# Dynamics of Structure and Charge at the Molecular Scale

*NSF NIRT Grant 0102950*

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**Goals.** The goal of this NIRT is to investigate the effects of fluctuations in atomic structure or electric charge on the electronic properties of nanoscale devices. As electronic device dimensions become smaller, two issues become increasingly important: the discreteness of atomic matter becomes significant in determining structural stability, and the discreteness of charge causes significant sensitivity of the device to fluctuations in the local electrostatic environment. Both issues are of fundamental importance to the design of any working nanoscale device. The Maryland NIRT brings together researchers with significant experience in studying charge fluctuations (Lobb) and structure fluctuations (Williams) with researchers who are constructing radically new molecular-scale electronic devices (Sita, Fuhrer).

**Systems to be Studied.** To accomplish this goal, the Maryland NIRT team is studying a range of model nanoscale devices in which to study the effects of changes in atomic structure and/or electrostatic potential on electronic properties. These devices include:

**Carbon Nanotube Devices.** The ease of conduction of carriers in a semiconductor is reflected in the mobility, the conductivity normalized by the number of charge carriers. Research by the NIRT has shown that semiconducting nanotubes have extraordinarily high mobilities[2]; we have set a lower bound on the hole mobility of 20,000 $cm^2/Vs$ at room temperature, approximately 40 times that of pure silicon. This high mobility also means high charge sensitivity; NIRT researchers found that the conduction through semiconducting nanotube devices was significantly influenced by the motion of single electrons into and out of charge traps near the nanotube, and this effect was exploited to demonstrate a single-electron memory device[3]. Scanned gate microscopy is used to identify charge-sensitive defects in nanotubes (see Figure 2). Future research will study the noise in these nanotube devices and thus the dynamics of the charges that are producing the noise. Also of interest is the role of the nanotube/metal interface – this molecular-scale junction should be enormously sensitive to its physical and chemical environment, and experiments are underway to change that environment through physisorption and chemisorption of particular species. Single-electron transistors with elevated operating temperatures and large coupling to the environment are being fabricated from carbon nanotubes; these should open up new areas for exploration of charge dynamics.

**Single Molecules.** The NIRT team is focusing on rational design of molecular two-state systems in which the rate of electron transfer through the molecule is modified by switching from one state to another. The model system consists of two ferrocene moieties linked by a conjugated organic bridge (see Figure 1). The switching is driven through the rearrangement of charge on the bridge for example by protonation, external electric field, or photoexctitation, which changes the oxidation potential of one ferrocene moiety. Thiol linkages enable chemisorption on gold surfaces. A concise and general synthetic route to the requisite 2,5-diethynylpyridyl-linked diferrocene dithiols and monothiols has been

achieved[4]. The fabrication of self-assembled monolayers (SAMs) on Au(111) has allowed quantitative electrochemical characterization of electron-transfer rates. DC and AC voltammetry have been used to measure the redox potentials and verify switching between states 1 and 2 of the molecule, and to probe electron transfer rates in states 1 and 2. Work in progress aims at attaching single molecules to electrical test structures, such as nanogap electrodes or gold nanoparticles tethered to gold surfaces by the molecules under study.

**Metal Films.** The NIRT team is studying structural fluctuations in metal films using several techniques. Magnetic force microscopy (MFM) has been used to quantitatively image the local current distribution in metal wires with fabricated defects. This technique will be pushed to smaller wires, with the goal of investigating fluctuation driven changes in the current distribution during electromigration and failure of nanoscale wires. The NIRT team is also using scanning tunneling microscopy to study thermal fluctuations of step edges in metal films (Ag, Pb) near room temperature[5] (see Figure 3). Structural fluctuations are probed in real time at the atomic scale while a driving current is passed through the sample. This study will be extended to narrow wires, in which the electrical noise and structural fluctuations will be simultaneously observed. Finally, nanoscale metal wires have been electromigrated to failure to form nanometer-scale gap junctions. These junctions have been spanned by nanotubes by starting with a wire deposited on top of the nanotube. This work will hopefully also provide an additional test bed for study of single molecule devices.

**Techniques.** A range of experimental techniques are being employed, often synergistically, to investigate the electronic properties of the devices mentioned above. Electronic transport measurements are performed at room temperature and at cryogenic temperatures. These include conductance measurements as well as characterization of the anomalous (1/f) noise in these systems. Transport measurements are coupled with scanned probe techniques to probe the local electronic properties of the devices. For example, electrostatic force microscopy (EFM) has been used to locate and study individual defects in carbon nanotubes; scanning tunneling microscopy (STM) will be used to monitor the atomic structures of thin metal films during electromigration; scanned gate microscopy (SGM) will be used to study the effects of local electrostatic potential variations on nanotubes and molecular devices.

**New Facilities.** Unique facilities are being developed to perform these measurements on samples in a range of environments. An environmental atomic-force microscope (AFM) has been modified to perform electronic measurements (EFM, SGM) in a range of environments, from pure gases to high vacuum, and from cryogenic temperatures (100 K) to high temperature (800 K). An ultra-high vacuum scanned-probe microscope is being developed which will feature a cantilever-type AFM, a field-emission scanning electron microscope, and *in situ* electrical measurement capability. This facility will allow preparation of clean samples in UHV, and the study of their electronic and structural properties without breaking vacuum.

