Room temperature negative differential resistance of a monolayer molecular rotor device

Mei Xue,¹,a) Sanaz Kabehie,² Adam Z. Stieg,³ Ekaterina Tkatchouk,⁴ Diego Benitez,⁴ Rachel M. Stephenson,² William A. Goddard,⁴ Jeffrey I. Zink,²,³ and Kang L. Wang¹,³

¹Department of Electrical Engineering, Device Research Laboratory, University of California, Los Angeles, California 90095, USA
²Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, USA
³California NanoSystems Institute, University of California, Los Angeles, California 90095, USA
⁴Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, USA

(Received 17 June 2009; accepted 12 August 2009; published online 2 September 2009)

An electrically driven molecular rotor device comprised of a monolayer of redox-active ligated copper compounds sandwiched between a gold electrode and a highly doped P⁺Si substrate was fabricated. Current-voltage spectroscopy revealed a temperature-dependent negative differential resistance (NDR) associated with the device. Time-dependent density functional theory suggests the source of the observed NDR to be redox-induced ligand rotation around the copper metal center, an explanation consistent with the proposed energy diagram of the device. An observed temperature dependence of the NDR behavior further supports this hypothesis. © 2009 American Institute of Physics. [DOI: 10.1063/1.3222861]

Negative differential resistance (NDR) is an essential property that allows fast switching in certain types of electronic devices such as Esaki diode and IMPATT diode.¹,² Beyond the traditional electronic devices, a number of nanoscale molecular devices have been studied and reported to exhibit NDR characteristics.³–⁷ Although various mechanisms have been proposed, including charging and discharging processes of electrons, chemical reaction, redox reaction, and the association-dissociation processes of molecules, their specific underlying physics remain unclear. These functional molecular units acting as state variables provide an attractive alternative to overcome the limits of conventional metal-oxide-semiconductor field-effect transistor technology due to their potential scalability, low cost, low variability, highly integrateable characteristics, and the capability to exploit self-assembly processes.⁸–¹⁰ Thus the elucidation of switching mechanisms and the development of different operational approaches have drawn a lot of attention. In this letter, we demonstrate an electrically driven sandwich-type monolayer molecular rotor switch with NDR. The observed NDR behavior is attributed to rotational motion on solid support. Both calculations of time-dependent density functional theory and an observed temperature dependence of the NDR behavior support this hypothesis.

Synthesized using a self-assembly approach, the molecular switch device shown in Fig. 1 is comprised of a heteroleptic copper compound covalently bonded to a highly doped silicon substrate. Each complex contains three subunits: a bifunctional stator [a bidentate ligand bonded to both a solid support (P⁺Si) and a Cu axle], the metal axle (Cu), and a diimine rigid rotator (2,9-dimethyl-1,10-phenanthroline). Preparation of the heteroleptic copper system was carried out through covalent grafting of a stator monolayer onto the hydroxylated surface of a P⁺Si substrate using silanol bonds.¹¹

The stators were then used to chelate a copper metal axle that subsequently bonds to the rotator subunit. The device was completed by deposition of a Ti/gold film through a shadow mask on top of the molecular layer to form the top electrode. The number of molecules per unit area and per unit devices tested is approximately 1.1 × 10¹⁴ cm⁻² and 8 × 10¹⁰, respectively. This copper compound exhibits two discrete, redox-dependent conformational states, Cu(I) and Cu(II). The Cu(I) form has tetrahedral geometry while the Cu(II) form is square planar.¹² The compounds undergo a one electron redox-induced rotational conformational change depending on the oxidation state of the copper metal. Interconversion between these two states provides the basis for a controlled, bistable nanoswitch.

I-V characteristics of the monolayer device are shown in Fig. 2. In this case, the silicon substrate represents the system ground and the dc bias applies from the top gold electrode. The bias sweep direction followed the arrows numerically as shown in Fig. 2. Unlike previously reported devices, the NDR observed here disappeared after reversal of the sweep.

FIG. 1. (Color online) The schematic structure of the molecular rotor device composed of a bisP⁺Si stator, a copper metal axle, and a diimine rotator. The diimine ligand on top, 2,9-dimethyl-1,10-phenanthroline, rotates upon reduction and oxidation in the direction as illustrated with arrows.

¹¹Author to whom correspondence should be addressed. Tel.: +1-310-206-0207. Fax: +1-310-206-8495. Electronic mail: mxue@ee.ucla.edu.
For a given device, the direction in the negative voltage regime is due to the conformational change in the active molecular layer. As seen in Fig. 2, state “1” and state “2” represent the molecular layer consisted of solely grafted stators or Cu ligated stators were prepared. Due to their lack of a liganding effect with redox-induced conformational switching, devices lacking the capability for rotation are observed among devices owing to the nonuniformity of the active molecular layer.

