Analysis and comparison of electrical characteristics for a single molecule wire with different electrode materials

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***Abstract*—In this paper, electrical characteristics of a phenyl dithiol molecule bridging between two electrodes of Pt are calculated and compared with a single molecule bridging between two electrodes of Au. The metal electrodes holding the same molecule have different transmission profiles, thereby leading to varying I–V characteristics. We use a simple model to analysis the I-V characteristic and investigate that the molecule with pt electrodes has higher current than that of with Au.**

***Keywords*—molecular electronics, single molecule devices, Fermi level, electrical characteristics.**

I. INTRODUCTION

The continuous miniaturization of electronic devices may ultimately require the use of single molecules or atoms as electronically active elements in a variety of applications [1]. Connecting a molecule as a bridge between two conducting electrodes is one of the fundamental challenges involved with the study of electron transport through molecular junctions. In recent years, the transport properties of single molecule systems (composed of a molecule bridging between metal electrodes), such as current-voltage (I-V) characteristics have been extensively studied due to their potential use as active components of unconventional and novel electronic devices. Some molecules can operate as diodes, wires, Coulomb blockade structures, or switching devices with high negative differential resistance at room temperature. So the investigation of electron transport in a single molecule junction is essential to the development of molecular electronics [2]. It is well known that such transport properties are very sensitive to the constituent materials. The chemical interaction between the molecule and the electrode is likely to modify the molecule's profiles such as electrostatic potential, electron density, and concomitantly the molecular energy levels or the barriers within the electrode and molecule junction.

So one of the most critical issues hindering the development of reliable devices is the lack of detailed understanding of the nature of the electrode–molecule interface and its role in modulating the conducting characteristics of the molecule placed between the metal electrodes Therefore, it is useful for future research to organize the dependence of the transport properties on constituent materials [3].

Since Aviram and Ratner suggested the possibility of using a single molecule as a rectifier, Reed et al first measured the current-voltage characteristics of the dithiol benzene system self-assembled to the Au electrodes, and further advances have been achieved. Theoretical approaches have also been exploited. Such as tight binding models (TB), and density functional theory (DFT) based calculations [4].

From the first-principles calculations, it is clear that the chemical nature of the metal electrodes may have strong effect on the conductance of a molecular junction. Hence, in studying the electron transport properties through a single molecule, it is important to design an appropriate molecule-electrode contact, because the contact plays a decisive role on the electron transport process through the molecule [5,6].

In the simple tunneling model, the conductance of the single molecular junction depends on the extent of the hybridization, energy difference between the molecular and metal orbitals and the local density of states of the contact metal atoms at the Fermi level. An effective hybridization and a small energy difference between the molecular and metal orbitals and large ρ of the contact metal atoms are essential for the single molecular junction to achieve high conductivity. Au is known to make good chemical contact with the thiol end groups but the ρ of Au is relatively low because of its *sp* state characteristics. Therefore, the Au–S bond is not always the best anchoring group for the single molecular junction with high conductivity. It is important to develop a pair of metals group other than Au–S to establish highly conductive single molecular junctions [6].

In this study, we compare the effects of Au and Pt electrodes on molecular electronic wires. Au is the most popular electrode material in molecular electronics. While a variety of organic molecules have been chosen by different research groups, the metal electrodes have been focused on Au, as its clean surface can be easily prepared which is essential for the formation of self-assembled monolayers (SAM). Also Au electrodes can be

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readily connected to a device molecule by gold thiol self-assembly.

A narrow 5d band is located at E_F for Pt. Thus, the ρ is high for Pt. The increase in the conductance could be expected for the single molecular junction with Pt electrodes [6].

A number of theoretical models have been developed for calculating the I-V characteristics of molecular wires using semi-empirical [7-9] as well as first principles theory [10-13]. In this paper we use an intuitive and downright explanation for the observed I-V characteristics of a single molecule bridging between two contacts, using simple models to illustrate the basic physics. In general, the tunneling current through a molecular junction depends on the electronic structure of the junction in the vicinity of the Fermi level.

In this paper it was shown that junctions with different metal electrodes result in qualitatively different conduction characteristics.

