

# Negative Differential Resistance Behavior of Thiolated Borazine Bonding with Gold Electrodes

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*Abstract:* - Electron transport properties of gold sandwiched thiolated borazine structure have been studied with first principles method Transiesta, which is based on density functional theory (DFT) and nonequilibrium Green's functions (NEGF's) to calculate the charge distribution for open metal-molecule-metal structures. The current-voltage (I-V) characteristics, density of states, and the transmission function of the structure are presented. The calculated results show that thiolated borazine has a nonlinear current-voltage characteristics with distinguishable negative differential resistance (NDR) behavior within bias range of 1.6V-3.0V. The origin of the mechanism leading to the characteristics is discussed based on density of states and transmission function. The NDR behavior is resulted from delocalization of the (HOMO) which is affected from applied bias voltages.

*Key-Words:* -*Ab initio* calculations, density functional theory, nonequilibrium Green's functions, quantum transport, molecular electronic structures, negative differential resistance, molecular electronics

## 1 Introduction

The field of molecular electronics has recently advanced to the point that some electronic components such as wires, diodes, and transistors have been demonstrated, based on single or self-assembled molecules instead of traditional inorganic materials. At very small dimension characteristic quantum effects become prominent. Devices could be built by exploiting the discretization of the electronic levels in molecular compounds. In particular molecular resonant tunneling diodes that are characterized by a negative differential resistance behavior (NDR) have been constructed [1]. This feature opens the way toward the development of molecular electronic switches and, by extension, memory and logic gate circuits.

The NDR behavior is often observed for molecules adsorbed on a gold surface when contacted by a scanning tunneling microscopy (STM) tip, as a result of the narrow density of states in the tip electrode [2]. NDR behavior has also been observed for compounds where the tunnel barriers leading to resonant tunneling processes are included within the molecular structure [3]. NDR behavior with a much lower peak-to-valley ratio was also demonstrated at room temperature for the same conjugated backbone substituted only with the nitro group [4]. More recently, it has been reported that the NDR behavior of molecular wires can be fine-tuned through attachment of electroactive

substituents along the conjugated backbone [5].

The origin of the mechanism leading to the sharp current peak at low voltage is still under intense debate. For the familiar double barrier resonant tunneling diodes fabricated using semiconductor heterostructures, NDR is due to shifting of the resonance states inside the tunnel barriers by the bias potential [6]. At small bias the resonance state is higher than the Fermi level of the electrode; therefore transport is off-resonance leading to a small current. At a larger bias, the resonance level is pushed down to align with the Fermi level of the source electrode leading to resonant tunneling, and larger current flows. At even larger bias, the resonance level is pushed below the edge of the conduction band of the semiconducting source electrode, giving rise to a drop in the tunneling current. This gives the familiar NDR of resonant tunneling diodes. This physical picture of NDR, however, does not apply to the organic molecular devices.

In this paper, we use *ab initio* method, Transiesta [7], to study the electron transport characteristics of thiolated borazine coupled to two Au(111) electrodes. The I-V characteristics are calculated based on density functional theory (DFT) and nonequilibrium Green's functions (NEGF's). The transmission behavior, particularly NDR behavior, is analyzed with transmission function and density of states, which are orbitals related.

## 2 System and Methods

We consider an atomic metal-molecule-metal system as shown in Fig. 1 to study the quantum transport of borazine with *ab initio* method. The geometries of the thiolated borazine and 3-D atomic golden electrodes are optimized separately first. Then the optimized molecule is sandwiched between gold (111) electrodes. The distance between left and right electrodes was adjusted and the whole structure was optimized in order to accommodate molecule properly by optimizing the total energy of the system.

The system can be divided into left electrode, device region and right electrode. Each electrode with two atomic layers and 3x3 atoms per layer represents semi-infinite lead that ends at the device region. The number of layers in the electrode is decided by Au basis set. The dimension of electrode is chosen by keeping enough distance between neighboring molecules to avoid van der Waals interactions and considering affordable computational complexity. The device region includes the thiolated borazine as well as two gold layers in each side. This can take more accurate accounts of mutual effects between the electrodes and the molecule and ease extending DFT, which is traditionally used for finite systems or periodic systems, to non-neutral open molecular systems [8].

We use the first-principles modelling method Transiesta [7] to investigate the system. With the Transiesta method, above infinite metal-molecule-metal system is approximated with a finite structure confined in the device region and the effects from semi-infinite leads on the device region are considered through self-energy, which can be viewed as effective Hamiltonians that arise from the coupling of the device with the electrodes. DFT within the local density approximation (LDA) is used to describe the electronic structure self-consistently and the self-consistent calculations are conducted only in the device region which is similar to a “super cell” and treated periodically in the directions perpendicular to the transport direction.

