

Room-temperature negative differential resistance in nanoscale molecular junctions

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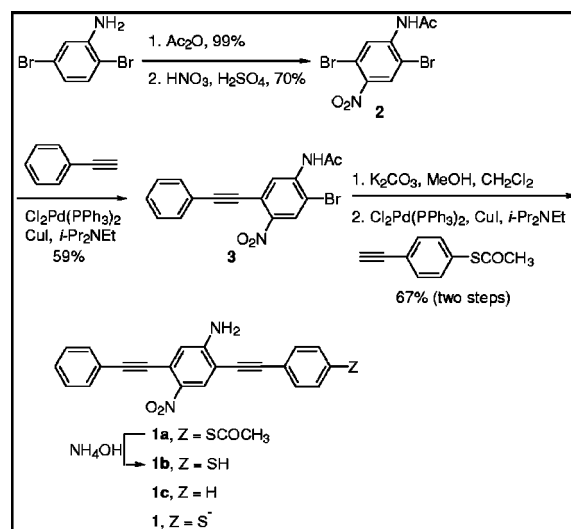
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Molecular devices are reported utilizing active self-assembled monolayers containing the nitroamine [2'-amino-4,4'-di(ethynylphenyl)-5'-nitro-1-benzenethiolate] or the nitro compound [4,4'-di(ethynylphenyl)-2'-nitro-1-benzenethiolate] as the active components. Both of these compounds have active redox centers. Current-voltage measurements of the devices exhibited negative differential resistance at room temperature and an on-off peak-to-valley ratio in excess of 1000:1 at low temperature. © 2000 American Institute of Physics. [S0003-6951(00)03234-4]

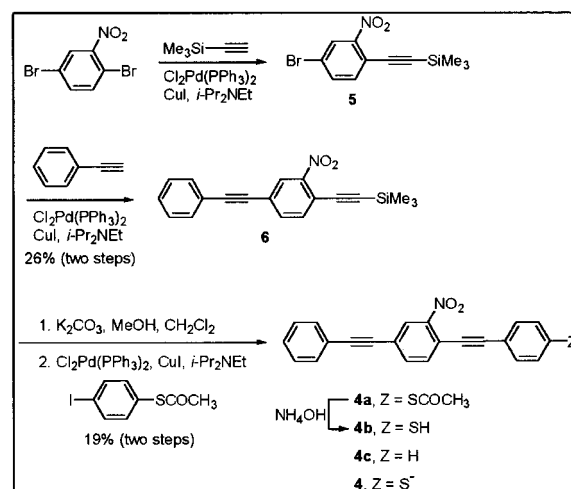
The discovery of negative differential resistance (NDR) in semiconductor diodes opened a new chapter in semiconductor device physics.¹ The physical basis of the Esaki diode is interband tunneling between the valence band and the conduction band. NDR can also result from resonant tunneling in semiconductor heterostructures.² The presence of NDR at room temperature allows for many practical applications.³⁻⁵ Here, we report on the observation of large NDR behavior, and room temperature operation, in an electronic device that utilizes molecules as the active component.

Electronic measurements were performed in a nanostructure consisting of top metal contact (Au)—self-assembled monolayer active region (30 to 50 nm in diameter)—bottom metal contact (Au), similar to that reported previously.^{6,7} The active electronic component was made from 2'-amino-4,4'-di(ethynylphenyl)-5'-nitro-1-(thioacetyl)benzene (**1a**) that was prepared as outlined in Fig. 1(a). Acylation and nitration of 2,5-dibromoaniline afforded **2**⁸ which underwent Pd/Cu-catalyzed coupling⁹ with phenylacetylene preferentially at the more electrophilic C-Br site to yield **3**. Acetate hydrolysis and coupling with 4-ethynyl(thioacetyl)benzene¹⁰ afforded the desired compound **1a**. As was previously established,¹¹ thioacetyl groups can be selectively hydrolyzed with ammonium hydroxide in tetrahydrofuran during the self-assembly step to afford the free thiol, 2'-amino-4,4'-di(ethynylphenyl)-5'-nitro-1-benzenethiol (**1b**), in this case. The actual assembly likely forms the thiolate [**1**: 2'-amino-4,4'-(diethynylphenyl)--5'-nitro-1-benzenethiolate] upon exposure to Au.¹¹ The other redox center-containing molecular compound used in this study is 4,4'-(diethynylphenyl)-2'-nitro-1-benzenethiolate (**4**). Its synthesis is shown in Fig. 1(b). 2,5-Dibromonitrobenzene was sequentially coupled to trimethylsilylacetylene and phenylacetylene using Pd/Cu catalysis⁹ to yield **6**. Exposure of the terminal alkyne and coupling with 4-thioacetyl iodobenzene afforded **4a**.

