Negative differential resistance and switch behavior of T-B_xN_y (x, y=5, 6, 11) molecular junctions

Shi-Liang Wang, Chuan-Lu Yang*, Mei-Shan Wang, Xiao-Guang Ma, and Jian-Guo Xin

School of Physics and Optoelectronics Engineering, Ludong University, Yantai 264025, the People's Republic of China

ABSTRACT: The electronic transport properties of T-B_xN_y (x, y=5, 6, 11) molecular junction are investigated based on first-principle density functional theory and non-equilibrium Green's function method. Strong negative differential resistance (NDR) behavior is observed for T-B₅N₆ molecule under negative and positive bias voltages, with an obvious switch effect for T-B₆N₅. However, only small NDR is shown for the complex of the two molecules. The projected device density of states, the spatial distribution of molecular orbitals, and the effect of transmission spectra under various bias voltages on the electronic transport properties are analyzed. The obvious effect of bias voltage on the changes in the electronic distribution of frontier molecular orbitals is responsible for the NDR or switch behavior. Therefore, different functional molecular devices can be obtained with different structures of T-B_xN_y.

1. INTRODUCTION

Boron and nitrogen are neighbors of carbon in the periodic table and have many similar properties to carbon. Boron nitride (BN) is a non-oxidative ceramic material, which is an isoelectronic system as to C₂ and has a similar crystal structure to the carbon of simple substance phase. The common BN includes hexagonal crystal structure (h-BN) and cubic crystal structure (c-BN) [1].

A series of cyclic 3D BN structures was recently proposed and was designated as T-B_xN_x (x = 4n - 1, n = 1, 2, 3...) by Zhang *et al.* [2]. They constructed bulk phase systems with optimization and lattice vibrational properties based on the T-B_xN_x unit and first-principle density functional theory (DFT). The structure exhibits intrinsic metallicity, although no

*Corresponding author. Tel: +86 535 6672870. E-mail address: ycl@ldu.edu.cn. (C.L. Yang).

metallic atom exists in the structure.

Inspired by the novel properties of the $T-B_xN_x$ unit, we construct several molecular junctions with 3D $T-B_xN_x$ unit, which are formed with orthogonal interlocking hexagons and Au electrodes. The sp^2 and sp^3 covalent bonds coexist in these 3D BN configurations, which display metallicity due to the electron-deficient feature of boron [2]. $T-B_5N_6$ and $T-B_6N_5$ units (represented with $T-B_xN_y$) exist in a $T-B_xN_x$ ($x=11$). The $T-B_xN_y-H$ ($x, y=5, 6, 11$) structures, in which the dangling bond was passivated by H, are also considered. We investigate the electronic transport properties of the $T-B_xN_y$ units, $T-B_xN_y-H$, and their complex structure to understand the change in the $T-B_xN_x$ structure and $T-B_xN_y-H$ as a molecular device. The curves of current–voltage ($I-V$) and the transmission spectra under different bias voltages are calculated. Obvious negative differential resistance (NDR) and switch behavior are determined and analyzed with transmission spectra and molecular projected self-consistent Hamiltonian (MPSH).

2. THEORETICAL MODEL AND CALCULATION DETAILS

In our calculation of molecular architectures, the $T-B_xN_y$ ($x, y=5, 6, 11$) and $T-B_xN_y-H$ ($x, y=5, 6, 11$) structures are optimized with the Dmol³ module in Materials Studio 6.0 [3]. The $T-B_xN_y$ ($x, y=5, 6$) structures are combined to build the $T-(BN)_{11}$ structure. The optimized $T-B_xN_y$ and $T-B_xN_y-H$ structures are located between two semi-infinite gold electrodes with (100) surface, as illustrated in Fig. 1. The ends of the molecules are attached to the top site of the electrodes via a thiol atom. The extended molecules or central scattering regions consist of the $T-B_xN_y$ molecule ($T-B_xN_y-H$) and the screen regions including four-layer gold atoms to consider the molecule–electrode-coupling and electrode-screening effects. In these screen regions, the electronic density and potential are calculated self-consistently to provide a smooth transition from the molecule to each electrode with bulk-like potential. Each semi-infinite gold electrode is simulated by a $3 \times 3 \times 4$ unit cell, and the bulk self-energy is calculated. The distance among the gold atoms is fixed to that of the bulk gold. The supercell is sufficiently large to avoid any interaction with molecules in the next supercell [4]. For convenience, the central $T-B_5N_6$, $T-B_6N_5$, and $T-(BN)_{11}$ molecules in Fig. 1 are represented by M1, M2, and M3, respectively.

