

Negative differential resistance in a bilayer molecular junction

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Negative differential resistance (NDR) is reported for a bilayer molecular junction. The system is comprised of a Hg–alkanethiol/arenethiol–Au bilayer molecular junction formed by bringing into contact a tetradecanethiol self-assembled monolayer (SAM)-coated drop of Hg with the surface of an oligo(phenylene-ethynylene) SAM on Au. Persistent, reproducible NDR is observed in the current–voltage characteristics with peak-to-valley ratios as high as 4.5 at room temperature. These results open a promising line of investigation of structure/function relationship and mechanisms in molecular NDR components. © 2003 American Institute of Physics. [DOI: 10.1063/1.1636520]

Molecules exhibiting negative differential resistance (NDR) could potentially provide the electrically active components required for information processing, memory, and other electronic applications at the nanoscale.¹ NDR, which refers to a region of a current–voltage characteristic in which the current decreases with increasing voltage, has been previously observed for metal–molecule–metal junctions comprised of nitro-substituted derivatives of oligo(phenylene-ethynylene) (OPE) molecules of the form $\text{Ph}-\text{C}\equiv\text{C}-\text{Ar}(\text{NO}_2)(\text{X})-\text{C}\equiv\text{C}-\text{PhSH}$. NDR has been observed for self-assembled monolayers (SAMs) of OPE molecules sandwiched between metal contacts in a nanopore structure² and formed on the metallic electrodes of a nanoparticle-bridged electrode gap.³ NDR has also been observed for a molecular layer comprised of OPE molecules inserted into an alkanethiol SAM probed by conducting atomic force microscopy⁴ and sandwiched between metallic nanorods.⁵

While NDR has been observed for this wide variety of structures, a considerable variation has been found for the current–voltage characteristics for the various structures in terms of peak voltage, current level, and peak-to-valley ratio. Control of the experimental conditions is hampered by the difficulty of obtaining reproducible, high quality contacts to both ends of the molecule. Although a high quality contact is readily obtained through a strong S–Au bond on the substrate side of a SAM using a thiol terminus for the molecule, the formation of a high-quality contact to the other terminus is difficult to achieve due to the need for additional chemical and physical processing. In the nanopore structure,² for example, this second contact is formed by vapor deposition of Au on a side of the SAM having no thiol termination, which results in a poorly defined physical and chemical interface and increases the possibility of damage to the molecules and of short circuits.

While various mechanisms based on charge transfer and conformational change have been proposed^{6,7} for the NDR observed in the earlier experiments, the origin of the NDR is not well understood. Since the electrical connection between a molecule and its electrodes is known to have a strong effect on the current–voltage characteristics of even simple molecular junctions,⁸ contacts could also play an important role in the charge transfer in these junctions. Conformational changes, such as bond rotation and changes in molecular orientation, could be strongly affected by the mechanical connection between the molecule and its contacts since this affects the freedom for molecular movement. Thus, experimental structures that allow the electrical and mechanical environment of the molecules to be systematically and reliably modified are of great interest for improved understanding and optimization of NDR effects.

In this letter, we report a study of NDR in a bilayer molecular junction. The junction is a two-layer structure comprised of a SAM based on tetradecanethiol molecules and a SAM based on nitro-substituted OPE molecules of the type discussed earlier. High-quality contacts are formed by strong bonds between the metal and thiol termini on both sides of the bilayer, and a van der Waals contact is formed at the interface between the two SAMs. The van der Waals contact represents a unique and potentially important feature of this junction with regard to electrical characteristics in that it modifies both the electrical and mechanical environments on one side of the OPE SAM from that in previously reported structures, as discussed later.

The OPE SAM is based on 4-[[2-amino-5-nitro-4-(phenylethynyl)phenyl]ethynyl] benzenethiol [OPE (*I*)] and the alkanethiol SAM is based on a tetradecanethiol (HSC_{14}). An idealized schematic representation of the junction is shown in Fig. 1. The OPE molecule (*I*) used in this junction has been found to exhibit NDR for a monolayer SAM in a nanopore configuration at temperatures up to about 150 K.⁹ The HSC_{14} molecule, which forms the other component of the junction, is known for its ability to form a high quality

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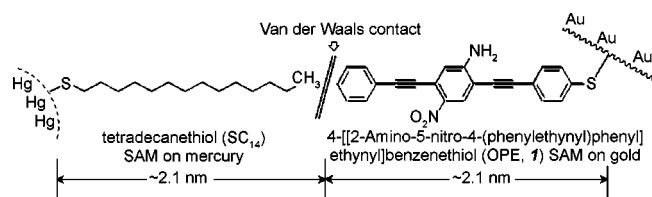


FIG. 1. Schematic diagram of the Hg-tetradecanethiol (SC_{14})/arenethiol [OPE (*I*)]-Au bilayer molecular junction. The symbol // represents the Van der Waals interaction at the interface between the terminal groups of the two SAMs.