Typical $I(V)$ characteristics of a Au-(1)-Au device are shown in Fig. 2(a), summarized here as previously reported.⁷ Positive bias corresponds to hole injection from the chemi-



(a)



(b)

FIG. 1. (a) Schematic of the synthesis of the active molecular compound **1** and its precursors (**1a** and **1b**). (b) Schematic of the synthesis of the active molecular compound **4** and its precursors (**4a** and **4b**).

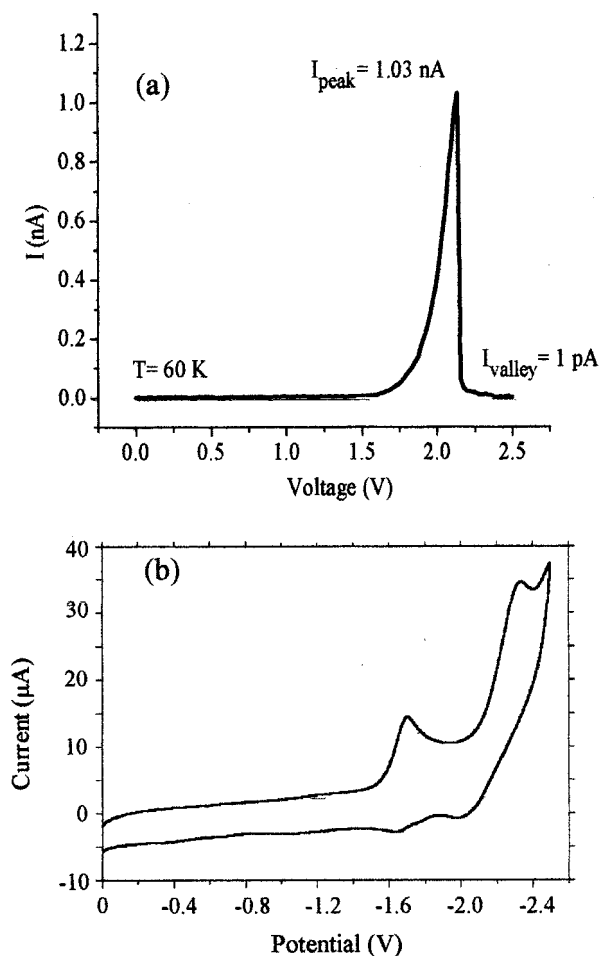


FIG. 2. (a) $I(V)$ characteristics of a Au-(1')-Au device at 60 K. The peak current density is ~ 50 A/cm², the NDR is ~ -400 $\mu\Omega$ cm², and the PVR is 1030:1; (b) cyclic voltammogram of compound **1c** showing two distinct reduction peaks.

sorbed thiol-Au contact and electron injection from the evaporated contact. At 60 K, the peak current density for this device was >53 A/cm², the NDR is <-380 $\mu\Omega$ cm², and the peak-to-valley ratio (PVR) is 1030:1. Unlike previous devices that also used molecules to form the active region,¹² this device exhibits a robust and large NDR. The $I(V)$ curve is fully reversible upon a change in this bias sweep direction; for a given device, small fluctuations (a few percent) were observed with consecutive positive and negative sweeps but could be attributed to temperature fluctuations of ~ 2 K (within the experimental thermal stability). The performance exceeds that observed in typical solid state quantum well resonant tunneling heterostructures.¹³⁻¹⁵ The intrinsic PVR of the molecule may be considerably greater than that reported here, because the valley currents observed (on the order of picoamperes) are comparable to typical leakage currents in the silicon nitride. The devices are stable for more than one year in ambient conditions.

Cyclic voltammetry measurements of compound **1** (for simplified analysis, specifically **1c**) were performed at room temperature on a BAS CV-50 W voltametric analyzer using an Ag/AgNO₃ reference electrode, and solvent system of dimethylformamide and 1 M *n*-tetrabutylammonium tetrafluoroborate with a scan rate of 100 mV/s. Figure 2(b) shows the cyclic voltammetry reduction curve where the first

