

Negative Differential Resistance in Metallic and Semiconducting Clusters

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One of the main goals of the multidisciplinary field of nanotechnology is to scale down electronic devices to the range of nanometers (nm) from the present feature size of ~ 50 nm in standard semiconductor integrated circuits. This challenge requires the use of small molecules or clusters to perform as electronic devices. Because a multitude of small organic molecules and clusters can be tailored to precise configurations emulating feature sizes equivalent to fractions of angstroms (10^{-10} m), they are potential electronic device candidates. Although it is not yet well established how these small systems can be addressed, they could be used as electronic devices if they present switching behavior. However, switching alone may not be enough; more complex nonlinear current–voltage (I – V) characteristics such as negative differential resistance (NDR) already reported in several experiments may be needed to compensate for the lack of direct addressing. It is demonstrated theoretically in this work that switching and NDR can be achieved because of electronic and electromechanical effects yielding cluster formation; therefore, electronic devices can be made not only from organic molecules but also from small clusters.

Introduction

It is an impressive fact that the microprocessors in our computers are in the range of one inch per side and have more than 60 million transistors; however, what it is really more impressive is the fact that those millions of transistors are perfectly interconnected, located, and manipulated to perform the required functions of a complex processor. We define these characteristics as addressing, which is possible because of the ability of modern lithographic techniques to resolve or to address features in the range of 45 nm.^{1–5}

However, small molecules cannot be addressed like transistors in an integrated circuit; thus, some other way of indirect addressing may be required because of the intrinsically random assembly or formation of molecular systems.² Molecular circuits or their interconnections must be reset or reprogrammed in order to trigger them to perform in a predetermined way. Reprogramming at the level of devices requires multivalued features such that an available space of configurations allow their programming into useful functions, and this was demonstrated to be possible if the devices show highly nonlinear characteristics such as NDR.⁴

Thus, devices having NDR characteristics may be essential because even the interconnection of only two NDR devices in series yields multivalued I – V characteristics for the composed system, which can eventually be programmed to perform a designated logic function regardless of their random arrangement.^{4,6}

However, the interpretation of experiments used to demonstrate the electrical characteristics of atomistic systems, such as NDR, is very difficult and uncertain and can lead to misleading conclusions.⁷

Certainly, NDR⁸ and switching observed in atomistic systems cannot be associated only with the organic molecules employed for that purpose but also to the contacts where the molecules

are attached. NDR was observed in nanocell experiments with and without molecules, suggesting that NDR was most likely due to the electromigration of deposited gold.⁹ Thus, NDR may originate from the creation and destruction of metallic filaments, involving several switching processes caused by changes in electronic, charge, conformational, or vibrational states as well as by chemical reactions yielding the creation and destruction of bonds.

An extraordinary help in solving these experimental questions comes from the “microscope” provided by quantum chemistry, which allow solutions of the molecular Schrödinger equation with “chemical precision” for small molecules. In addition, with the complement of molecular dynamics simulations, a very acceptable description of the molecular environment and external conditions could be obtained. We perform *ab initio* density functional theory (DFT) calculations combined with a Green function approach for electron transfer^{4,10,11} and molecular dynamics (MD) simulations^{5,12} to analyze the possible mechanisms of observed NDR in experiments involving metallic gold systems.

Bridge Breaking and Formation

When a current passes through a nanosized filament, it is heated, and the local temperature may rise to 1000 K and higher values until the filament breaks (*vide infra*). This is not the average temperature of a macroscopic sample but that of a localized region of nanometer dimensions. After the breaking, the electron-tunneling probability decreases as well as the current, thus decreasing the local temperature. However, the effect of the electric field on broken filaments or in contacts very close to each other (e.g., in discontinuous gold films) can yield the formation of bridges between the separated terminals through small filaments or clusters of gold atoms with properties such as NDR (*vide infra*). Figure 1 shows a few frames from molecular dynamics simulations illustrating the breakage and formation of atomic bridges that are able to produce switching in gold filaments. Then, the bias voltage can pull atoms to bridge

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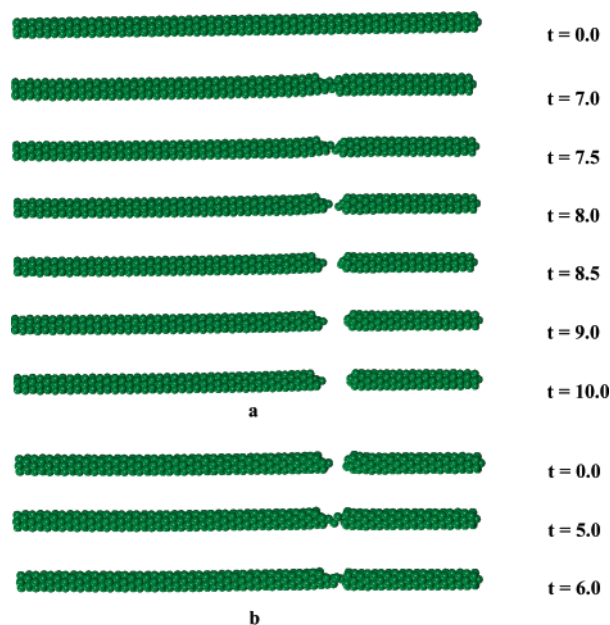