II. METHODOLOGY

Figure 1 shows the configuration outline of a single molecule wire bridging between two electrodes and scetched in ADF tool. The conductive channel is phenyl dithiol molecule which consists of a phenyl ring with thiol (-SH) end groups ($C_6H_4S_2$). This end group can attach easily to metal surfaces allowing the molecule to function as a nanoelectronic interconnect.

The first step in understanding the current (I) vs. voltage (V) curve for a molecular conductor is to draw an energy level diagram and locate the Fermi energy.

A molecular channel must have an energy spectrum which is separated into three bands at the beginning state. The valence band of an inorganic semiconductor corresponds to the highest occupied molecular orbital (HOMO), while the lowest unoccupied molecular orbital (LUMO) represents the conduction band (the difference between the energy levels of the HOMO and LUMO) [14].

A number of authors have performed detailed calculations to locate the Fermi energy with respect to the molecular levels for a phenyl dithiol molecule bridging between two contacts, but there is considerable disagreement. Different theoretical groups have placed it close to the LUMO or to the HOMO. The density of states inside the HOMO-LUMO gap is quite small making the precise location of the Fermi energy very sensitive to small amounts of electron transfer, a fact that could have a significant effect on both theory and experiment. As such it seems justifiable to treat E_f as a "fitting parameter" within reasonable limits when trying to explain experimental I-V curves [15].

The band gap energy is wide enough so that no electron receives thermal effect. Without applying a voltage, the beginning energy level distributed so that, the Fermi level is in middle of the band gap [15]. As shown in figure 2 the supply voltage $V \neq 0$ leads to the electrochemical potential difference $\mu_1 - \mu_2 = eV$ between electrodes.

Contact 1 would like to see $f_1(\varepsilon)$ and contact 2 would like to see $f_2(\varepsilon)$ electrons occupying the state, where f_1 and f_2 are the contacts Fermi functions. The average number of electrons N at steady state will be some number intermediate between $f_1(\varepsilon)$ and $f_2(\varepsilon)$. The steady-state current per spin is determined by:

$$I = 2\frac{e}{h}\frac{\Gamma_1\Gamma_2}{\Gamma_1+\Gamma_2}(f_1(\varepsilon)-f_2(\varepsilon)) \quad (1)$$

The strength of coupling of the molecule to the contacts is important in determining the current flow. The stronger the coupling, the larger the current. A useful quantitative measure of the coupling results from broadening Γ of the molecular energy levels. This broadening Γ can also be related to the time that τ takes for an electron placed in that level to escape into the contact ($\Gamma = \hbar/\tau$). In general, the broadening Γ, could be different for different energy levels. Also it is convenient to define two quantities Γ_1 and Γ_2, one for each contact, with the total broadening $\Gamma = \Gamma_1 + \Gamma_2$ [15].

Eq 1 is the current I without charging effects. For including this effects, potential U_{SCF} added due to the change in the number of electrons from the equilibrium value ($f_0 = f(\varepsilon_0, E_f)$) [15].

$$U_{SCF} = U(N - 2f_0) \quad (2)$$

Where the level ε shifts up or down by this potential:

$$\varepsilon = \varepsilon_0 + U_{SCF} \quad (3)$$

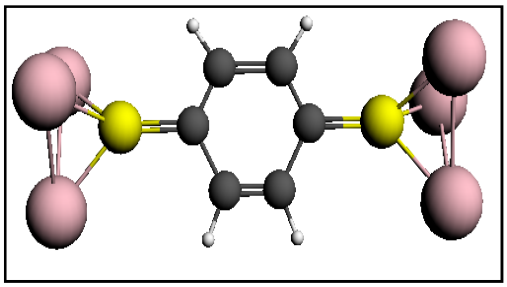

Figure 1. Schematic structure of a single phenyl dithiol molecule bridging between two electrodes (Au or Pt).

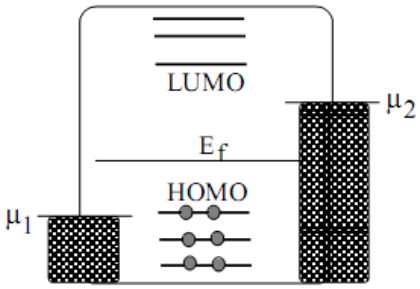

Figure 2. Energy level diagram of a metal molecule-metal structure when contact 1 is positively biased. When a positive voltage V is applied externally to the drain with respect to the source, then the drain has an electrochemical potential lower than that of the source by eV : $\mu_2 = \mu 1$-eV.

