations, respectively. Charge storage stability was tested up to retention of 600 hours, as compared to the longest retention of a few hours previously reported for one-bit-per-cell molecular memories. Comparison between silicon and molecular devices shows that multilevel molecular memory enables low-power, ultra-dense and high-performance nonvolatile data storage to go beyond the silicon technology scaling limit. 1. Dept. of E.E.-Electrophysics, University of Southern California, Los Angeles, CA 90089, USA. 2. Elliott Laboratory, MS 229-1, NASA Ames Research Center, Moffett Field, CA 94035, USA. 3. MS 229-1, NASA Ames Research Center, Moffett Field, CA 94035, USA. a. To whom correspondence should be addressed: chongwu@usc.edu

9:45 AM T6.4
Scanned Probe Imaging of Nanoscale Switching Centers in Metal/Molecule/Metal structures. Chun Ning Lau1, Duncan Stewart2, R. Stanley Williams2 and Marc Bockrath1; 1Bell-Lettett-Packard Labs, Palo Alto, California; 2Applied Physics, California Institute of Technology, Pasadena, California.

Molecular conductance switching has been experimentally observed in a number of different systems covering a wide variety of molecular insulators. Understanding the switching mechanisms, which remain controversial to date, is essential for design and fabrication of functional nanoscale switches. Here we describe a new switching mechanism revealed by a novel scanned-probe technique that yields an image of the mechanism-electrical response of a Pt/stearic acid/Ti structure device. Such a device switches reversibly between "on" and "off" states with unusually high on/off ratio (105) under appropriate bias voltages. However, because stearic acids have a simple molecular structure and are electrical insulators, previously proposed switching mechanisms such as molecular conformational changes are not likely to account for switching in our system. Using our technique, a single switching event was directly imaged and its current-voltage characteristics determined. First, we will discuss theoretical studies on small organic molecules linking metal/insulator/metal junctions. I will discuss theoretical studies on small organic molecules linking metal/insulator/metal junctions.
effect for a shorter molecule. We will also discuss measurements of the
C60 fullerene and C70 dimer (C140). In C140 devices, the transport
measurements are affected by an intercage stretching vibrational
mode that has an energy of 11 meV. We make comparisons between
the observed tunneling rates and those expected from the
Franck-Condon model.

11:30 AM T6.7
The Kondo Effect in C60 Single-Molecule Transistors.
Douglas Natelson1,2 and Lam H. Yu1; 1Physics and Astronomy, Rice
University, Houston, Texas; 2Electrical and Computer Engineering,
Rice University, Houston, Texas.

We have used an electromigration technique to fabricate C60-based
single-molecule transistors. We describe in detail the process statistics
and the protocols used to infer the successful formation of a
single-molecule transistor. At low temperatures each transistor acts as
a single-electron device in the Coulomb blockade regime. In several
devices we observe conductance features characteristic of the Kondo
effect, a coherent many-body state comprising an unpaired spin on
the molecule coupled by exchange to the conduction electrons of the
leads. The inferred Kondo temperature can significantly exceed 100 K.
Signatures of molecular vibrational modes are also observed in the
Kondo regime.

11:45 AM T6.8
Phenyldithiol-based Molecular Transistors with Strong Gate
Effects. Hiroshi Inokawa, Hiroshi Nakashima, Kazuaki Furukawa,
Kenji Yamazaki, Junzo Hayashi, Yasuo Takahashi and Keiichi
Torimitsu; NTT Basic Research Laboratories, Atsugi, Kanagawa
Pref., Japan.

We introduced a new method to efficiently fabricate Au nano-gaps, in
which length and width of suspended masks were systematically
varied to obtain gaps of 1 nm directly, and contacts that could be
converted to nano-gaps later by break-junction technique. These gaps
were made on a 20-nm-thick gate SiO2 that could reliably apply
electric field of \(4.3\) MV/cm. 4,4'-terphenyldithiol SAM was
deposited from a solution under an inert-gas atmosphere to bridge the
gaps. The nano-gap devices showed noisy \(I_d-V.gs\) characteristics at
room temperature, but they became stable and exhibited peaks as the
temperature decreases. At 30 K, more than 40 % of devices showed
\(I_d-V.gs\) with on/off ratios larger than 10 at \(V_d\) = 0.1 V, and some
had ratios of more than 1000. A group of devices having “on” current
around 1 nA displayed large on/off ratios and clear Coulomb
diamonds with conductance gaps of up to 0.6 V. This presumably
indicates that the number of molecules involved in these devices is
small, and the molecular conductance is of the order of 10 nS.
Single-electron charging is not generally considered to play a major
role in electrical conduction through Au-terminated phenyldithiols [1].
However, in view of the reported conductance values much lower than
the quantum conductance (\(e^2/h\)) and the Coulomb blockade effects
observed in slightly larger molecules [2,3], the present results could be