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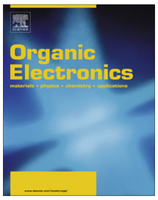

Altering regularities on resistances of doped Au–alkanedithiol–Au junctions

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ABSTRACT

The electronic transport properties of alkanedithiol molecular junctions doped by boron (B) or phosphorus (P) on different sites are investigated by using the non-equilibrium Green's function method combined with the density functional theory. Results show that B or P doping can decrease the resistances of alkanedithiol molecular junctions obviously and the direct-current conductance becomes stronger gradually when doped sites vary from side to center. Namely, the B or P doped effects are not uniform which are sensitive to its doped sites. Interestingly, significant negative differential resistance behaviors are only found in B-doped molecular junctions and peak-to-valley ratios are also sensitive to the B doped sites.

1. Introduction

To overcome the increasing difficulties and fundamental limitations on the miniaturization of the semiconductor industry, the functional devices based on the single molecules have been proposed as potential building blocks for future nanoelectronic systems. For achieving this aim, the scientists do their best to fabricate the various functional molecular devices such as rectifier [1–3], switch [4–6], negative differential resistance (NDR) [7–9], field-effect transistors [10,11], and spin filter [12–14]. On the other hand, the fundamental studies on transport properties of simple molecular structure including nanowire, nanosheet, nanoribbon, nanotube also attracted much attention [15–18]. Because the studied conclusions can help us explore the mechanisms of the above functional molecular devices and do better in future nanoelectronic industry.

Although a mass of exciting achievements have been made, there are still a number of challenges in researching of the molecular device. First of all, exact measurement of conduction at the single molecule level is still an extremely difficult task due to the lack of the uncontrollable experimental details. So far, one of successfully measured systems is the alkane molecular junction who can be thought of as being a model of molecular wire and is important to the research field of molecular electronics. Such a device is becoming even more interesting because different laboratories reported transport data that were quantitatively consistent with each other [19–21]. In addition, theoretical researchers also do their utmost to explore the effects of length, end groups, bonding sites, and interface states on the transport properties of alkane molecular junction [22–24]. The same conclusion was obtained from the above experimental and theoretical works: the resistance of alkane molecule is enormous. In other word, the alkane molecule is not a good conductor which limits its potential as a lead in future molecular integrate circuit greatly.

How to enhance the electronic transport ability of alkane molecular junction with minimal damage on its structure? Chemical doping with foreign atoms should be the most suitable way [25,26]. For instance, boron atom

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doping or nitrogen atom doping can effectively modulate the electronic transport properties of Au–C_{60}–Au junction and make the intrinsic NDR behavior disappear [27]. For the graphene nanoribbons, the hybridization of boron nitride nanoribbon can transform it from insulator to metal realized by changing the unit number of zigzag graphene nanoribbon [28]. The doping of boron atom and phosphorus atom on silane chain can also induce the above phenomenon [29]. Therefore, with an aim to enhance the electronic transport ability of alkane molecular junction, we theoretically study the transport properties of alkane molecular junctions doped by boron atom or phosphorus atom in this paper.

2. Model and computational details

The molecular devices are illustrated in Fig. 1. In order to focus on the role of the doped site, we choose the centrosymmetric heptane as a studied candidate of alkane molecules. The calculated configurations used in our transport studies correspond to the structures in the experiment which the molecule bonds to the pyramidal gold electrodes through two sulfur atoms [19].

The first-principles transport calculations for a two-probe system are performed using the non-equilibrium Green's function (NEGF) method combined with the density functional theory (DFT) [30,31]. The exchange–correlation potential is described by the local density approximation (LDA), which works rather well for light elements and systems where electrons are delocalized. Single-zeta plus polarization (SZP) basis set for Au atoms and double-zeta plus polarization (DZP) basis set for other atoms are adopted. The criterion of convergence in the NEGF/DFT self consistent calculations is 10^{-5} and the number of energy-points used for the integration to calculated the current is 200. The Hamiltonian, overlaps, and electronic densities are evaluated in a real-space grid defined with a plane wave cut-off of 150 Ry to achieve a balance between calculation efficiency and accuracy. The geometries are optimized until all residual force on each atom is smaller than 0.05 eV/Å. The optimized C–B and C–P bond lengths are 1.559 Å and 1.781 Å which are a little longer than C–C bond length. Therefore, the changes of alkane's structure induced by B or P doping are very small as compared with the other modulated methods.