To further explore the correlation of the observed NDR effect with redox-induced conformational switching, devices whose molecular layer consisted of solely grafted stators or Cu ligated stators were prepared. Due to their lack of a ligated rigid rotator, these devices lack the capability for rotational motion upon oxidation or reduction of the Cu metal axle. The lack of observed NDR effects in these cases implies that the source of the observed NDR in the full device is due to the conformational change in the active molecular layer. As seen in Fig. 2, state “1” and state “2” represent the low and high conductivity states, respectively. The turning voltage between state “1” and state “2” is determined by the redox energy of the copper system. Variations in the turning voltage between the extracted activation energy and the theoretical quenching energy supports the proposal that the observed NDR effect in this device is due to rotational motion within the molecular layer. The peak and background currents at 0.5 and −0.5 V, respectively, were plotted versus 1000/T and displayed different temperature dependences, as shown in the inset of Fig. 3. The weak temperature dependence of both background currents is indicative of electron tunneling between the two device electrodes.

The proposed mechanism for the observed device I-V characteristics shown in Fig. 2 is based on an electron tunneling induced molecular rotation behavior that serves to modify the band diagram of the active molecular layer. Density Functional Theory (DFT) calculations have been employed in an attempt to reconcile the sequence of carrier transport processes and the role of energy states, which helped formulate the proposed band diagram presented in Fig. 4. Application of a bias potential to the top gold electrode shifts the energy positions of molecular states relative to both gold electrode and P+Si band edges. As the rotary motion around the molecular axle is controlled by electron transfer, a portion of the applied potential is used to initiate the redox process within the molecular layer. First, theoretical calculations of the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) band gap for the Cu(I) and Cu(II) complexes by time-dependent DFT (TD-DFT) yielded values of approximately 2.7 and 3.4 eV, respectively. Similar methods have been used in the study of organocopper complexes. Additional calculations of the molecular redox energy produced a value of 0.3 eV by exponentially fitting the curve of the measurement data higher than 244 K. The inset shows the peak current as well as the background current at 0.5 V and −0.5 V, respectively. The weak temperature dependence of the background current implies tunneling transport of electrons.

$$E_a = -R \frac{d \ln k}{d(1/T)}$$

where $E_a$ is the activation energy, $k$ is the rate constant of chemical reactions, $T$ is the temperature, and $R$ is the gas constant. Curve fitting of the data acquired for $T>244$ K yielded a rotational activation energy of approximately 0.3 eV, and this value is consistent with the theoretical quenching energy of the rotation in solution. This solid agreement between the extracted activation energy and the theoretical quenching energy supports the proposal that the observed NDR effect in this device is due to rotational motion within the molecular layer. The peak and background currents at 0.5 and −0.5 V, respectively, were plotted versus 1000/T and displayed different temperature dependences, as shown in the inset of Fig. 3. The weak temperature dependence of both background currents is indicative of electron tunneling between the two device electrodes.

![FIG. 2](Image)

FIG. 2. (Color online) I-V characteristics of the monolayer device with the bisP stator. State “1” represents the low conductivity state, while state “2” is the high conductivity state. The turning voltage between state “1” and state “2” is determined by the redox energy of the copper system. The difference in value of the turning voltage between positive and negative ranges is due to the different contact energy barriers of the two electrodes. The arrows show the sequence of the voltage scan. Arrows “4” and “5” correspond to the band diagrams in Figs. 4(a) and 4(b), respectively (to be discussed later).

![FIG. 3](Image)

FIG. 3. (Color online) Arrhenius plot of the peak minus background current. The activation energy of rotation was extracted to be 0.3 eV by exponentially fitting the curve of the measurement data higher than 244 K. The inset shows the peak current as well as the background current at 0.5 V and −0.5 V, respectively. The weak temperature dependence of the background current implies tunneling transport of electrons.
The tunneling transport. Furthermore, the thickness of the temperature dependence of the background current implies port mechanisms, the current would show different tempera-
port, which one might consider. For both of these two trans-
port mechanisms, the activation energy of the rotation was estimated to be 0.3 eV from the Arrhenius plot. The proposed band dia-
gram was used to explain the electron transport behavior during the device operation.

The authors would like to thank the FCRP-FENA center for support.

16. All calculations were performed on model system [Cu(2,9-dimethyl-1,10-phenanthroline)3] in the gas phase with Gaussian 03 using the density functional B3LYP with the 6-31G(d) basis set. (Frisch, M. J. Gaussian 03, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.) The LANL2DZ basis set was used for Cu and the 6-31G(d) basis set for C, N, and H.
18. X. J. Wang, C. Lv, M. Kubo, and A. Miyamoto, J. Organo-
23. N. F. Mott and E. A. Davis, Electronic Processes in Non Crystalline Ma-