

Charge storage model for hysteretic negative-differential resistance in metal-molecule-metal junctions

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Experimental results on the electrical characteristics of Hg-alkanethiol/arenethiol-Au molecular junctions are used to develop a physical model for the hysteretic negative-differential resistance (NDR) for these, and possibly other, metal-molecule-metal junctions. The dependence of the room-temperature current-voltage characteristic on sweep direction and sweep rate is examined. Based on several specific electronic behaviors, it is concluded that the NDR is caused by slow charge capture (reduction or oxidation) during the forward sweep and the resultant effect on tunneling. The implications of this model on potential electronic applications are discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2195696]

On the basis of detailed experimental findings, we wish to suggest a model for the hysteretic negative-differential resistance (NDR) observed for certain metal-molecule-metal junctions. This model provides an explanation for the electrical behavior of these junctions and has implications for their possible use in electronic circuitry.

The metal-molecule-metal junction examined in this study [Fig. 1(a)] was a bilayer molecular junction composed of two self-assembled monolayers (SAMs) sandwiched between metal contacts.¹ A nitrosubstituted oligo(phenylene-ethynylene) (OPE) was chosen for one component of the junction because NDR has been reported by various groups for a variety of junctions containing this molecule and other nitrosubstituted analogs,^{2–8} although we note that NDR has also been observed for other molecular junctions.^{9–15} An alkanethiol was chosen for the other component because of its well known electrical characteristics, which are attributed to tunneling.¹

As in our earlier reported studies,⁶ the specific molecules used here were 4-([2-amino-5-nitro-4-(phenylethynyl)phenyl]ethynyl)benzenethiol (1) and tetradecanethiol (HSC₁₄H₂₉). The chemical protocols used for OPE synthesis and SAM preparation were also identical to the ones used before.⁶

Due to the poorly reproducible construction and limited stability of most metal-molecule-metal junctions exhibiting NDR, an extensive study of NDR behavior has previously not been possible. The data have usually been limited to a few characteristics taken at one sweep rate in one direction only. Although bilayer junctions offer some advantages in this regard, reproducibility has also been a factor in our experiments. Typically, only one in ten of our junctions exhibits NDR. Nevertheless, we have observed NDR with good peak-to-valley ratio in over 40 junctions and have obtained char-

acteristics that are sufficiently repeatable to allow a systematic study of electrical behavior.

The current-voltage (*I-V*) characteristic shown in the inset of Fig. 1 is typical of our best junctions and is comparable to the best reported for other metal-molecule-metal junctions at room temperature. Figure 1 shows the *I-V* characteristics for nine consecutive sweeps from -0.5 to 1.5 V. The vertical shift of the characteristic with each sweep, which is typical of these junctions, represents a current scaling with each sweep. Microscopic observation showed no change in the contact area during the measurement, indicating that conduction through a fraction of the molecules is somehow lost with each sweep. Possible mechanisms for this include a cleavage of thiol-metal bonds⁹ or a change in the molecule-molecule interface. Significantly, even though the overall current drops by orders of magnitude, the peak-to-valley ratio changes little over the entire set of forward sweeps, indicating that the NDR is caused by some different mechanism.

The most striking behavior revealed by the data in Fig. 1 is the hysteretic feature in the range of 0.50 – 0.75 V. The

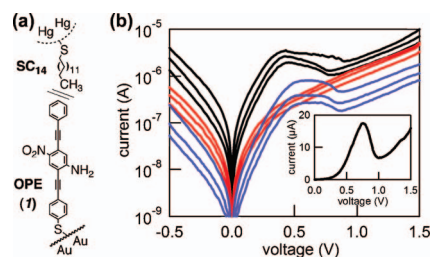


FIG. 1. (Color) (a) Schematic of the Hg-SC₁₄//OPE(1)-Au bilayer molecular junction. (b) A series of consecutive *I-V* sweeps performed in three sets: the first three sweeps (black) were taken in the forward-sweep direction, the next three (red) in the reverse-sweep direction, and the last three (blue) again in the forward-sweep direction. Bias voltage refers to the potential with respect to the Hg drop. Junction diameter of $170\ \mu\text{m}$. Sweep rate of $130\ \text{mV/s}$. All data taken at room temperature. Inset: *I-V* characteristic for a single sweep in the forward-sweep direction.

