Molecular conductance measurements through printed Au nanodots

W. Jiang\textsuperscript{a} and E. Garfunkel

\textit{Department of Chemistry, Rutgers, The State University of New Jersey, New Jersey 08854}

N. Zhitenev, D. Abusch-Magder, and D. Tennant

\textit{Bell Laboratories, Lucent Technologies, 600 Mountain Ave., Murray Hill, New Jersey 07974}

Z. Bao

\textit{Department of Chemical Engineering, Stanford University, Stanford, California 94305}

\begin{quote}
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Gold pads with \(\sim 100\) nm diameter are imprinted on self-assembled monolayers of alkane dithiols of different lengths using nanotransfer printing. The pads are contacted by conductive atomic force microscope tips, and electron transport was measured as a function of force. Atomic scale topography at the metal-molecule interface is essential to describe the conductance-stress relationship. A finite force (1–10 nN) deforms devices resulting in two competing effects: (a) a larger contact area and (b) deformation of the interfacial bonds and/or tilting of the molecules. The estimated conductance of molecules is significantly smaller than results suggested in previous experiments and calculations. © 2006 American Institute of Physics. [DOI: 10.1063/1.2345613]

Because of the potential application of organic molecules in micro- and nanoelectronics, researchers have worked extensively on attempting to measure the conductance of molecules and trying to understand the nature of molecular conductance.\textsuperscript{1,2,6,10,12} Measuring the molecular conductance requires one to connect both ends of molecules to electrodes. Different techniques have been applied to measure conductance, including scanning probe microscopy,\textsuperscript{1,3,4,6,10,12} nanopore,\textsuperscript{5} cross wire,\textsuperscript{5} Hg drop electrode,\textsuperscript{8} and break junction.\textsuperscript{2,6} However, making reliable devices at such a small scale remains a significant challenge. Some of the issues requiring better experimental control are metal diffusion, bonding, topography and stress at the interfaces, and interaction between molecules.\textsuperscript{4,6,8,13}

Conductive atomic force microscopy (CAFM) has been broadly applied to study molecular conductance.\textsuperscript{1,2,6,12} The technique has certain advantages over other methods, as one can examine the structure concurrent to measuring conductance, choose spatial location, and easily accumulate statistically significant data sets. However, there are up to three orders of magnitude differences in molecular conductances measured by different groups using CAFM of the same molecule.\textsuperscript{6} The nature of the contact between a CAFM tip and a molecule, stress introduced by the tip and the corresponding molecular deformation, and the possible penetration of the tip inside the molecular layer have been extensively examined to remove the experimental controversy.\textsuperscript{12} Cui \textit{et al.}\textsuperscript{1} found that chemical bonds may strongly enhance tunneling through the molecules (through bonds tunneling) as opposed to tunneling between neighboring molecules (through space tunneling). The notion that monolayers of dithiols are more conductive than layers of monothiols has been both corroborated\textsuperscript{12} and challenged\textsuperscript{14} in the literature.

In this work, we combine nanofabrication and CAFM techniques to extend the measurement of molecular conductance into a significantly lower pressure range than in previous experiments. Nanotransfer printing\textsuperscript{15} (nTP) techniques were applied to pattern 100 nm size Au dots on top of alkanedithiol self-assembled monolayers (SAMs). Strong and nonmonotonous dependence of \(I-V\) curves on the contact pressure is found already at effective pressures that are one to two orders of magnitude smaller than the typical exerted pressures in the past experiments. The estimated conductance of the molecules is three to six orders of magnitude lower than previously reported in CAFM experiments.

Octanethiol (C8) and decanethiol (C10) were studied in this letter. As shown in Fig. 1(a), patterned Au film was

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig1.png}
\caption{(Color online) (a) Diagram of patterned dot transfer onto SAM; (b) \(I-V\) curves for octanethiol (C8) and decanethiol (C10) measured at the same force; left upper corner is the image of tip on sample with imprinted Au dots (AFM image).}
\end{figure}
imprinted onto the thiol-terminated molecular monolayer previously prepared on Au. Detailed information about the process can be found on our previous publication. In this work, the Au dot size was chosen to be ~100 nm, which is large enough to significantly reduce the stress while still being smaller than the typical domain size of alkanethiol monolayer, avoiding transport through domain boundary/defects. The potential deformation of Au pads caused by the CAFM layer, avoiding transport through domain boundary/defects.

