

Electrical measurements of a dithiolated electronic molecule via conducting atomic force microscopy

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We describe a method of measuring the electrical properties of a molecule via conducting atomic force microscopy (AFM). A dithiolated molecule is chemically inserted into defect sites in an insulating self-assembled monolayer formed on an epitaxial Au substrate and the top thiol terminus of the molecule is reacted with a Au nanoparticle. A Au-coated AFM probe is used to contact the molecule through the nanoparticle, thus electrical data can be obtained. We report preliminary transport measurements of two test molecules. Our data shows qualitative agreement with previously published results for similar molecules deposited in a nanopore containing approximately a thousand molecules. This work indicates that the measured negative differential resistance is not an intermolecular phenomenon. © 2002 American Institute of Physics.

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Over the last decade molecular electronics has developed from an area of research,¹ that many defined as surrealism, to being recognized as Science magazine's "breakthrough of the year" for 2001.² The conventional "top-down" fabrication approach utilized by the semiconductor industry is challenged by the increasingly daunting technical challenges of miniaturization and rising costs (Moore's Law). Molecular electronics may allow for further, cheaper miniaturization by utilizing small organic molecules for ultra-dense logic and memory circuits that can be fabricated via a "bottom-up" approach based on thermodynamically driven assembly.³

The inability to rapidly screen a single molecule in a reliable, defined, and facile manner is an issue that molecular electronics presently encounters. Many test devices of electronic molecules rely on bulk measurements of thousands of molecules.^{3,4} Whether these measurements represent the true electronic properties of a single entity or collective intermolecular characteristics is ambiguous. Furthermore, most methods involve evaporation of the top metal contact (nonchemisorbed) that results in uncertainties in the physical and electronic characteristics of the metal/molecule interface. Albeit, there have been experiments on direct measurements of a simple single molecule via a break junction⁵ yet this measurement is difficult to execute and characterize.

Herein, we report a nonlithographic approach for probing of a molecule with chemisorbed connections of the thiol "alligator clip" to the Au contacts on both termini. Figure 1 is a schematic representation of the test structure. On an epitaxial Au (111) surface an "insulating" self-assembled monolayer (SAM) of dodecanethiol is formed. In the naturally occurring defect sites in the SAM, dithiolated electronic molecules are inserted by self-assembly,⁶ followed by the assembly of Au nanoparticles onto the unreacted top thiol

termini.^{7,8} We then utilize conducting atomic force microscopy (cAFM) to collect electrical data on these molecules by making contact with a Au-coated AFM probe to the Au nanoparticle capped system.⁹ In this letter we report $I-V$ measurements on that assembly for two candidate molecules, 1-nitro-2,5-di(phenylethynyl-4'-thioacetyl)benzene and 2,5-di(phenylethynyl-4'-thioacetyl)benzene (compounds **1** and **2**, respectively). These molecules are similar to the ones previously studied using the nanopore configuration in which a monothiolated version of compound **1** is reported to exhibit room temperature negative differential resistance (NDR).¹⁰

Figure 2 shows a series of scanning tunneling microscopy (STM) images taken at various stages of the sample preparation process. Figures 2(a) and 2(b) show a dode-

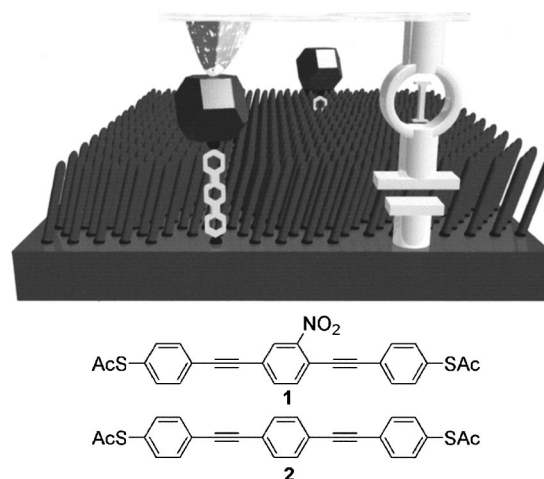


FIG. 1. Schematic representation of the test structure. (Not drawn to scale) Dithiolated electronic molecules are self-assembled in naturally occurring defect sites in a dodecanethiol SAM. A Au nanoparticle is then attached to the top unreacted thiol terminus of the molecule and a Au-coated AFM probe is utilized to make contact. Chemical structures for the two test molecules, **1** and **2**, are also shown.

