NIRT: Single-Molecule Electrical Transport: Collaborative Nanoscale Research Bridging Chemistry and Physics

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Introduction

This program encompasses two complementary research efforts aimed at achieving detailed understanding of electronic transport through individual molecules. The first section outlines a systematic study of electron tunneling through small molecules in order to provide a quantitative basis for the study of more complex systems. The second section describes experiments to measure the electrical transport properties of individual DNA molecules with greatly increased control over the contacts, molecular geometry, and chemical environment.

1. Electrochemistry On The Nanometer Scale: An Electrochemical Study Of Electron Tunneling Through Solvents and Molecular Bridges

This work aims to address key issues of electron transfer through solvents and simple molecular bridges, an understanding of which is immediately relevant to molecular-scale electronics and electrochemical processes such as photosynthesis. We are investigating these issues by *directly* exploring tunneling events through solvents and simple molecular bridges using metal electrode pairs, which are separated by experimentally controlled and known distances. A large volume of phase space can be explored by varying the electrode separation, electrode composition, and (in solvent studies) the chemical potential of the solvent relative to the electrodes.

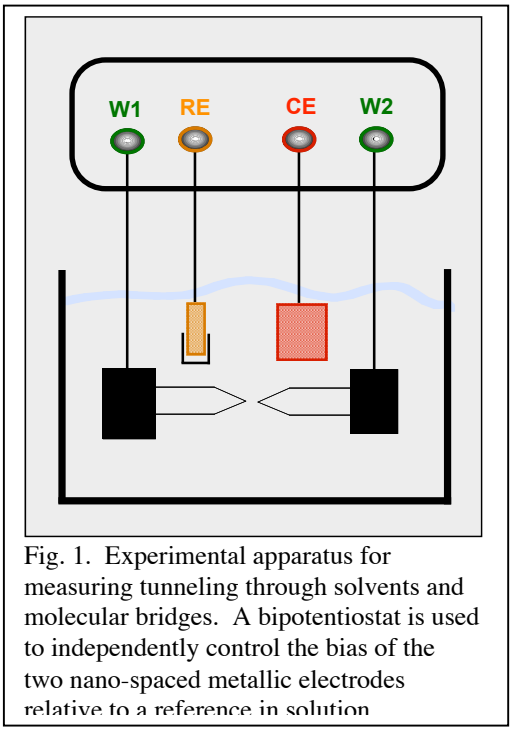

Fig. 1. Experimental apparatus for measuring tunneling through solvents and molecular bridges. A bipotentiostat is used to independently control the bias of the two nano-spaced metallic electrodes relative to a reference in solution

The first step in this work is the fabrication of electrode pairs with controlled separation. We have achieved progress using two methods: (1) gap-narrowing by electroplating[1,2]; (2) electromigration of a weak link in a metal wire[3]. Both of these methods have been used by other groups to make contacts to nanometer-scale structures; in particular, electromigration-induced gaps have recently been used to study single-molecule transport[4,5]. Figure 2 shows the formation of a gap by electroplating of Pt. This method produces high quality structures with a small grain size; we were unable to reproduce reported results using gold. Figure 3 shows the formation of a gap by electromigration. The weak link is created by e-beam lithography and angle evaporation of gold,

so that the 'neck' has a thickness of only ~20 nm. In the best devices, a nano-gap can be created by 'gently' breaking the wire, paying extra attention to heat sinking and minimizing the current.

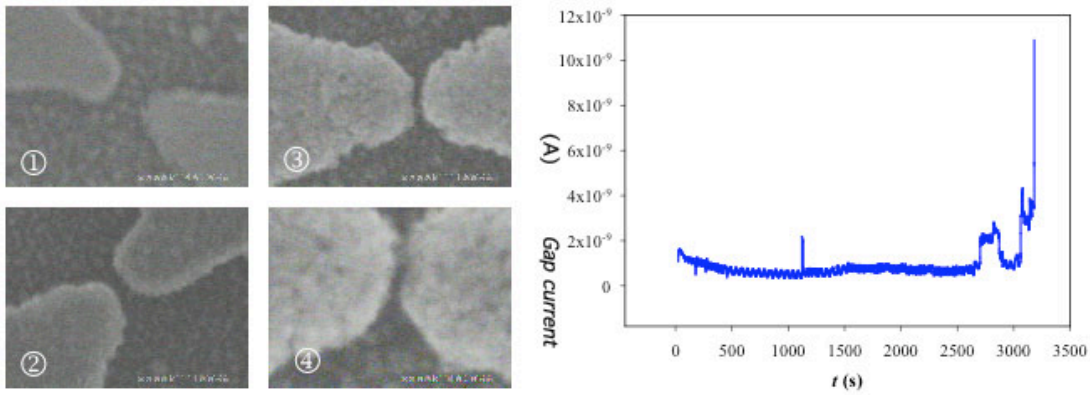

Fig. 2 Nano-gap formation by electroplating of Pt. The gap between the two electrodes closes from ~60 nm to <5 nm (images 1-4); the tunneling conductance increases rapidly as the electrode separation enters the nm range.