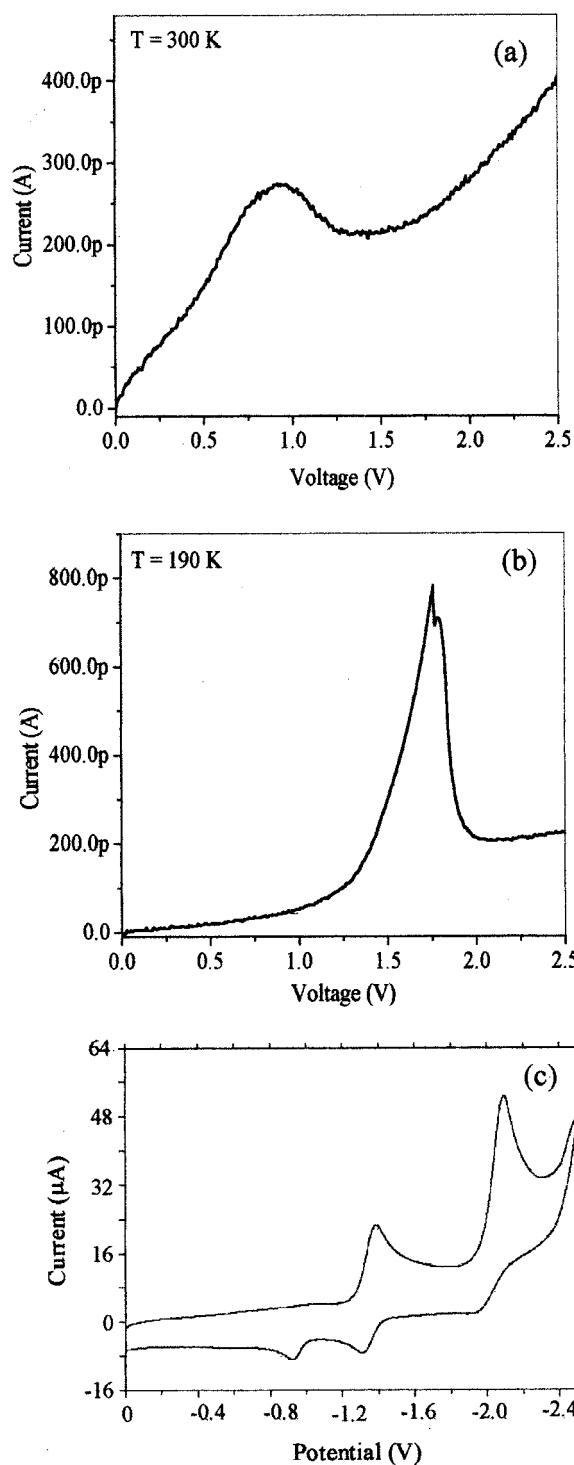


FIG. 3. $I(V)$ characteristics of a Au-(4)-Au device at: (a) 300 K; (b) 190 K; (c) Cyclic voltammogram of compound **4c** showing two distinct reduction peaks.

and second reduction potential for compound **1c** are -1.70 V and -2.33 V, respectively.

A candidate mechanism for NDR is a two-step reduction process that modifies charge transport through the molecule.⁷ As the voltage is increased, the molecule initially undergoes a one-electron reduction, turning on the conduction channel; a further increase in voltage causes a second-electron reduction with subsequent blocking of the current.¹⁶ The width of the $I(V)$ peak correlates well with the difference in the two-electron reduction potentials. The NDR behavior is absent in

the control molecule (no amine or nitro moieties),¹² indicating that the nitroamine redox center is responsible for the NDR behavior of the devices.

Similar NDR behavior was also observed in devices with nitro only moiety (**4**). The PVR is smaller than that of **1**, but NDR behavior persisted from a low temperature to room temperature. $I(V)$ characteristics of a Au-(**4**)-Au device at 300 K are shown in Fig. 3(a). The device has a peak current density $>16 \text{ A/cm}^2$, NDR $<-144 \text{ m}\Omega \text{ cm}^2$ and a PVR 1.5:1. At 190 K [Fig. 3(b)], the NDR peak is much sharper, although its PVR is not as large as that of **1**. The degradation in PVR (decreasing in peak current) can probably be caused by increased inelastic scattering with increased temperature. Figure 3(c) shows the cyclic voltammogram curve for compound **4c** where the reduction potentials peaked at -1.39 and -2.09 V , respectively. The reduction potential difference is in approximate agreement with the width of the $I(V)$ peak. The fact that **4c** is more readily reduced than **1c** (the reduction potential of **4c** is 0.3 V less than that of **1c**) could be responsible for the observation of room temperature NDR in **4** but not in **1**. The NDR behavior is absent in amino only molecule [2'-amino-4,4'-di(ethynylphenyl)-1-benzene-thiolate]. This observation suggests that the nitro group is responsible for the NDR behavior. Further understanding of the underlying mechanism and experimentation with various redox centers should allow us to further modify and engineer molecular compounds.

We have reported on molecular devices that exhibit room temperature NDR behavior and large PVR NDR at low temperature. Good agreement between the transport measurements and the electrochemistry experiments suggests that reversible electrochemical redox reaction could be re-

sponsible for the NDR behavior. The performance of molecular NDR devices can be improved by changing the chemical structure of the molecules, a conceptually different approach than solid state NDR devices.

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