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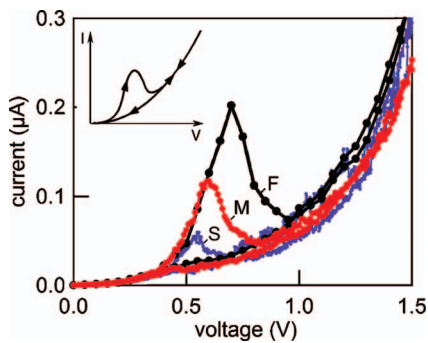


FIG. 2. (Color) Cyclic I - V characteristics for three different sweep rates: slow (S) ± 21 mV/s, moderate (M) ± 83 mV/s, and fast (F) ± 415 mV/s. Each continuous cycle of the voltage shows a current peak in the forward-sweep direction and no peak in the reverse-sweep direction (see inset). The diameter of the junction was $180 \mu\text{m}$.

first and last sets of curves were swept in the forward direction, while the middle set was swept in the reverse direction. In this and other experiments, the NDR was observed only in the forward-sweep direction. This hysteretic behavior provides an important clue for understanding the underlying mechanism for the NDR itself. Note that, except for the current scaling, the characteristics for successive sweeps closely repeat for both directions, i.e., the process seems to reverse. The results below confirm this reversibility.

Some junctions exhibited highly repeatable characteristics with virtually no drop in current over many sweeps, allowing a systematic study of the sweep rate dependence to be made. Figure 2 shows I - V characteristics for three different sweep rates. In each case, the voltage was swept in a continuous cycle from 0 to 1.5 and back. (No other bias was applied between sweeps.) Figure 2 shows that the sweep rate has a significant effect on the peak position and height.

A series of over 20 consecutive sweeps taken at different rates in a random order confirmed the repeatability of the characteristics for stable junctions and the validity of the sweep rate dependence in Fig. 2. An analysis of the data was performed to search for quantities that were independent of sweep rate and that might explain the systematic sweep rate dependence. Even though the I - V characteristic in the peak region changes dramatically as the sweep rate is varied by a factor of 20, the integral of the current from the peak to the valley is nearly constant for all rates (within a factor of about 2). The integral is 0.25, 0.21, and $0.10 \mu\text{C}$ for sweep rates of 21, 83, and 415 mV/s, respectively. The integral, which we call Q_F , is the amount of charge that flows through the junction while the voltage sweeps through the NDR region. The fact that Q_F is nearly constant suggests that the NDR is the result of a charge storage process within the junction.

The cyclic I - V data in Fig. 2 are replotted on semilog axes in Fig. 3. In the forward-sweep direction, the current increases exponentially as the voltage increases toward the peak. The current then drops with increasing voltage and becomes exponential again but with a different slope. When the sweep direction is reversed, the characteristic initially retraces the forward-sweep characteristic for voltages above the current valley but then continues to decrease instead of retracing the NDR branch. The reverse-sweep characteristic then abruptly changes slope and retraces the forward-sweep characteristic again. Although various mechanisms could produce the exponential dependence, the two exponential branches of the characteristic can most simply be explained

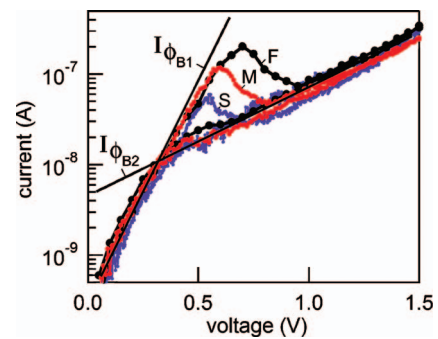


FIG. 3. (Color) The cyclic I - V data from Fig. 2 replotted on a log I vs V graph. The lines labeled $I_{\phi_{B1}}$ and $I_{\phi_{B2}}$ are linear fits to the low- and high-voltage data. ϕ_{B1} and ϕ_{B2} refer to the effective tunneling barrier heights for these regimes. $\phi_{B2} = \phi_{B1} + \Delta\phi$, where $\Delta\phi$ represents the change in the barrier height due to charge storage.

by tunneling transport in which the effective tunneling barrier is changed by some process.