Figure 1. (a) Frames from molecular dynamics simulations of gold filaments showing the breaking of the filament when reaching 1010 K. (b) Formation of an atomic bridge on the broken filament under the effect of an electric field applied in the axial direction; the bridge is formed when 15 V is applied at 473 K. The time in picoseconds is shown on the right. The filament does not break below 1000 K, but it breaks when the local temperature rises above 1010 K.

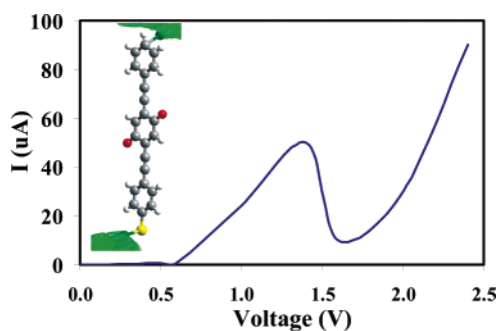


Figure 2. Molecular NDR predicted for a dioxo molecule.⁴ The sharp drop may be from a change in the charge state of the molecule due to the bias potential.

the gap between the broken filaments. The thermal motion can be constrained at low temperatures⁹ but electromigration cannot.

Molecular NDR

Switching and NDR from organic molecules can be demonstrated theoretically; NDR was attributed to a combination of charge and torsional effects in an organic molecule,¹³ and later, another study demonstrated that the dioxo molecule, shown in the inset of the Figure 2, presented NDR behavior due to electronic and charge effects.⁴ These calculations showed unambiguously that NDR can be a molecular property. It is mainly attributed to charging (changes in the charge state of the molecule) and, to a lesser degree, electronic effects (changes in the molecular orbitals). Other effects may also participate in the switching of these devices, such as the torsional displacements in oligophenylene rings.^{14,15} Electronic orbitals, known as molecular orbitals (MO), are the conduction channels whose shape and energy determine the electron-transfer characteristics in small nanometer-sized systems. Thus, switching and NDR take place in organic molecules because of changes in the occupation, shape, and energy of the MOs.

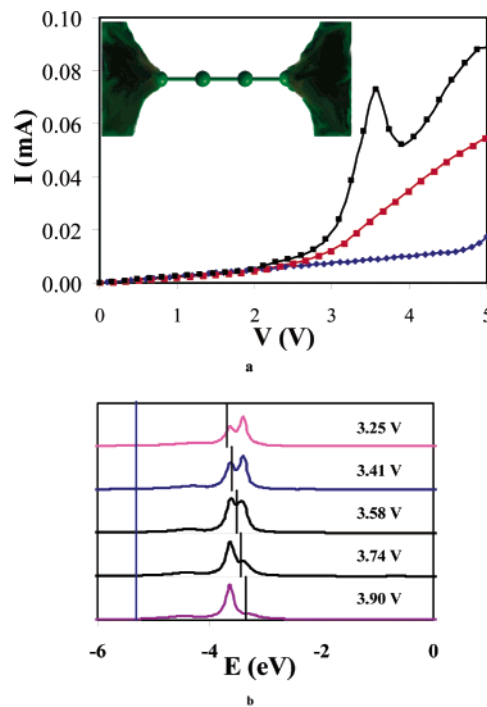


Figure 3. (a) Current–voltage characteristics for the Au_2 anion (black) and for neutral Au_2 when the field (red) and no field (blue) approximations are used. (b) Evolution of the transmission as the bias voltage (left) increases. The line on the left indicates the Fermi level for the gold cluster, and the lines on the right represent the upper limit of the integration window used to calculate the current. The vertical axis for each bias voltage corresponds to the linear range from 0 to 1 for the transmission probability.

Cluster NDR

Switching and NDR properties are also predicted in small systems composed of a few atoms, not necessarily of organic molecules. For instance, a negatively charged dimer of gold atoms connected to metallic contacts as shown in Figure 3a exhibits NDR (black curve). The peak centered at ~ 3.5 V results from changes in the electronic structure of the cluster under the external bias voltage, which needs to be explicitly considered in the calculations. The blue (red) curves correspond to the neutral gold cluster when the electrical field is (is not) considered in the calculation, respectively. The mechanism of NDR for the negative cluster can be explained by the set of transmission probabilities (Figure 3b) obtained at several bias voltages in the neighborhood of the peak resonance; the transmission probability changes rapidly as the bias voltage changes around the peak voltage. The area between the vertical lines under the curves is proportional to the current. At the peak (3.58 V), the transmission probability has the widest shape, and the current reaches a maximum.