In order to carry out the DFT analysis, one must calculate the charge distribution for the system. Traditionally, it is constructed from the Kohn-Sham eigenstates. However, it is very difficult to determine the bound states that exist inside the scattering region. To overcome this difficulty, NEGF’s is used which naturally includes the contributions of scattering states as well as bond states in the charge density.

The density of states (DOS) can be calculated

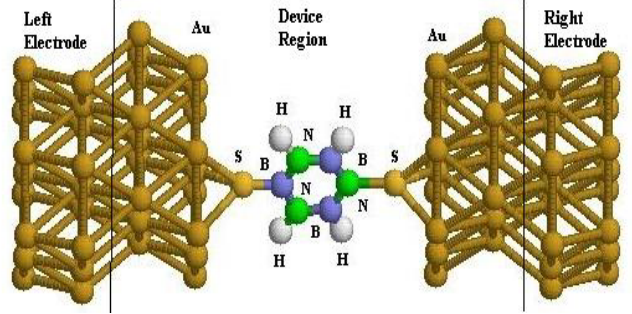


Fig 1. Atomic structure of thiolated borazine sandwiched between Au (111) electrodes

through Green’s function  $G(E)$  by [9]

$$D(E) = \frac{\text{Tr}\{i[G(E) - G^*(E)]S\}}{2\pi} \quad (1)$$

where  $S$  is the overlap matrix. The transmission function  $T(E, V)$  is the sum of the transmission probabilities of all channels available at energy  $E$  in bias  $V$  and can be calculated as [10]

$$T(E, V) = \text{Tr}[\Gamma_L(V)G(E, V)\Gamma_R(V)G^*(E, V)] \quad (2)$$

where  $\Gamma_L$  and  $\Gamma_R$  are coupling functions, which are the imaginary parts of the left and right self-energies, describing the coupling at left and right electrodes, respectively. The current flowing from the left electrode to the right electrode can be calculated via the Landauer formula [11]

$$I(V) = \frac{2e}{h} \int_{\mu_{\min}}^{\mu_{\max}} dE (f_L(E, V) - f_R(E, V)) \cdot T(E, V) \quad (3)$$

where  $f_L(E, V)$  and  $f_R(E, V)$  are the Fermi–Dirac functions for left and right electrodes under the bias voltage  $V$ .

## 3 Results and Discussion

Transmission function (TF) and density of states (DOS) of the system shown in Fig. 1 were calculated by using combined DFT--NEGF’s approach Transiesta. Fig. 2 shows the overall DOS (solid green line) and TF (dashed red line) of surface and molecule atoms under zero bias. Fermi level ( $E_f$ ) is labeled by red solid line in the middle of the figure. The DOS near  $E_f$  is mainly contributed by  $\pi$  electrons of thiolated borazine, while the DOS from surface Au atoms should be located much below of  $E_f$ . The TF is mainly characterized with a broaden feature due to coupling with the gold electrodes. This also causes that the peaks of DOS are a little shifted from those of TF.

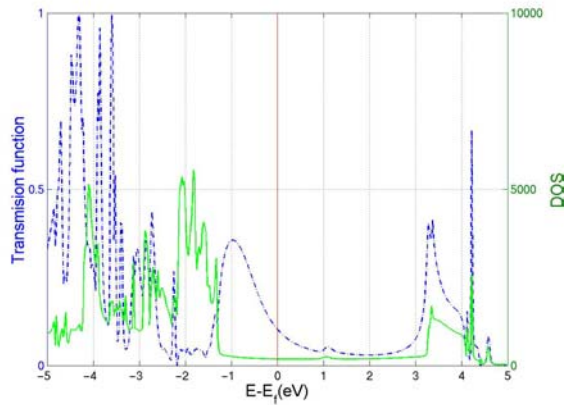


Fig 2. Density of states and transmission function under zero bias voltage.

The transmission is dominated by the HOMO, located at the first peak below the Fermi level  $E_f$  in the Fig. 2. The LUMO is located at the peak  $3.2eV$  above  $E_f$  and is farther away from  $E_f$  and thus does not significantly contribute to the current in small bias range. HOMO is the first level to be reached by electrons from the electrodes as the applied bias voltage increases. Therefore, the shape of TF and states at the HOMO determines the conduction at low bias.

The current is obtained using the Equ. (3). The energy region  $\mu_{min}--\mu_{max}$ , which contributes to the current integral, is from  $E_f - eV_{bias}/2$  to  $E_f + eV_{bias}/2$ . Since the current is the integral of the TF, it is strongly associated with the TF behavior. Fig. 3 shows the I-V characteristics in the bias ranging from 0 to 3.4V. It shows nonlinear characteristics with a NDR feature.

The conduction directly depends on the energy levels from molecular orbitals separation from the  $E_f$  of the electrodes, while the slope in the I-V curve depends on the delocalized nature of these orbitals. The more delocalized the orbitals, the higher the slope of its I-V curve. The full electronic delocalization of the HOMO is responsible for the current peak in the I-V characteristics at around 1.6V.

