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Effect of electrode materials on transport properties of asymmetric biphenyl molecular junctions

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ABSTRACT

We analyze the effect of electrode materials Y (Y=Ag, Cu, and Pt) on electronic transport properties of asymmetric biphenyl molecular junctions using first-principles calculations. To introduce coupling asymmetry in these junctions, one end of the biphenyl molecule is terminated by conjugated double thiol (model A) and single thiol (model B) anchoring groups, while the other end is terminated by Cu atom. We reveal that, for Ag and Cu electrode, conjugated double thiol exhibit stronger rectifying performance in contrast to nonconjugated single thiol group. Further, when the molecule is connected to the Pt electrode through single thiol and Cu atom, multifunctional behavior with excellent rectifying performance and clear negative differential resistance (NDR) are observed for the first time. The present results will pave a new roadmap for designing functional molecular devices.

1. Introduction

Rapid development and growing popularity of silicon-based integrated circuits have attracted the scientific community viz. academic researchers and engineers to miniaturized electronic devices. In recent years, a wide range of nanometer-scale electronic devices have been developed that provide various fascinating properties, such as electronic switching [1], molecular rectification [2–4], negative differential resistance (NDR) behavior [5,6], and single-electron characteristics [7]. In particular, the molecular rectifier, first proposed by Aviram and Ratner [2] is the basic functional element for building an electronic circuit. In the near future the multifunctional molecular devices, which show rectification, NDR, and switch behavior simultaneously [8,9], have the potential to further improve the integration density of molecular circuits.

It is well known fact that contacts asymmetry has significant impact on transport properties of molecular junctions [4,10–13]. Rectification was reported for dithiocarboxylate ($-CS_2$) [12,13] anchoring group that have two thiols connected to one end of the Au electrode whereas a single thiol ($-SH$) group is connected to the other. Wang et al. [14] reported that symmetric metal–molecule connection through Cu anchoring groups produces weak coupling than that of thiol anchoring groups. Moreover, such weak coupling of Cu enhances the rectifying performance of molecular devices when asymmetrically connected to thiol groups [15].

However, the studies were carried out on Au electrodes, as it can be simply fabricated by using self-assembled monolayers (SAMs), due to its clean surface [16]. In practicality, real life applications desire the junctions to be easily integrable as well as reliable and should show stability at room temperature. Nijhuis et al. [17] investigated SAM-based molecular junctions using Ag electrodes, and observed rectification effects at room temperature. Recently, it is reported that Cu electrodes are a better choice for replacing Au electrodes in rectification devices [18,19]. In fact, molecule–copper contact provides high device yield and good junction reproducibility [20,21]. Among different noble metals, we believe that Pt electrode is a good choice for investigation due to the following reasons: Firstly, Pt electrodes fabricated by using a self-breaking electromigration method, shows long-term stability at room temperature [22]. Secondly, the conductance of a single-molecule connected to the Pt electrodes is higher than that of the Au electrodes, due to a narrow 5*d* band located at the Fermi level [23]. These properties motivated us to investigate the transport properties of a biphenyl molecule with different interface anchors for Ag, Cu, and Pt electrodes.

2. Model and computational method

The modeled molecular junction configurations are depicted schematically in Fig. 1. Models A1–A3 and B1–B3 correspond to Ag, Cu, and Pt electrodes (illustrated with wire boxes), respectively. The junction system was divided into three regions: the left electrode, the

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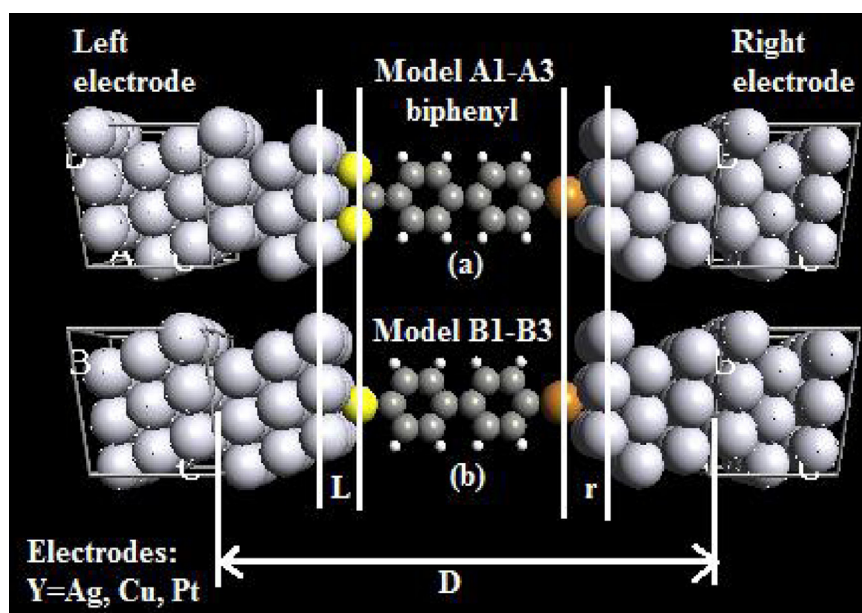
Fig. 1. (Color online) Structure of a biphenyl based molecular devices where models A1–A3 and B1–B3 correspond to Ag, Cu and Pt electrodes, respectively. (a) The molecule is connected to the electrodes via dithiocarboxylate (–CS$_2$) anchoring group and Cu atom, (b) the (–CS$_2$) is replaced by a thiol (–SH) group.

