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Molecular conductance measurements through printed Au nanodots

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Gold pads with ~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 measuring the conductance of molecules and trying to understand the nature of molecular conductance.[1–11] 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,[1,3,4,6,10,12] nanopore,[9] cross wire,[5] Hg drop electrode,[8] and break junction.[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.[4,6,8,13]

Conductive atomic force microscopy (CAFM) has been broadly applied to study molecular conductance.[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.[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.[12] Cui *et al.*[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[6] and challenged[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[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.

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

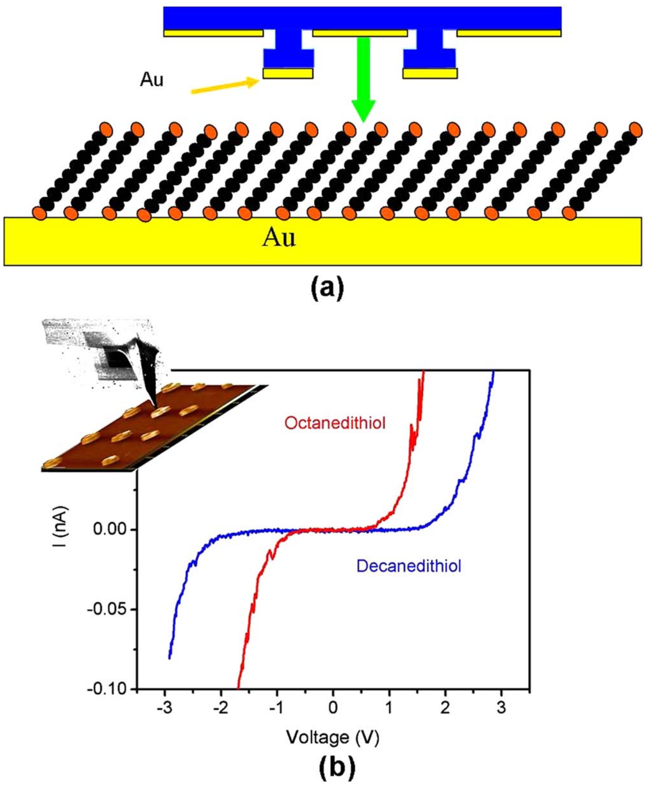

FIG. 1. (Color online) (a) Diagram of patterned dot transfer onto SAM; (b) *I*-*V* curves for octanedithiol (C8) and decanedithiol (C10) measured at the same force; left upper corner is the image of tip on sample with imprinted Au dots (AFM image).

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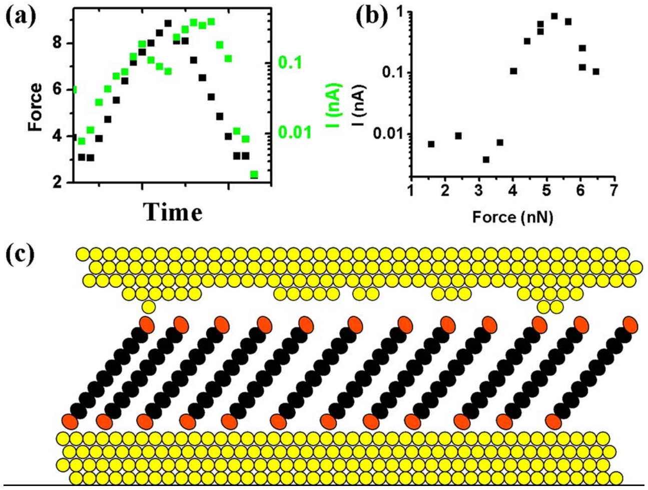

FIG. 2. (Color online) (a) Force (black) vs current (green) curve with time of C10 dithiol at 2.5 V bias; (b) current vs force curve of C8 dithiol at 2.3 V bias; (c) structural diagram of SAM/Au interfaces.

imprinted onto the thiol-terminated molecular monolayer previously prepared on Au. Detailed information about the process can be found on our previous publication.[16] 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 tip will also affect the conductance measurements. With a maximum applied force $F=9$ nN and Au pad thickness $d=10$ nm, we estimate that the strain at SAM surface[12] will be ~0.05%, or estimated maximum compression of alkane monolayer will be less than 0.02 Å, which suggests that the deformation effect is minimal. The atomic force microscope (AFM) is first run in a tapping mode to check the film morphology and to determine the dot locations. Then, the tip is placed on top of Au dot, and the AFM operation is changed to a static contact mode for *I*-*V* measurements at different force settings. The measurements were repeated on ten dots fabricated on different samples to enable meaningful statistics to be determined.