SAM and for its well established electron tunneling characteristics.¹⁰

The acetyl-protected precursor of OPE (*I*), OPE-Ac (*I*-Ac), was synthesized by us according to procedures described elsewhere¹¹ and was de-protected by base-promoted adsorption¹² immediately prior to SAM preparation. An OPE (*I*) SAM on Au was formed by placing the Au substrate in a vial containing 300 μL of a 0.5 mM solution in tetrahydrofuran (THF). This solution was prepared by *in situ* hydrolysis of *I*-Ac with about 0.5 μL of concentrated NH_4OH for at least 48 h. Before use, each SAM-coated Au substrate was ultrasonically cleaned in THF for 10 min and blown dry with argon. The gold substrates were prepared by thermal evaporation of 25-nm-thick Au layer (0.5 $\text{\AA}/\text{s}$) with 15 nm Cr adhesion layer (0.2 $\text{\AA}/\text{s}$) onto 1 cm \times 1 cm single-crystal silicon pieces under a vacuum of $\sim 10^{-6}$ Torr. An alkanethiol SAM on a Hg drop was prepared by immersing a drop of liquid mercury extruded from a syringe needle (1 μL SGE syringe) into a 10 mM alkanethiol solution in isooctane for at least 10 min.

Bilayer junctions were formed by bringing into contact the OPE (*I*) SAM-coated Au surface with the HSC_{14} SAM-coated Hg drop in distilled isooctane, following the experimental approach pioneered by Rampi and Whitesides.¹³ The contact area was calculated from the measured diameter (50–200 μm) of the circular interfacial contact area from a captured digital microscopic image of the junction. The Au film and the Hg drop are used as electrodes and the *I*-*V* characteristics were recorded using an HP4145B semiconductor parameter analyzer (noise current floor <10 pA).

Hg- SC_n // C_nS -Au alkanethiol bilayer junctions of different lengths were also prepared for use as control structures in this experiment. Figure 2 shows the *I*-*V* characteristics measured in our system for four different lengths of alkanethiol molecules, corresponding to $n=6, 8, 10$, and 14. The bias voltage for this and all other data refers to the potential of the Au substrate with respect to the Hg drop, and all measurements were carried out at room temperature. It is seen that the currents are nearly symmetric with bias voltage and vary exponentially with bias over a large range. A plot of the current at 0.5 V versus junction thickness for the bilayer junctions in Fig. 2 (not shown) revealed an exponential dependence of current on thickness, in agreement with previous studies¹⁰ and with what is expected for tunneling transport.⁸ Thus, the alkanethiol bilayer control samples are well behaved and exhibit the expected tunneling characteristics.

Current-voltage characteristics for a Hg- SC_{14} //OPE (*I*)-Au junction are shown in Fig. 3 for successive bias sweeps from -1.5 to 1.5 V. As shown, a highly asym-

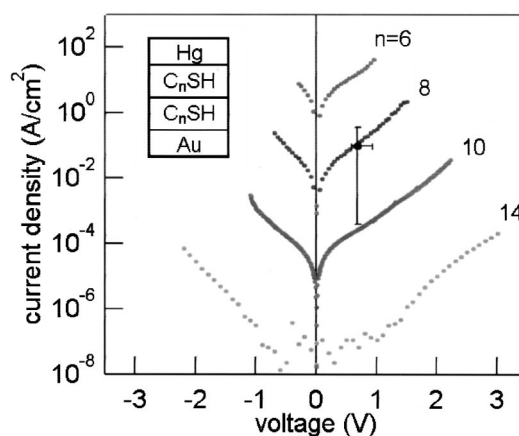


FIG. 2. Current-voltage characteristics for Hg- SC_n // C_nS -Au alkanethiol bilayer junctions for $n=6, 8, 10$, and 14. These junctions represent control structures for these experiments [no OPE (*I*) molecule]. The solid circle with its error bars (quoted as minimum and maximum values) represents the range of peak currents and peak voltages observed for the Hg- SC_{14} //OPE (*I*)-Au bilayer molecular junction in Fig. 1.

metric characteristic is observed with a region of NDR in the positive bias range and no NDR in the negative bias range. The peak voltage and peak-to-valley current ratio of the NDR are approximately 0.7 V and 1.3, respectively. A reduction in the current density is observed for successive sweeps, however, the NDR persists and exhibits little shift in peak position and little change in peak-to-valley ratio. A further observation made from the data in Fig. 3 is that the current for successive sweeps is scaled by nearly the same factor independent of bias. A possible explanation for the drop in current seen in this figure is a reduction in the effective area of the junction. Since negligible change in the interfacial contact area was observed in the microscope image, the current reduction may be the result of a decrease in the number of effectively contacted molecules due to changes at one of the metal contacts or at the van der Waals interface. It was also found that some junctions exhibit a partial recovery in current level after a delay of several minutes between sets of successive bias sweeps (not shown), which is consistent with the re-establishment of structural features during the anneal-