right electrode and the central scattering region. The central region also contained parts of the electrodes so that the screening effect could be included in the calculations. The most common Y (1 1 1) surface [24,25] was used with (3 × 3) periodic boundary conditions. For model A, biphenyl molecule with conjugated double thiol (dithio-carboxylate) group was connected to Y electrode on the left side and Cu atom connected to Y on the right side. For model B, dithiocarboxylate (–CS$_2$) was replaced with a single thiol (–SH) group. Here, L is the optimized distance from the surface of the left electrode Y to the left end group and r is the distance from the right end group to the surface of right electrode Y. Moreover, D is the distance between left and right electrodes. For models A1–A3, the distance L are found to be 2.0, 2.0, 2.81 Å and r becomes 1.77, 1.74, 2.0 Å. For models B1–B3, L and r become 1.67, 1.55, 1.61 Å and 1.74, 1.74, 2.0 Å respectively.

Geometry optimization and transport property calculations were carried out by using an ab-initio package ATK-VNL [26], which combines self-consistent density functional theory (DFT) and none-quilibrium Green's functions (NEGF) formalism. The current through the device was calculated using the Landauer–Buttiker formula [27,28]. For calculations, we used Troullier–Martins nonlocal pseudo-potential to describe the atomic core and Perdew–Zunger local density approximation (LDA) for the exchange–correlation functional. For metal atoms, electron wave function was expanded in double zeta plus polarization (DZP) basis set, while for other atoms, single zeta plus polarization (SZP) was used. The geometry optimizations ended when the residual force on each atom was less than 0.05 eV/Å. To obtain a good balance between computational time and accuracy of the results, a cutoff energy of 150 Ry and k-mesh of (1 × 1 × 150) were used. The NEGF/DFT self consistent calculations were controlled by a numerical tolerance of 10^{-5}.

3. Results and discussion

3.1. I–V Characteristics

The current–voltage (I-V) curves for models A1–A3 and B1–B3 are shown in Figs. 2 and 3(a) respectively. For models A1 and A2, the current under the positive bias region is higher than that of same negative bias over the whole bias region. While for

model A3, an increase in current occurs at a higher positive bias voltage (+1.6 V) and then it shows a weak negative differential resistance (NDR). The asymmetry of the I–V curve is illustrated in Figs. 2 and 3(b) by the rectification ratio, which is defined as $R(|V_b|) = I(+|V_b|)/I(-|V_b|)$. For models A1 and A2 stronger rectifying performance are observed as compared to model A3. For example, the value of rectification ratio reaches 2.7 at around 1.0 V for both models A1 and A2 while only 1.89 at 2.0 V for model A3. Moreover, for A3, $R_{max}(|V_b|) < 1$ when the bias voltage is between ∼0.5 and ∼1.4 V.

In comparison with models A1 and A2, models B1 and B2 having a single thiol group, reduces the metal–molecule coupling and thus show weak asymmetry in I–V curve, as shown in Fig. 3(a) and (b). This indicates that conjugated double thiol (dithiocarboxylate) induces a stronger rectifying performance than nonconjugated single thiol group due to increase in interface coupling in biphenyl molecular devices. Zhao et al. [13] also employ additional thiol groups to enhance the electronic coupling and found enhanced rectifying behavior in porphyrin-based molecular junctions. Furthermore, for model B1, the current under negative bias is higher than the positive bias voltage in the entire bias range considered. Model B3, however, displays a dramatic increase in current till the bias voltage reaches +0.6 V and then exhibit NDR under positive bias voltage. It concludes that Model B3 manifests multifunctional behavior, which exhibit the excellent rectifying performance (the maximum rectification ratio is 10.1) and clear NDR at +0.6 V. Our proposed device has a wide range of applications including high-speed switches, high frequency oscillators, amplifiers, logic, as well as, has the potential to improve the integration density of molecular circuits in the near future.

3.2. Transmission spectra under zero bias

The transmission spectra of all the models at zero bias are shown in Fig. 4(a) and (b). The average Fermi level, which is the average value of the chemical potentials of the left and right electrodes, is set to zero. The first transmission peak that appears below and above the Fermi level are assigned to the conduction properties through the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) state of models respectively. In case of A1