In the conductive channel, the energy spectrum is expanded to a band with density of state (DoS) denoted by D(E). For both spins over the energy level of ε we obtain Eq 4.

$$D_{\varepsilon}(E) = 2\frac{\frac{\Gamma}{2\pi}}{(E-\varepsilon)^2 + (\Gamma/2)^2} \quad (4)$$

The number of electrons (N) and the current (I) show the energy level with extended effect [14]. The related equations for I and N can obtain from Esq. 3,4.

$$N = 2\int_{-\infty}^{\infty} dED(E)\frac{\Gamma_1 f(E,\mu_1) + \Gamma_2 f(E,\mu_2)}{\Gamma_1 + \Gamma_2} \quad (5)$$

$$I = 2\frac{e}{h}\int_{-\infty}^{\infty} dED(E)\frac{\Gamma_1\Gamma_2}{\Gamma_1 + \Gamma_2}(f(E,\mu_1) - f(E,\mu_2)) \quad (6)$$

III. RESULTS AND DISCUTION

In this section, the result of simulating a single phenyl dithiolate molecule bridging between two Pt electrodes has been investigated and compared with the previous experimental [16] and simulation results of the Au electrodes. We use the ADF tool to calculate the energy levels of molecule.

The most important factor in determining the conductance of a molecular wire is the location of the Fermi energy of metallic contact relative to the energy levels of molecule (HOMO and LOMO) and the extent of the hybridization and energy difference between the molecular and metal orbitals.

In our simulation, the applied voltage between two contacts is 4V and $\Gamma_1 = \Gamma_2 = 0.2$.

As shown in figure 3, current through the molecule bridging between Pt electrodes is larger than that of a molecule bridging between Au electrodes. We find in figure 4 that platinum-contacted molecules would exhibit even higher conductance than Au-contacted molecules.

It was mentioned in Ref [17] that Hitachi Advanced Research Laboratory (Japan) indicates that PDT molecular wire junctions based on Pt electrodes can also be easily formed, therefore pt electrodes can use practically as the electrodes of molecular junctions.

The higher conductance is the result of smaller difference between the Fermi level and molecule (HOMO-LOMO) level for Pt. Figure 6 shows the density of states for the PDT molecule with Au and Pt electrodes. As shown in figure 5 and 6 the difference between the Fermi energy and nearest molecule level in the molecule with Pt electrode is smaller than Au. In other words, Pt has a higher density of states in the adjacency of the Fermi level than Au.

The Fermi energies used in this simulation were E_f=-5.3 eV for Au and E_f=-5.9 eV for Pt.

The experimental results [16] of current-voltage characteristic for Au electrod is similar to the simulation results in figure 3.

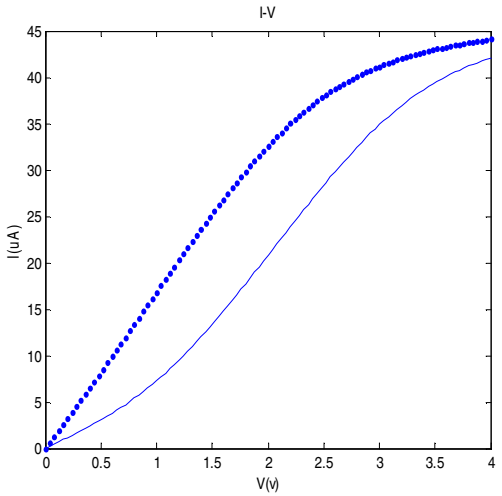

Figure 3. Current-voltage (I-V) characteristic of a phenyl dithiolate molecule bridging between two: a)Au electrodes (solid lines). b) Pt electrodes (dashed lines). The current for molecule with Pt electrodes is higher than with Au.