On the other hand, the electric field induced by the bias voltage strongly affects the DOS and transport properties at the HOMO and its neighbor levels. Fig. 4 shows the TF for different bias voltages in the range 1.0V-3.2 V. The HOMO located at around 1.0V in Fig.2 is shifted to  $E_f$  and the magnitude of TF through HOMO decreases with bias voltage increase. The neighboring orbitals located at lower energy levels are also shifted to  $E_f$  but the TF magnitudes at lower energy levels increase. In other words, the peak of transmission coefficients shifted to the lower energy levels from

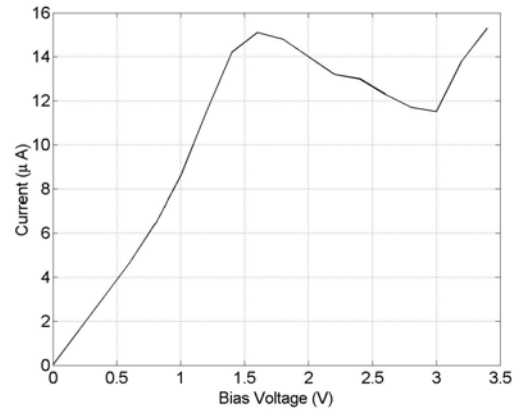


Fig 3. Current-voltage curve of gold sandwiched thiolated borazine

higher energy levels with bias increase.

These effects are responsible for the high current slope between 1.0-1.4V and the NDR feature observed between 1.6V and 3.0V in Fig. 3. When bias increases to 1.0V, transmission takes place partially through HOMO. The HOMO can not be fully accessible for conduction till 1.6V bias voltage. As a result, the slope of current increases from 1.0V bias to 1.4V and the current increases till bias of 1.6V. When bias increases above 1.6V, the magnitude of TF through HOMO and nearby orbitals continue to decrease. The coupling of the HOMO states of the molecule to the electrodes becomes worse as bias continue to increase. The LUMO will not be accessible yet. These result that the slope of current becomes negative and lead to the negative differential resistance feature. At the same time, when bias continue to increase the transmission at lower energy levels increases as showed at the left in Fig. 4. These orbitals can not be accessed at lower bias. However when bias exceeds 3.0V, they can be

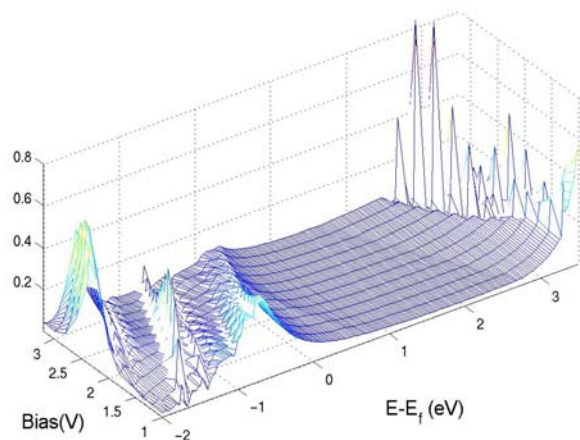


Fig 4. Transmission function under different bias voltages.

accessible gradually. This leads to the increase of current again and ends the NDR region.

The mechanism of NDR appeared in the STM experiments [2] could help to understand the NDR further in our case. Narrow features in the density of states can be found if the tip is in the atomic scale in STM experiments. When the tip is near the sample surface, the narrow tip DOS feature can be tuned to align with localized states of the sample by the bias potential. Therefore, the tunneling current is low at small bias before the alignment; at a larger bias when alignment occurs the current becomes high; and it becomes low again at even higher bias when the DOS feature of the tip is off alignment. In our case, the states related to HOMO are partially then fully localized with bias increase from zero to 1.6V and the DOS features become worse when bias continue to increase. This is the same scheme as pre-alignment, alignment and off-alignment in the STM experiments.

## 4 Summary

We have investigated quantum transport properties of thiolated borazine sandwiched between gold (111) surfaces using *ab initio* technique which is based on DFT and NEGF's. Nonlinear I-V characteristics with a NDR region are observed for thiolated borazine. The current flow through borazine is directly associated with the transmission spectrum which is mainly caused by the density of states raised from  $\pi$  electrons. HOMO is believed to be mainly constructed by  $\pi$  orbitals of thiolated borazine and has dominant contributions to the electron transport. The transmission spectrum is changed with applied bias. When bias increases, the peak of transmission spectrum located HOMO moves to the Fermi level and its magnitude decreases. This leads to NDR behavior within bias of 1.6V-3.0V. The mechanism of reported NDR can be further understood through that established in the atomic scale STM measurement in which NDR results from the narrow features in the density of states. This theoretical study of thiolated borazine leads us to conclude that a variety of molecules could be studied with *ab initio* methods in order to design molecular electronic devices with specific properties.

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