Formation of Metal−Molecule−Metal Tunnel Junctions: Microcontacts to Alkanethiol Monolayers with a Conducting AFM Tip

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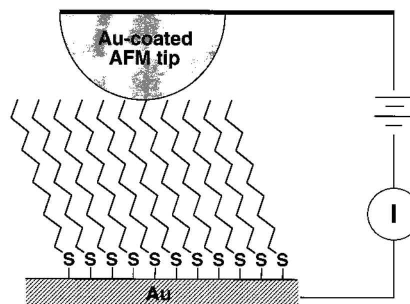
We report the characterization of metal−molecule−metal tunnel junctions made by contacting Au-supported self-assembled monolayers (SAMs) of alkanethiols with a conducting atomic force microscope (AFM) tip, Scheme 1. The electrical properties of individual molecules and molecular assemblies are currently of heightened interest because of potential applications in molecular electronics and new opportunities for understanding charge transport in organic systems.[1] Molecular level electrical transport studies require innovative approaches for making electrical contacts to oriented molecules. Scanning tunneling microscopy (STM)[2] and electrochemical methods[3] have been used for a number of years to examine transport in surface-confined molecules. In STM and electrochemistry, the molecules are in direct contact with one metal electrode and charge is delivered by vacuum tunneling or redox molecules, respectively. More recently, metal−molecule−metal junctions have been fabricated by assembling molecules inside metal-capped nanopores[4] and mechanical "break junctions",[5] or between mercury drops,[6] nanofabricated electrodes,[7] and crossed wires.[8] Metallic nanoparticles have also been used as electrical contacts to molecular monolayers supported on metal surfaces.[9] Self-assembly or Langmuir−Blodgett techniques are commonly employed in these studies because they are convenient approaches to immobilizing molecules at metal surfaces.

Scheme 1. Formation of a Metal−Molecule−Metal Junction by Contacting an Alkanethiol Self-Assembled Monolayer with an Au-Coated AFM Tip[a]



[a] $I-V$ traces are obtained as a function of load applied to the tip-SAM contact, or as a function of number of carbons in the alkane chain.

Conducting probe atomic force microscopy (CP-AFM)[10] provides an attractive approach to electrically contacting monolayer films and the formation of metal−molecule−metal junctions. In CP-AFM, a metal-coated AFM tip is placed in direct contact, under controlled load, with the material to be probed. The technique differs from STM in that the probe is positioned using normal force feedback, which decouples probe positioning from the sample conductivity and facilitates interpretation of the tip location with respect to the sample (i.e., in contact or out of contact). In previous studies, CP-AFM has been used to measure the resistances of individual carbon nanotubes,[10c] semiconductor nanoparticles,[10g] Langmuir−Blodgett films,[10d] adsorbed molecules on graphite,[10e] and organic semiconductor microcrystals.[10a,b] In an early study using metallic levers with high force constants, Salmeron et al. measured current and cantilever deflection simultaneously as the lever was brought into contact with a SAM of $CH_3(CH_2)_{11}SH$.[10i]

We show here that CP-AFM may be used to make mechanically stable electrical contact to SAMs of alkanethiols on Au. We have probed the current−voltage ($I-V$) characteristics of the resulting junctions as a function of the number of methylenes in the alkane chains and the load applied to the tip−sample contact. The resistance of these junctions increases exponentially with monolayer thickness, as expected for tunneling through a dielectric film, proving that we can probe reproducibly the electrical properties of the junctions as a function of molecular length.

We prepared SAMs of alkanethiols, $CH_3(CH_2)_nSH$, $5 \le n \le 9$, on polycrystalline Au and contacted these SAMs with an Au-

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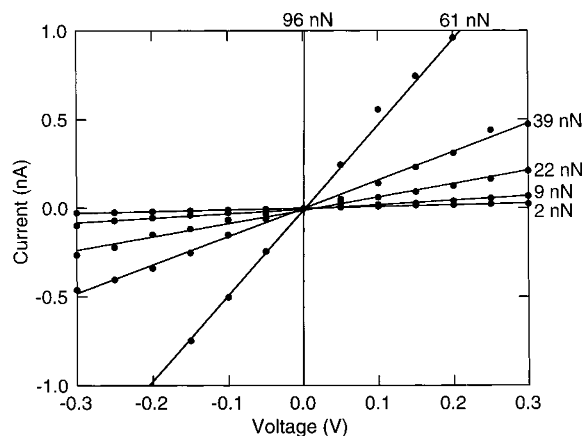

Figure 1. Current-voltage characteristics as a function of applied load for an Au tip in contact with a SAM of $CH_3(CH_2)_9SH$. The data are indicated by the filled circles and the lines are linear fits. At 2 nN load, the current at +0.3 V is 0.15 nA. Data points for the 96 nN load are not visible because of the current scale.

coated Si_3N_4 AFM cantilever, as shown in Scheme 1.[11] $I-V$ measurements were obtained in ambient conditions under a constant, controlled load at a fixed point on the SAM using external electronics described previously.[10a,b]

Figure 1 shows $I-V$ characteristics for an Au probe in contact with a decanethiol SAM for applied loads ranging from 2 to 96 nN. The $I-V$ traces were acquired with the same tip at the same location and were reproducible at different locations on the sample surface. At each load, the traces are linear through the −0.3 to +0.3 V range. When the tip is just in contact with the SAM at a load of 2 nN, the resistance is 1.3×10^{10} Ω. Applying higher loads results in the probe penetrating the SAM, thereby reducing the resistance. We can apply enough force (typically ~100 nN for decanethiol) to punch through the film to make Au−Au contact. In such cases, we measure resistances as small as ~20 Ω. The significance of the Figure 1 data is that while the junction resistance is clearly load dependent, changes in load on the order of a few nN result in small changes in resistance. We estimate that the load precision in our experiments is approximately 0.2 nN, which corresponds to resistance variations of a few percent.