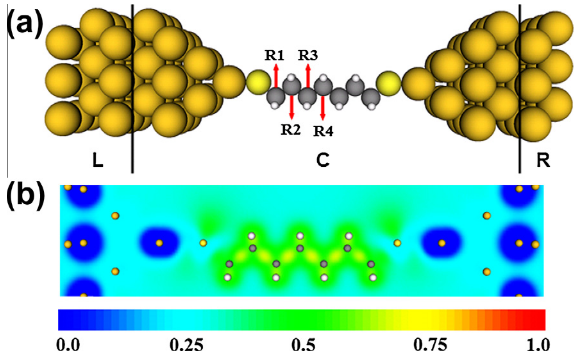

Fig. 1. (a) Schematic diagram of a two-probe junction, where *L*, *R*, and *C* correspond to the left electrode, right electrode, and center scattering region which contains a portion of electrodes to screen the perturbation from the central molecule. The R1, R2, R3 and R4 are four different doped sites varying from side to center on the heptane molecule. (b) Electrostatic potential distribution of the undoped heptanedithiol molecular junction.

The nonlinear current through the contact is calculated using the Landauer formula:

$$I(V_b) = \left(\frac{2e}{h}\right) \int_{\mu_L}^{\mu_R} T(E, V_b) dE, \tag{1}$$

where $\mu_{L/R}$ are the electrochemical potentials of the left and right electrodes [32]. With the applied bias potential V_b, the difference in the chemical potentials are given by eV_b, and we use $\mu_L(V_b) = \mu_L(0) - eV_b/2$ and $\mu_R(V_b) = \mu_R(0) + eV_b/2$. The transport coefficient $T(E, V_b)$ as a function of the energy level E at a certain bias V_b can be calculated using the well-known formula:

$$T(E, V_b) = Tr[\Gamma_L(E) G^R(E) \Gamma_R(E) G^A(E)], \tag{2}$$

where $G^R(E)$ and $G^A(E)$ are the advanced and retarded Green's functions respectively, and $\Gamma_{L,R} = i(\sum^R_{L,R}(E) - \sum^A_{L,R}(E))$ is the coupling functions of the conductor to the left and right electrodes, $\sum^R_{L,R}(E)$ and $\sum^A_{L,R}(E)$ are the self-energy matrices used to include the effect of the left (right) semi-infinite electrode, which is explicitly include in the Kohn–Sham calculation for the extended molecule system.

3. Results and discussions

Fig. 2a shows the *I*–*V* characteristic of the undoped heptanedithiol molecular junction in the range from 0.0 V to 2.0 V. From the figure, we can see that the current increases with the bias linearly and the magnitude of the current value is nanoampere. That means the direct-current conductance of the alkanedithiol molecular junction is very small and it is not a suitable candidate of electronic leads in future molecular integrate circuit. The values of our calculated current are higher than the measured data of octane and lower than the measured data of hexane in the experiment which confirm the accuracy of our calculations [19]. The poor conductance of the alkanedithiol molecular junction can be explained from its transmission spectrum in Fig. 2b. The Fermi energy of the junction defines the zero of energy. It can be seen clearly that the average transmission coefficient is very small and two short transmission peaks are far from the Fermi energy. Therefore, the electrons in the Au electrode are very difficult to pass through the heptanedithiol molecular junction and become the conduct current.

The *I*–*V* curves of doped heptanedithiol molecular junctions are shown in Fig. 2c and d. For simplicity, the system after doping is named as the type of dopant and its doping sites. The systems with substitutional boron or phosphorus atoms at site R1–R4 are denoted as the B1–B4 or P1–P4 systems. From the figures, we can see the currents increase obviously when one carbon atom is replaced by one B atom or one P atom. Furthermore, the increased magnitudes of current are sensitive to the doped sites and show a strong regularity. While the doped sites on the heptanedithiol