The curves can be crudely approximated with an exponential model. From Fig. 2b, the current at the peak corresponds to parallel conductance of molecules bonded at both ends, with a maximum peak current of 0.8 to 1 nA per C10 dithiol molecule. In our experiment, the measured conductance is about two orders of magnitude larger than the conductance of single molecules. The current decrease observed at high force may be related to a distortion of molecules or bonds at the interfaces. AFM and interfacial microscopy experiments suggest that ~2 GPa is needed to tilt long alkyl chains (C$\geq$14). The pressure needed to tilt short alkyl chains is smaller.

Nonlinear-optical experiments show that at pressures of several tens of megapascals, terminal gauche defects are generated that tilt the symmetric dipole of the terminal group. The tilting or the gauche defects may increase or decrease the conductance in different models. In our experiment, the conductance is consistently decreased in all measured samples. In fact, a small dip in the current seen in Fig. 2(b) at ~3 nN force is possibly caused by the same mechanism. The conductance of molecules bonded to the lowest terrace decreases with force before the second Au terrace is brought into contact with molecules.

Further numerical estimates can be made based on our simple model. From Fig. 2(b), the current at the peak corresponding to the parallel conductance of molecules bonded between the substrate and the second terrace of the Au dot is about two orders of magnitude larger than the current at small force. Similarly, the area of the second terrace is likely two orders of magnitude larger than the area of the first terrace which is bonded to the monolayer during nTP. Hence, the contact area between the printed dot and monolayer at zero pressure is less than 1% of the Au dot dimension, or less than $10^{-16}$ m$^2$. In the C8 samples, the conductance starts to increase at about 3 nN, which suggests that the critical pressure to tilt short chain alkanedithiol monolayers is larger than 30 MPa. The whole process of contact deformation is close to reversible in all force ranges studied. Typically, the average current in the reverse curve is slightly higher than at the forward curve.

The I-V curves shown in Fig. 1(b) were measured at the forces corresponding to the current peaks in Figs. 2(a) and 2(b) (7 nN for C10 sample and 5 nN for C8 sample) where maximum conductance is reached. Typical current values observed in previous experiments at 0.5 V bias range from 1.3 to 15 nA per single C8 dithiol molecule, and from 0.8 to 1 nA per C10 dithiol molecule. In our experiment, the measured current is below the noise level (~1 pA) at biases smaller than 1.5 V. Based on the discussion above, there

![Image](https://example.com/image.png)
should be at least 100 molecules bonded to each Au dot, so that current per molecule is below $10^{-14}$ A in the small bias range examined, many orders lower than in earlier experiments. Often, low current level is assigned to absence of bond at interfaces. We note that the formation of chemical bonds at both interfaces in our devices is proven to be better than in other experiments.20–25 The transfer printing works only if exposed bonds are present at the top SAM interface and the printed dots passed the scotch tape test.

At large bias, it is possible to compare the current levels through C8 and C10 devices to estimate a tunneling decay parameter $\beta$. In the simplest model of tunneling under a rectangular barrier, dependence of conductance as a function of molecular length is approximated by $\sigma(l) = \sigma_0 e^{-l\beta}$. Further assuming that C8 and C10 devices have similar contact resistance and number of molecules under each dot, $\beta$ can be determined by plotting $\ln(I_{C8}/I_{C10})$. From Fig. 3, one can see that the $\beta$ value is about 0.7 Å at 1.5 V and it increases toward zero bias. The slope is about −0.3/V, so that linear extrapolation gives $\beta = 1.15$ Å. This $\beta$ value is somewhat larger than typical $\beta \sim 1$ but it is still not large enough to self-consistently account for undetectably small conductance at zero bias. The extrapolation from large bias to zero bias is likely not justified.

In conclusion, we have studied the conductance of molecular junctions using a combination of fabrication and measurement techniques. Fabricating top contacts using nTP technique ensures formation of chemical bonds at metal–molecule interfaces. A finite contact force affects the local structure of the contact, which in turn affects the transport in at least two opposing ways. We interpret our results as implying first an increase of the number of wired molecules per Au dot with increasing pressure, followed by a decrease in the apparent conductance resulting from deformation of the interfacial bonds and/or tilting of the molecules.

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