Figure 1(b) shows representative *I*-*V* curves measured on C8 and C10 dithiol SAMs. As expected, shorter C8 molecules are more conductive than C10 ones. The current level is below the noise floor (~1 pA) at small applied voltages. The curves can be crudely approximated with an exponential dependence. *I*-*V* curves measured on different dots on the same SAM are qualitatively similar.

At a given voltage, the current is sensitive to the force applied to the AFM tip. Figure 2(a) shows the force curve (black) and the corresponding current curve (green) of C10 at 2.5 V bias (tip positive) as force is applied and released. The current is below the detection limit until the applied force reaches 3 nN; then the current increases with force until the force reaches about 7.5 nN. The current decreases in the force range between 7.5 and 9 nN (maximum applied force). The dependence is close to reversible with a slight hysteresis. Figure 2(b) shows the current-force relationship measured at 2.3 V on C8. We note that the voltage settings are different for C8 and C10 samples to analyze a broader range of forces. For C8 [Fig. 2(b)], only a 1.5 nN initial force is needed to observe a current above the noise floor. Qualitatively, the force dependence is similar for Au dots on both C8 and C10.

Three different force ranges can be identified. We suggest that the current plateau at the smallest forces (below the noise floor on C10 samples) corresponds to parallel conductance of a small percentage of molecules bonded at both ends to the metal contacts. It was established that the formation of chemical bonds at the top molecule-metal interface is the necessary condition for successful nTP of Au dots;[15] however, the density of these bonds can be rather small.[16] Au dot curvature and microscopic roughness present at the surface prevent concurrent bond formation over the full diameter of the dot [Fig. 2(c)]. As depicted in Fig. 2(c), the Au surface forms 0.3 nm high atomic terraces. At small forces, only the most exposed (highest) terraces are mutually aligned with the atomically flat Au substrate yielding small density of bonded molecules. At a larger force, the imprinted Au dots will be pushed into the organic monolayer, the contact area will increase, and more molecules should bond to the top Au contact. We believe that the steep rise of current by approximately to orders of magnitude is likely caused by this effect. Finally, 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 ($C>14$).[17] The pressure needed to tilt short alkyl chains could be smaller. Nonlinear-optical experiments[18] 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.[19] 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[6] 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

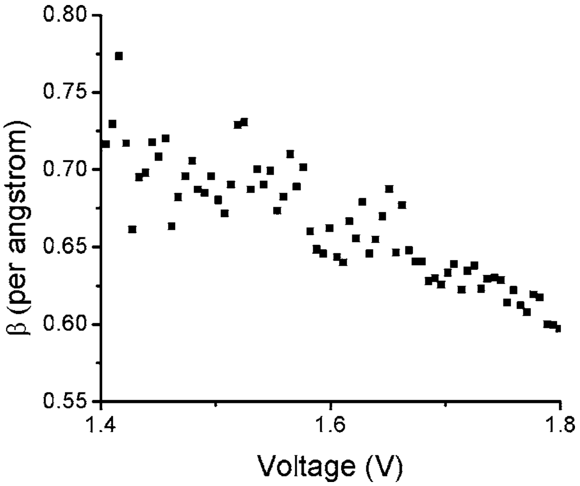

FIG. 3. β vs voltage. β is tunneling decay constant.

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 good 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 β. In the simplest model of tunneling under a rectangular barrier, dependence of conductance as a function of molecular length is approximated by $\sigma(l)=\sigma_0 \exp(-\beta l)$. Further assuming that C8 and C10 devices have similar contact resistance and number of molecules under each dot, β can be determined by plotting $\ln(I_{C8}/I_{C10})$. From Fig. 3, one can see that the β value is about 0.7 Å at 1.5 V and it increases toward zero bias. The slope is about $-0.3/\mathrm{V}$, so that linear extrapolation gives $\beta=1.15$ Å. This β 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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