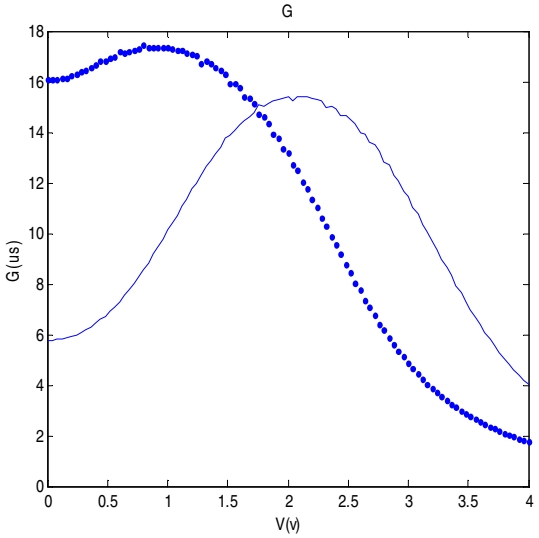

Figure 4. Conductance of a phenyl dithiolate molecule wire bridging between: a) Au electrodes (solid lines), b) Pt electrodes (dashed lines)

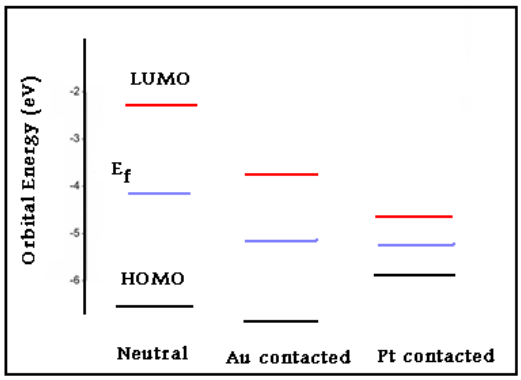

Figure 5. Comparison of the energies of HOMO and LUMO levels of the neutral gold-,and platinum-contacted molecules. The Fermi energy (E_F) is the average of the HOMO and LUMO energies.

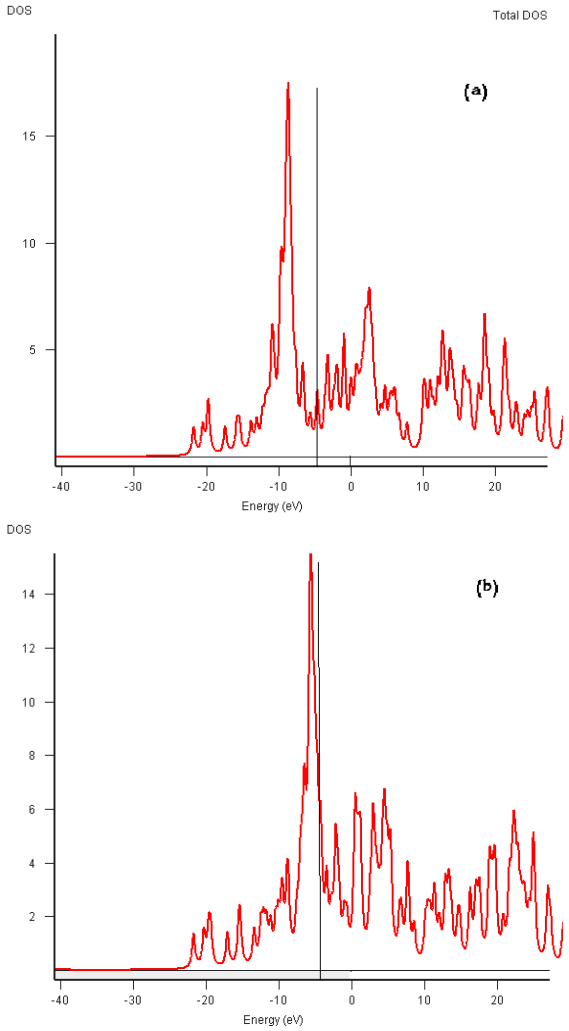

Figure 6. Density of states for a single PDT molecule between: a)Au electrodes, b) Pt electrodes. Pt has a higher density of states in the adjacency of the Fermi level than Au

IV. CONCLUSION

It is obvious from the results that Pt makes better electrodes than Au metals, due to a closer positioning of the transmission resonance to the Fermi level. So the current and conductance of a molecule with Pt electrodes is mainly larger than that of a molecule with Au electrodes.

In this paper we investigated that changing the electrode material, would efficiently improve the characteristics of a metal–molecule-metal junction.

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