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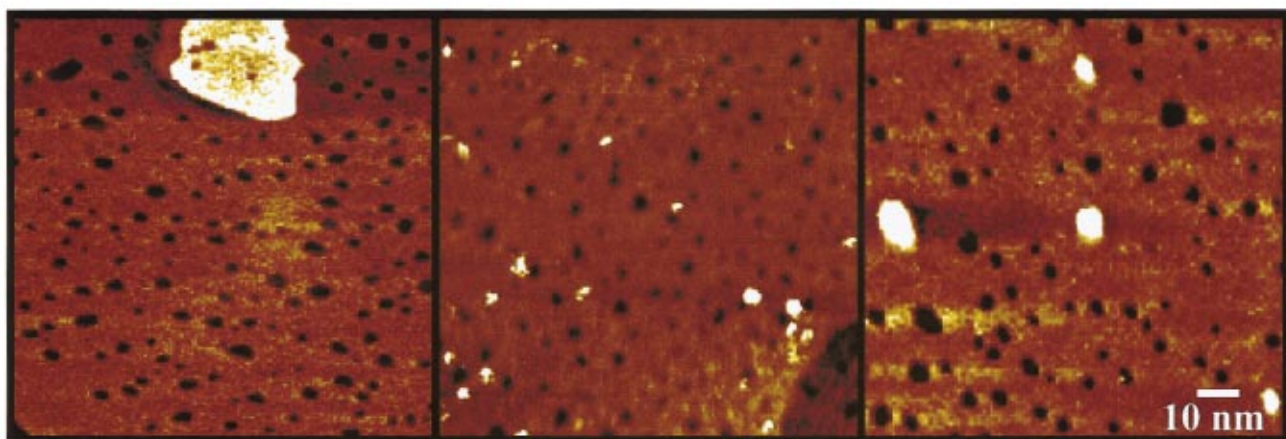


FIG. 2. (Color) STM study of the insertion of molecules in defect sites of a dodecanethiol SAM formed on an epitaxial Au (111) surface. All images are $100 \times 100 \text{ nm}^2$. (a) Image of SAM before insertion; pits in the SAM appear darker than the surrounding matrix. (b) Image obtained after insertion of molecule 1 into defect sites. Molecule 1, being more conductive with respect to the dodecanethiol SAM, appears brighter. (c) Image taken after the attachment of $\sim 2 \text{ nm}$ Au nanoparticles to the top thiol termini of molecule 1.

canethiolate SAM on a Au (111) film before and after insertion of the dithiolated molecules, respectively. The molecules can be identified as the small bright white spots [Fig. 2(b)], inserted preferentially at the domain boundaries and less frequently in the domains (pits in the film appear as dark spots).⁶ The sparse density of the inserted molecules illustrate the tight packing of the dodecanethiolate SAM and, hence, a high quality insulating layer. This precludes that the dithiolated molecules are parallel to the Au surface but rather inserted vertically with one thiol terminus attached to the Au (111) film and the other thiol terminus extending beyond the insulating SAM.⁶ Figure 2(c) shows the attachment of 2 nm Au nanoparticles to the top of the inserted dithiolated molecules. It should also be noted that the density of Au nanoparticles is in close approximation to the density of the inserted molecules. Furthermore, we did not observe any Au nanoparticles attached to the dodecanethiol SAM when the dithiolated molecules were not inserted into the SAM.