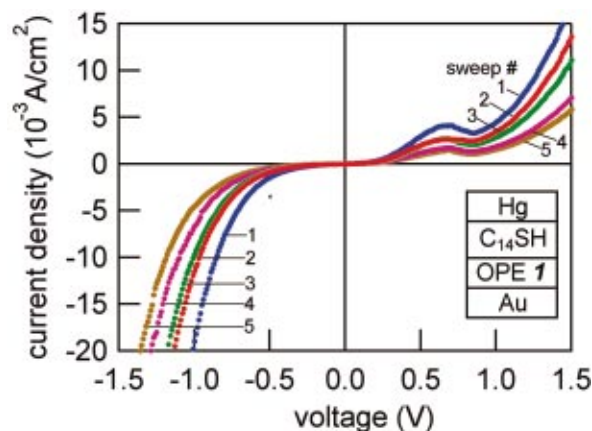


FIG. 3. (Color) Current-voltage characteristics for successive bias sweeps for a single Hg- SC_{14} //OPE (*I*)-Au bilayer junction at 300 K. The voltage was swept from -1.5 to +1.5 V with a sweep rate of 0.13 V/s and a delay of approximately 30 s between sweeps. The contact area was $1.7 \times 10^{-4} \text{ cm}^2$.

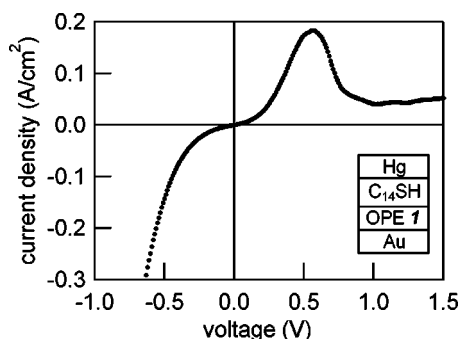


FIG. 4. Current-voltage characteristic for a Hg-SC₁₄//OPE (I)-Au bilayer junction with a high value of peak-to-valley ratio at 300 K. The peak-to-valley ratio and peak current are 4.5 and 0.18 A/cm², respectively. The voltage was swept from -1.0 to +1.5 V with a sweep rate of 0.13 V/s. The contact area was 1.2×10^{-4} cm².

ing period. However, I - V characteristics that were nearly identical on two successive sweeps and characteristics that changed only within the NDR region were also observed in a few junctions, and a more detailed study is needed to fully characterize this time-dependent behavior.

NDR characteristics similar to those in Fig. 3 were obtained for more than 14 different bilayer junctions formed on several different samples of the OPE (I) SAM. The NDR characteristic is also reproducible in that (1) the NDR persists over successive sweeps of the bias and (2) the variation in the peak voltage over many junctions is small. In particular, the average peak voltage was 0.69 V with a standard deviation of 0.12 V. The characteristics exhibited a wide range of variation in terms of current level, however. The values of peak current density for different junctions ranged from 4.7×10^{-4} to 4.6×10^{-1} A/cm². This nearly three orders-of-magnitude variation, while large, is not much greater than the approximately two orders-of-magnitude current variation we observe for different junctions for a given Hg-SC_{*n*}//C_{*n*}S-Au alkanethiol bilayer control. Because OPE is an aromatic molecule, the current level for the Hg-SC₁₄//OPE (I)-Au junction is expected to be many orders of magnitude higher than that for the Hg-SC₁₄//C₁₄S-Au control, in agreement with Fig. 2. An approximate upper bound for the Hg-SC₁₄//OPE (I)-Au current would be equal to the current for a Hg-SC₇//C₇S-Au bilayer since this bilayer contains the same number of methylene groups as in a Hg-SC₁₄ monolayer. This is also in agreement with the data in Fig. 2 by extrapolation. Thus, both the observed current values and range of these values seem reasonable.

Finally, the current-voltage characteristic for the junction exhibiting the highest peak-to-valley ratio is presented in Fig. 4. The peak-to-valley ratio and peak current density for this junction are 4.5 and 0.18 A/cm², respectively.

In conclusion, we have observed negative differential resistance in a bilayer molecular junction. The junction is based on a Hg-alkanethiol/arenethiol-Au system comprised of two different SAMs, each of which is contacted by a S-metal bond at one end and shares a common van der

Waals interface. One SAM is based on an alkanethiol molecule with well established tunneling characteristics while the other SAM is based on a nitro-substituted OPE molecule for which NDR was previously reported for monolayer SAMs at temperature up to approximately 150 K. Persistent, reproducible NDR is observed in the current-voltage characteristics with peak-to-valley ratios as high as 4.5 at room temperature. Within the context of previously reported results for NDR in OPE monolayer SAMs, the bilayer results presented here suggest that (1) a NDR mechanism for such SAMs can be accessed by tunnel injection through an alkanethiol SAM and (2) the bilayer junction provides a favorable electrical and mechanical environment for this mechanism. In light of the present incomplete theoretical understanding of NDR in molecular systems, however, alternative mechanisms for the observed characteristics more specific to the bilayer junction should also be considered. In particular, the exact nature of the noncovalent interaction between the methyl and phenyl termini of the Hg-bound and Au-bound monolayers and its possible role in determining the current-voltage characteristics raise interesting questions for future investigation. The robust and reproducible bilayer molecular junction system offers the opportunity to systematically vary the molecular components to investigate various hypotheses of structure/function relationships and mechanism.

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