Figure 2a shows typical $I-V$ characteristics between −0.3 and +0.3 V for the *same* Au probe in contact with SAMs of $CH_3(CH_2)_nSH$, with $5 \le n \le 9$.[12] All measurements were taken at the same nominal load of 2 nN. Again, within the sweep range, the $I-V$ traces are linear. Figure 2b shows a semilog plot of the average resistance for each type of junction as a function of the number of carbon atoms in the chain. The error bars represent the estimated standard deviation.[13]

Figure 2b shows that the resistance increases exponentially with chain length. An exponential increase is not surprising since (1) the SAM thickness increases linearly with the number of methylenes[14] and (2) the transport mechanism is likely to be tunneling, based on previous STM[2a,g] and electrochemical studies.[3a,c−e] The decay constant calculated from the data in Figure 2b is $\beta = 1.45$ per methylene unit.[15] This is in reasonable agreement with the values of 1.5, 1.21, and 1.14 per methylene published by Weiss and Allara,[2a] Chidsey,[3e] and Majda,[3d] respectively.

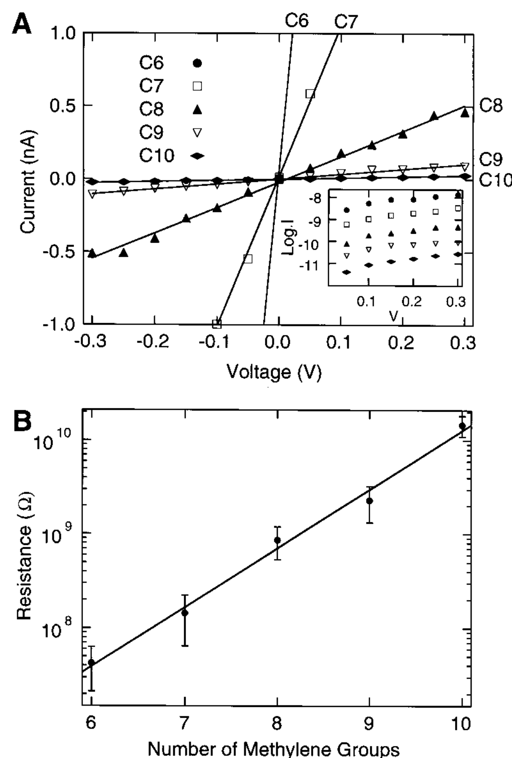

Figure 2. (A) Current−voltage characteristics of tip/SAM/substrate junctions as a function of the number of carbons in the alkane chains. The inset shows a semilog plot from 0 to +0.3 V. (B) Resistance vs number of carbons in the alkane chains. The lines in both panels A and B are linear fits.

Our data show that it is possible to put a conducting probe in reproducible mechanical contact with SAMs and to obtain $I-V$ characteristics that show predictable dependence on the SAM thickness. An advantage of CP-AFM measurements is experimental simplicity, providing a convenient alternative to labor-intensive microfabrication methods for making metal−molecule−metal junctions. In comparison to STM studies,[2] interpretation of the $I-V$ characteristics is simplified by the absence of an additional tunneling gap between the CP-AFM probe and the SAM. Thus, CP-AFM is a promising approach for studying transport through molecular junctions and its dependence on conjugation, functional group distributions, orientations, and molecular dimensions.

A potential limitation of our present setup is the irradiation of the junction with scattered light (~670 nm) from the optical beam used to detect the lever deflection. The optical gap of alkanethiols (~6 eV) is much greater than the photon energy (1.8 eV) so direct excitation of the molecules cannot occur. However, in future experiments involving conjugated molecules, optical absorption may play an important role in the measured transport characteristics. In some cases, it may be desirable to eliminate the optical beam, or to use the beam to intentionally stimulate electronic or vibrational transitions of molecules in the junction.

In summary, we have shown that it is possible to make stable electrical contact to SAMs of alkanethiols by AFM. The resulting metal−molecule−metal junctions behave as tunneling junctions, in which the resistance increases exponentially with SAM thickness. Contacting SAMs with metallized AFM tips should be a general approach to probing the conductance of molecular junctions as a function of the bonding and functional group architecture of the constituent molecules.

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(11) Si_3N_4 cantilevers (nominal force constant 0.06 N/m) were coated with 40 Å Cr followed by 400 Å of Au. All measurements were done using a Digital Instruments Nanoscope 3a Atomic Force Microscope.

(12) $I-V$ traces were recorded sequentially for SAMs of $CH_3(CH_2)_5SH$, $CH_3(CH_2)_6SH$, $CH_3(CH_2)_7SH$, $CH_3(CH_2)_8SH$, and $CH_3(CH_2)_9SH$, respectively. After completing the series of measurements, rerecording the $I-V$ on SAMs of $CH_3(CH_2)_6SH$ showed that no substantial changes to the tip had occurred.

(13) The standard deviation was calculated for each chain length using ~20 resistance values taken from five different points on the sample.

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(15) β is the decay constant of the transconductance (G). $G = Be^{-\beta l}$, where l is the length of the molecular bridge.