A typical $I-V$ plot of the Au nanoparticle/molecule 1/Au test structure was taken with cAFM at room temperature (red/blue curves, Fig. 3). A NDR peak is observed near 1 V with a peak-to-valley (PV) ratio of 2:1. Repeated scanning of the $I-V$ curve often showed a slight degradation of the PV ratio as well as a slight shift of the peak towards higher voltages. Presumably, the large current density flowing through the molecules results in their breakdown. Nevertheless, the NDR peak is similar to that reported in the literature.¹⁰ The ohmic background in molecule 1 is not correlated with the size or position of the NDR peak, a feature that appears to be well reproduced in molecules with very different ohmic background currents [Fig. 3(a)]. For comparison, we have also taken $I-V$ plots of the Au nanoparticle/molecule 2/Au film test structure [black curve, Fig. 3(a)] and the dodecanethiol SAM and we have not observed any NDR behavior in several hundred $I-V$ plots.

The method of Cui *et al.*, compiling the $I-V$ data by the integer multiples of current according to the number of molecules in each junction, was not possible in this work due to variation in characteristics between molecules.⁹ To circumvent this problem posed by large current fluctuations at large bias, we characterized the $I-V$ curves by their slopes in the

low bias (0.1 to -0.1 V) region. These were good fits to straight lines, thus molecular resistances were obtained from these slopes. Data for molecule 1 yielded a wide range of resistances as illustrated [inset (b), Fig. 3, some very high resistance points have been omitted]. Data from molecule 2 were much more tightly clustered [inset (c), Fig. 3] but not as tightly as observed in the case of alkanedithiol molecules. Nonetheless, the distribution shown for this molecule is narrow enough to make the possibility of multiple molecules in parallel unlikely. Furthermore, this distribution as well as previous work on single molecule insertion with similar molecules^{6,9} leads us to conclude that molecule 2 probably inserts as a single molecule. The similarity of the NDR-peak from molecule to molecule [Fig. 3(a)] is evidence that molecule 1 also inserts as a single molecule. As an additional

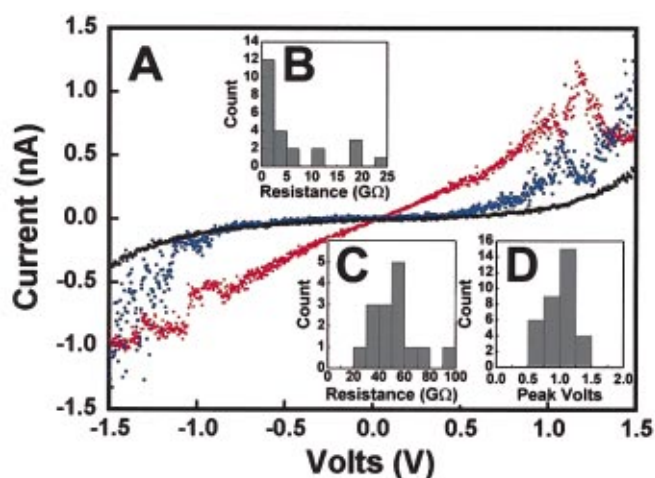


FIG. 3. (Color) Representative current–voltage characteristics (a) for molecule 1 (red/ blue curves) and molecule 2 (black curve). Molecule 1 (red/ blue curves) exhibits both the negative differential resistance peak and a wide range of background ohmic currents. The distribution of resistances is shown by the histogram inset (b). In contrast, molecule 2 (black curve) shows no NDR-like features and resistances in the ohmic region are much more tightly clustered [$51.6 \pm 18 \text{ G}\Omega$, $N=15$, see histogram inset (c)]. The NDR-peak voltage is $1 \pm 0.21 \text{ V}$ ($N=32$); the corresponding distribution is shown in (d). The resistances measured with the tip in contact with the surrounding alkanethiol monolayer were extremely large and could not be determined accurately in the low bias region.