We also analyze a few clusters that may be formed in gold–silicon interfaces because of differences in the structural (geometric) properties of Si and Au (Figure 4a). Two of the possible orientations of Si_{13} are shown, Si_7Si_6 and Si_6Si_7 , as well as the biatomic clusters Au_3Si_3 and $\text{Au}_6\text{Si}_{13}$. The Si_{13} cluster is a fused three-ring system having their atoms distributed in two parallel planes having six and seven atoms. In one case, the Si_7 plane is connected to the gold terminal, and the Si_6 plane is connected to the silicon $[\text{Au}_{\text{bulk}}\text{Au}_7]-[\text{Si}_7\text{Si}_6]-[\text{Si}_{13}\text{Si}_{\text{bulk}}]$ and vice versa in the other case $[\text{Au}_{\text{bulk}}\text{Au}_6]-[\text{Si}_6\text{Si}_7]-[\text{Si}_{13}\text{Si}_{\text{bulk}}]$. In this notation, $([\text{X}_{\text{bulk}}\text{X}_n]-[\text{M}]-[\text{Y}_m\text{Y}_{\text{bulk}}])$, $\text{X}_{\text{bulk}}\text{X}_n$ and $\text{Y}_m\text{Y}_{\text{bulk}}$ represent the left and right contacts, respectively, made of a bulk contribution terminated in few (n and m) atoms