**Impact.** The research will have a significant impact on nanoscale science and technology. Nanoscale memory elements will require the control of charge and structure at the level of a single charge or defect. Understanding the sensitivity of devices to their structural and electrostatic environments will allow the design of new nanoscale sensors of charge and structure, which may be used as sensitive detectors of defects, dopants, electric fields, or chemical species. Understanding how nanoscale devices interact through electrostatic and

structural fluctuations may guide the development of new logic elements. The research provides excellent training for undergraduates, graduate students and postdocs in nanoscience.

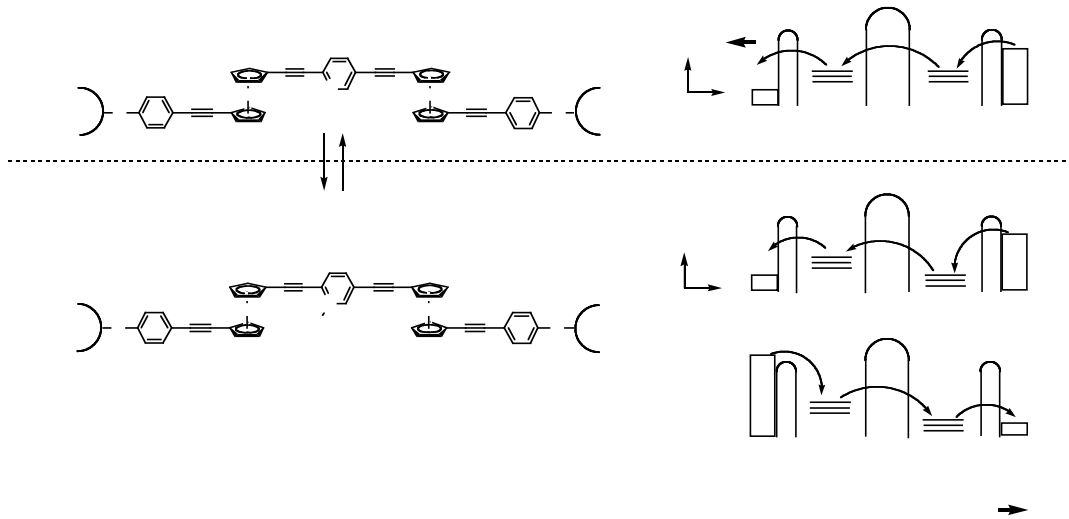

**Figure 1.** Scheme for molecular diode based on 2,5-diethynylpyridyl-linked diferrocene dithiol. Protonation of the 2,5-diethynylpyridyl linker raises the oxidation potential of ferrocene 1 resulting in asymmetric transport.

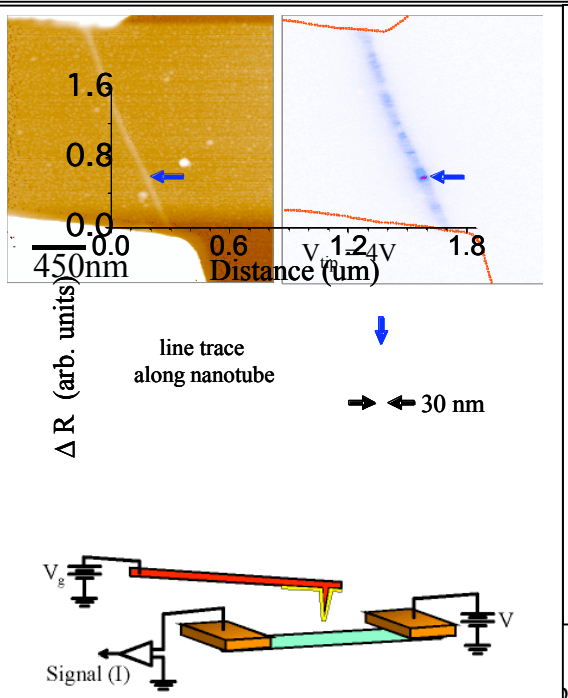


**Figure 2.** AFM topograph (top left) and scanned-gate image (top right) of carbon nanotube device with a single defect.

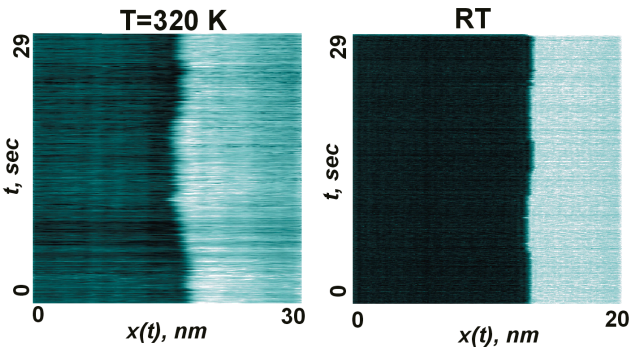


**Figure 3.** Scanning tunneling microscope "movie" of step edges on Ag (111) surface. A step edge is scanned continuously in the horizontal direction, and a time series of horizontal scans is shown in the vertical direction. Fluctuations in the step edge position are significantly larger at T=320 K than at room temperature.

://www.physics.umd.edu/condmat/mfuhrer/NIRT/ or email

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