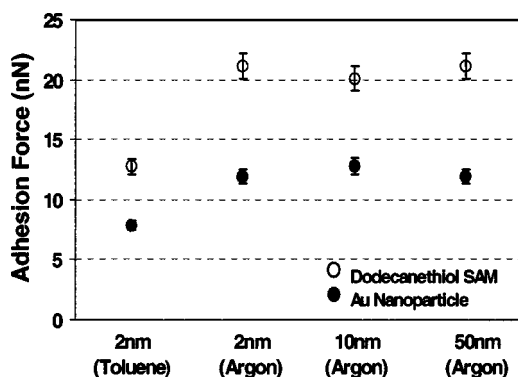


FIG. 4. Adhesion curve comparisons with regards to the Au-coated AFM probe contacting the dodecanethiol SAM or a Au nanoparticle (ranging from 2 to 50 nm in diameter), measured in toluene or argon. The difference in adhesion force in all cases is sufficiently large to distinguish the two materials.

check on reproducibility, experiments were carried out in parallel at both Arizona State University and Motorola [Fig. 3(a), blue/red curve, respectively]. The fine structure is essentially identical, despite the disparity in the background ohmic currents.

This work has demonstrated that the NDR peak is intrinsic to single molecules containing an electroactive nitro moiety. There is considerable evidence that peaks in the current-voltage curves of electroactive molecules occur when the electron injection energy aligns with the formal potential for a redox process.¹¹ Electron transfer via sequential reduction and subsequent oxidation (return to pre-reduction charge state) leads to additional current at the formal potential. This potential is not well defined in a solid environment and in the absence of a supporting electrolyte and potential control.

Figure 4 shows the adhesion forces between the AFM probe and the nanoparticle that is used to characterize precise location of the probe tip before and after $I-V$ measurements. Measurements of these highly specific interaction forces, which differ as much as 40%, ensure continuous contact with the Au nanoparticle during data acquisition. Presented are averaged data sets from adhesion curves collected on and off Au nanoparticles (ranging from 2 to 50 nm in diameter), examined in toluene and argon environments using optimal spring constants of 0.06 and 0.32 N/m, respectively. This approach allows for junction formation, with assured contact of the cAFM probe to the nanoparticle, under a controlled force.

In conclusion, we have developed a method of electrically testing molecules via conducting atomic force microscopy for potential use as molecular electronic components. Our method provides a more defined method of testing single molecules and could be used to efficiently test libraries of

candidate electronic molecules. Furthermore, results of our transport measurements demonstrate qualitative agreement with previously reported data and we propose that the exhibited NDR behavior of compound **1** is an intramolecular phenomenon.

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⁸ Epitaxial Au (111) on mica substrates were purchased from Molecular Imaging, Phoenix, AZ. All glassware was either cleaned via piranha solution (1:3 hydrogen peroxide/ sulfuric acid) and washed with 18.3 MΩ cm water or purchased ultracleaned (Wheaton Clean-Pak precleaned container). Epitaxial Au (111) on mica was annealed using a reducing H₂ flame to remove organic contaminants and then immediately immersed in a 1 mM solution of dodecanethiol in ethanol (10 mL) for ~12 h. The substrate is spin rinsed with ethanol and transferred to an inert atmosphere, where insertion of the desired electronic molecules is achieved by placing the sample in a 0.5 mM solution of molecule 1 or 2 in particulate-free, distilled tetrahydrofuran (THF) and ammonium hydroxide (10 μL) for 30 min (see Ref. 6). The sample is rinsed with THF and immersed in a solution of prepared Au colloids, (see Ref. 7), 1 mg per 30 mL of THF, for ~12 h. The sample is then rinsed with THF and immediately used for cAFM measurements. We have noticed a slight degradation of the cleanliness of the surface after a few days; presumably, from contaminants in the air.

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