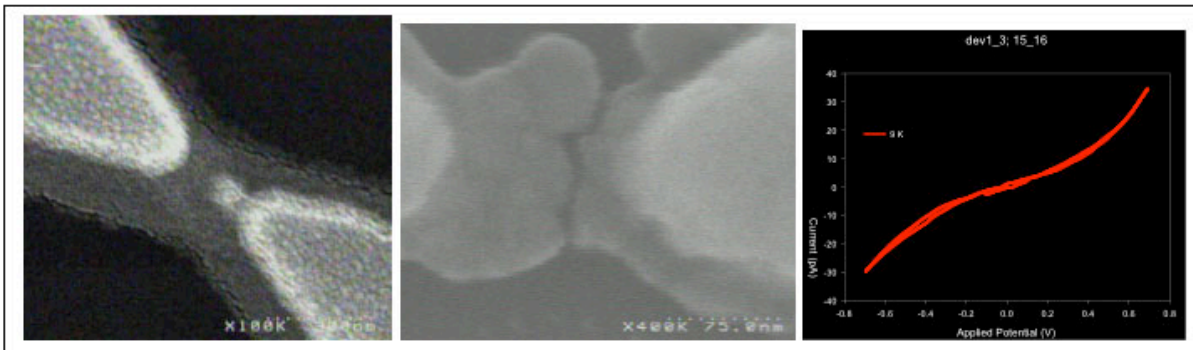

Fig. 3. (left) A weak link structure; the light areas are 100-nm thick Au; the gray areas are 20 nm thick. (middle) A similar structure after electromigration, with a gap < 5 nm. (right) I-V curve at 9 K for the same structure.

Our work in fabricating and characterizing these structures, as well as the paucity of data on the electronic and structural properties of such nano-gaps, has led us to attempt to more rigorously correlate their structure and electronic transport. We are investigating the role of many factors, such as the presence of an adhesion layer, the type of metal used, the temperature of breaking, etc. on the structure of the gaps, and performing careful I-V measurements with varying applied 'gate' potentials to clarify the nature of the electronic transport in these devices. Furthermore, we are fabricating devices on thin Si membranes, so that the gaps can be examined by high-resolution TEM to understand their sub-nm structure.

2. Conductivity of Individual DNA Molecules

In many ways, DNA is an ideal candidate for true molecular electronics, given the degree to which self-assembly techniques should be possible. However, the extent to which DNA can fill the role of a molecular wire is far from clear, because the experiments to date on the conductivity and electron transfer rate disagree so strongly with one another[6]. To address this disparity, a systematic approach that incorporates a high degree of detailed characterization and control over the relevant physical and chemical parameters of the system is needed.

Our planned work involves using shadow-masking techniques to attach metal leads to DNA molecules without damage to the molecule, and then measuring the conductance under carefully controlled fluid conditions. The first stage of this work, which is already underway, involves fabricating electrodes with sub-micron spacing and attempting to contact dense films of DNA. Figure 4 shows an AFM image of two gold electrodes patterned by shadow-masking on

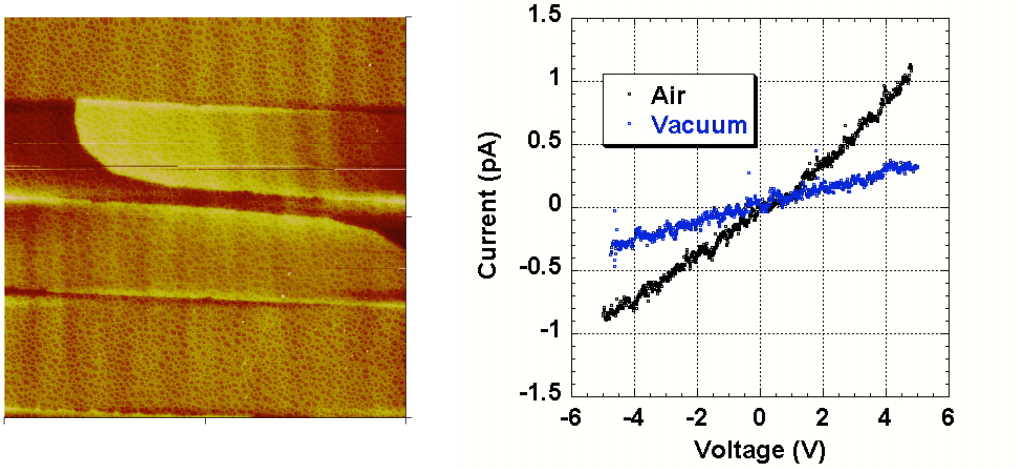

Fig. 4. Left: 10 μm × 10 μm (left) atomic force microscope image of a network of DNA molecules on a mica surface, with Gold-Palladium contact pads on top. Right: measured I-V characteristics.

top of a film of λ-DNA on a mica substrate, and I-V characteristics of the film.

The next stages will involve both reducing the electrode spacing to the 10-100 nm level, and introducing micro-fluidic systems that will allow us to measure DNA in its 'native' environment. In addition to varying the environment of the DNA, we will vary its sequence, for instance by introducing base mismatches that disrupt the base stacking, and vary its electronic structure by introducing intercalants. In related work, we are using STM to probe the electronic transport properties of films of DNA in fluids.

References

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