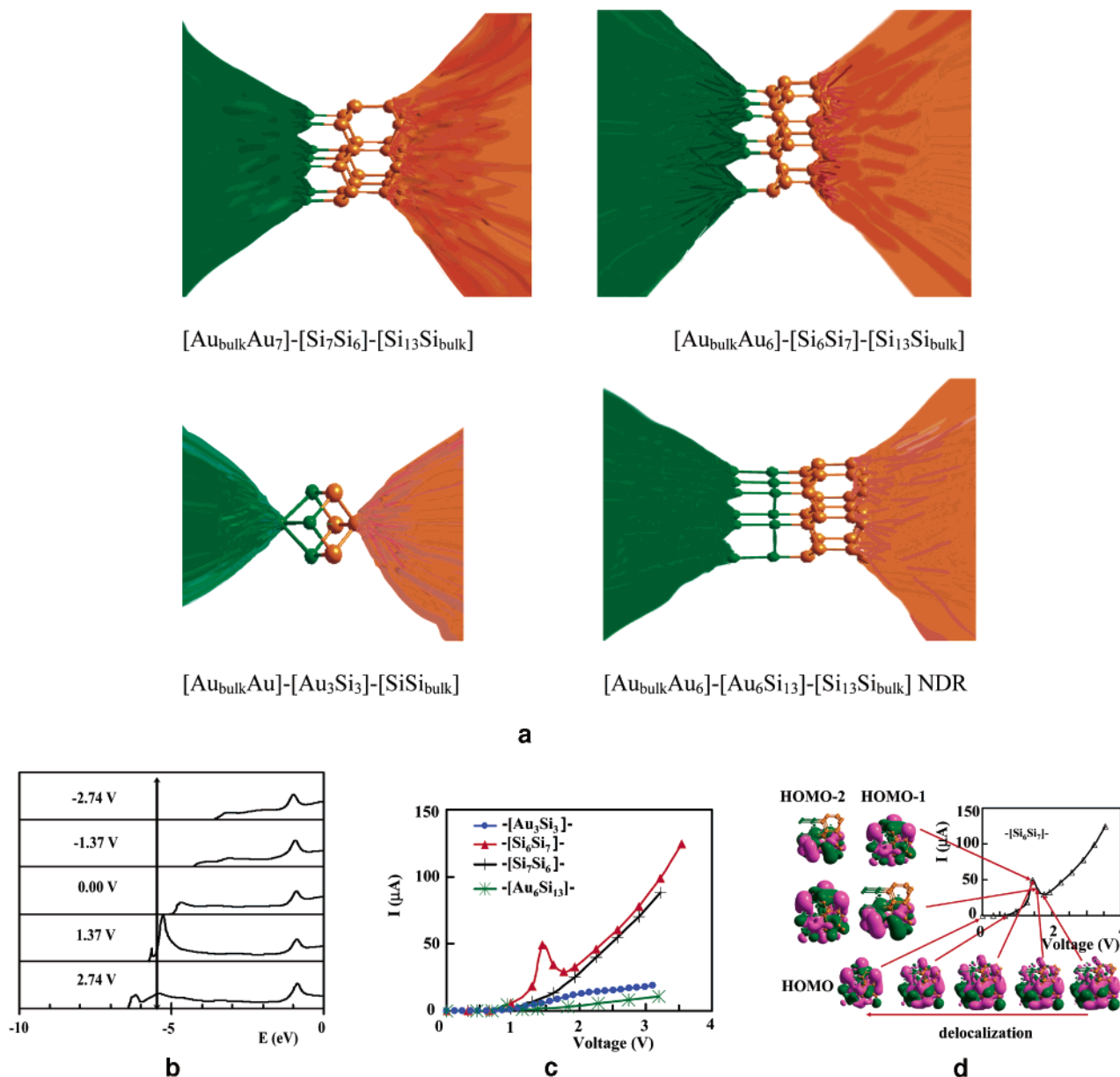


Figure 4. (a) Gold–silicon nanostructures attached to semi-infinite contacts forming the gold–silicon interfaces. (b) Transmission probabilities of the $[\text{Au}_{\text{bulk}}\text{Au}_6]\text{--}[\text{Si}_6\text{Si}_7]\text{--}[\text{Si}_{13}\text{Si}_{\text{bulk}}]$ junction for several applied voltages. The vertical axis is the transmission probability ranging linearly from 0 to 1, and the horizontal axis is the energy of the incoming electrons in electronvolts. The vertical line inside the plot indicates the location of the Fermi level of bulk gold. (c) $I\text{--}V$ characteristics of the four interfaces. (d) Selected molecular orbitals of the extended system $[\text{Au}_{\text{bulk}}\text{Au}_6]\text{--}[\text{Si}_6\text{Si}_7]\text{--}[\text{Si}_{13}\text{Si}_{\text{bulk}}]$ at different bias voltages: HOMO-2 and HOMO-1 (top left) are shown at a bias of 1.448 V (peak) and at 1.770 V (valley). The HOMO orbitals (bottom) are shown at bias voltages of 0, 0.685, 1.448, 1.609, and 1.770 V.

extending the molecule M to $X_n\text{--}M\text{--}Y_m$, which is used to calculate the properties of the interface and the molecule itself. Typical n and m values used in interfaces representing the attachment of the molecule to the contact atoms are for only few atoms because in most cases atoms from a molecule attach to only one or two atoms^{14,16,17} in the metal and because most interactions are local in nature; however, a good level of theory is required to describe the chemistry of such an interface correctly. The current–voltage characteristics (Figure 4b) show NDR for one of the Si_{13} and for the $\text{Au}_6\text{Si}_{13}$ clusters with a peak-to-valley ratio of ~ 2 ; the $\text{Au}_6\text{Si}_{13}$ NDR shows a smaller peak current; the other two systems do not show any sign of NDR. As expected, these results imply a strong dependence on the interface geometry.^{16,18} A simple explanation of the NDR in the Si_6Si_7 cluster can be provided by the shift in energy because of the effect of the variable bias voltage in the

transmission probability (Figure 4c). The peak above the Fermi level at a bias voltage of 1.37 V strongly contributes to the NDR. The electronic orbitals, yielding different delocalizations as the electric field is varied, are shown in Figure 4d for the extended molecule $\text{Au}_6\text{--Si}_6\text{Si}_7\text{--Si}_{13}$. The highest occupied MO (HOMO) (Figure 4d, bottom) at 0, 0.685, 1.448, 1.609, and 1.770 V shows delocalization changes gradually as the bias voltage is applied. The next occupied MOs (HOMO-1 and HOMO-2) show an energy crossing at the peak current. Thus, molecules are not the only systems that show NDR; small clusters of atoms may also show it. Notice that the two Si_{13} clusters yield higher currents than the $\text{Au}_6\text{Si}_{13}$ and Au_3Si_3 clusters because there is one more layer of gold atoms in the later clusters making the tunneling distance longer than the former distances in an environment in which the attachment to silicon is not perfect.

Conclusions

Our theoretical simulations and analyses show that NDR, in addition to the known organic molecule NDR, may occur because of bond breaking due to the local thermal motion of atoms in nanosystems followed by the displacement of atoms by electromigration and by the formation of clusters between interfaces, in agreement with experimental results. The effects giving rise to NDR phenomena are similar in organic molecules and clusters, and they can be thoroughly studied using theoretical chemistry techniques. The potential for practical applications based on the NDR phenomenon in small clusters of atoms is also similar to those of organic molecules and therefore to those of the stable organometallic systems that yield NDR. As a side conclusion of the present work, we can state that the characteristics of electronic devices depend exclusively on the small number of atoms clustered at interfaces.

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