On the basis of the above results, we suggest the following physical picture. As the voltage is increased, the current at first increases exponentially due to tunneling with an effective barrier height ϕ_{B1} (see Fig. 3 legend). After a critical voltage is reached, a slow charge capture process begins, eventually resulting in the buildup of charge within the junction. Since we do not know what specific component of the junction becomes charged nor whether it gains or loses an electron (i.e., is reduced or oxidized), we refer to this event, simply, as charge capture. The essential point is that the capture acts to slowly change the electronic properties of the junction in such a way that ϕ_B is increased. This charge storage causes the current to gradually decrease. The number of accessible charge storage centers in the junction is fixed. Once these centers become saturated, the barrier assumes a constant value ϕ_{B2} and the current increases exponentially again but at a lower rate due to the increased barrier height. Simply put, current flows by tunneling throughout the entire characteristic and charge storage changes the effective tunneling barrier ϕ_B at some point during the sweep.

Within this model, the NDR is a dynamic effect resulting from an overshoot of the current beyond its steady-state value during a slow charge capture process. The capture process is characterized by a critical voltage and a small capture cross section, i.e., a small probability for capture. When the voltage is swept faster, the overshoot is larger and the peak position and height increase accordingly.

The small capture probability is an important part of the model and was key in our interpretation of the data. When the probability of capture is small, many carriers transit the junction for each captured carrier. This means that Q_F , which is the amount of charge that flows during the storage process, should be a multiple of the charge stored in the junction, Q_S . The multiplication factor is governed by the capture probability of the center. If a junction has a limited number of accessible charge storage centers, then Q_S , and hence Q_F , should be fixed for that junction, independent of sweep rate.

The maximum density of molecules for a SAM on Au(111) is $\sim 5 \times 10^{14} \text{ cm}^{-2}$. This provides a rough upper bound for the area density of stored electrons in the junction Q_S/q . The value of Q_F/q for the junctions examined in our study was in the range of $5 \times 10^{15} - 7 \times 10^{16} \text{ cm}^{-2}$. The corresponding ratio Q_S/Q_F gives a maximum probability of capture of roughly 1/10–1/100 for these junctions.

The fact that the reverse characteristic does not retrace the forward-sweep characteristic in the NDR region is consistent with our model. In the reverse-sweep direction, the current should follow the φ_{B2} line in Fig. 3 until the critical voltage is approached from the right. At this point the characteristic should slightly overshoot the φ_{B1} line if charge emission (or the relevant reverse process) is slow. The fact that the characteristic changes abruptly from one line to the next without overshoot indicates that emission is faster than capture (and faster than the sweep rate) for these centers. The voltage where the characteristics cross over from $I_{\varphi_{B2}}$ to $I_{\varphi_{B1}}$ behavior in the reverse sweep direction is independent of sweep rate. Hence, this voltage is probably related to a characteristic voltage of the system, such as a reduction (or oxidation) potential or a critical electric field.

Based on the above, we conclude that the observed characteristics are the result of a slow reduction (or oxidation) during the forward sweep and a fast oxidation (or reduction) during the reverse sweep, where slow and fast refer to the rate of charge capture or release compared to the sweep rate. The slow rate of capture implies that the capture mechanism must have a small probability, which suggests that the reduction may involve a structural (e.g., conformational) rearrangement of a molecule having a large reorganization energy. This structural rearrangement would likely be the major contributor to the overall energetic barrier that is responsible for slow charge storage. While the redox-active nitrosubstituted OPE molecule in this junction is an obvious candidate for the charge storage center, the reduction (or oxidation) of centers associated with extrinsic constituents cannot be ruled out.

Although reduction/oxidation processes have been implicated in other studies of NDR in molecular junctions,^{8,10,12} the suggested role in each case was different from that proposed here. It has been suggested that charge capture¹⁵ and molecular reorganization^{13,14} may also play a role in the conductance switching (persistent bias-induced conductance changes) observed in other molecular junctions. Although conductance switching and NDR are distinctly different behaviors, their underlying mechanisms may share some common features.

In this study, we have probed the electrical behavior of Hg-SC₁₄//OPE(1)-Au molecular junctions and used our results to develop a physical model for these junctions. We conclude that the observed NDR is a dynamic effect caused by a slow reduction or oxidation during the forward sweep and its resultant effect on tunneling through the junction. This model has important implications on potential elec-

tronic circuit applications for these junctions. Because the behavior results from a slow dynamic process, these junctions cannot provide the gain or oscillation needed for high-speed signal processing or logic applications. Further analysis is needed to determine whether the junctions are locally active in the NDR region and, hence, could offer other useful electronic functions.¹⁶

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