The geometrical optimization of the extended molecules through the junctions is conducted by using DFT, and the electronic transport properties are calculated with the DFT combined with the non-equilibrium Green's function (NEGF) method [5, 6], in which the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) [7] is adopted for the exchange correlation potential. The GGA has been extensively used to explore the transport properties of molecular junctions [8–10]. A single- ζ -plus-single polarization atomic orbital basis set for the gold atoms and a double- ζ -plus-single polarization basis set for the other atoms are employed. We set the K-point to 5, 5, and 100 along the two vertical directions and the parallel direction of the electronic tunneling transmission, respectively. All calculations for the two-probe system are performed with the package Atomistix ToolKit [11].

In NEGF theory, the transmission function $T(E, V)$ of the system is a sum of transmission probabilities of all tunneling paths at energy E under external bias voltage V [12], as follows:

$$T(E, V) = \text{Tr}[\Gamma_L(E, V)G^r(E, V)\Gamma_R(E, V)G^a(E, V)], \quad (1)$$

where $G^r(E, V)$ and $G^a(E, V)$ are the retarded and advanced Green's functions of the central scattering region, respectively. $\Gamma_{L/R} = i[\Sigma_{L/R}^r(E, V) - \Sigma_{L/R}^a(E, V)]$ denotes the line width function. $\Sigma_{L/R}^r(E, V)$ and $\Sigma_{L/R}^a(E, V)$ represent the self-energy of the scattering, which includes the effects of the electrodes.

The tunneling current is calculated from the Landauer–Büttiker formula, as follows [12]:

$$I(V) = \frac{2e}{h} \int dE [f(E - \mu_L) - f(E - \mu_R)] T(E, V), \quad (2)$$

where $f(E - \mu_{L/R})$ and $\mu_{L/R}$ represent the Fermi distributions of the electrons in the left or right electrode and the chemical potential, respectively. $\mu_L = E_F + eV/2$ ($\mu_R = E_F - eV/2$), where e and V denote the elementary charge and the bias voltage, respectively. $E_F = \mu_{L/R}(0)$ is usually the Fermi level, and $[\mu_L(V), \mu_R(V)]$ is generally referred to as the bias window, in which the energy integral area contributes to the tunneling current.

3. RESULTS AND DISCUSSION

3.1 Characteristics of the molecular junctions

The I - V curves of the $T-B_xN_y$ molecular junctions are calculated in the bias voltages ranging from -2.0 V to 2.0 V, with a step of 0.1 V, and shown in Fig. 2. ~~The I - V curves of the $T-B_xN_y-H$ molecular junctions are shown in the Supplementary Information.~~ For the $T-B_xN_y$ molecular junctions, For the molecular junctions without the passivated H atoms, Fig.2(a) shows the curve of M1 is approximately symmetry about the origin of coordinate and demonstrates obvious NDR behavior [13–16]. The peaks of the current appear at approximately ± 1.3 V. The current is expected to be used to manufacture an oscillator because of the characteristics of the obvious peak and lower bias. The molecular junction of M2 shows obvious switch behavior. The electron can easily tunnel through the junction when the bias is higher than ± 0.5 V. This junction is a preferable switch molecular device for the low open voltage and the fast saturated current [17, 18]. The M3 junction, which is composed of M1 and M2 molecules, loses the characteristics of both M1 and M2. The I - V curve is not symmetrical with the origin of the coordinate, which is different from other molecular junctions [19]. Only weak NDR behavior is observed near 1.8 V. The light NDR of M3 with a small peak and a high voltage is less application in comparison with that of M1. For the I - V curve of $T-B_xN_y-H$ molecular junctions in Fig. 2(b), the magnitude of current with H-passivation is much less than that of the current without H-passivation. Compared with the $T-B_xN_y$ molecular junctions, the relative magnitudes of I - V of the three molecular junctions are similar. For brevity, we only further discuss the $T-B_xN_y$ molecular junctions.

3.2 MPSH eigenstates

We calculate the MPSH eigenstates for each junction to fully understand the various characteristics of the molecular junctions [20]. Fig. 3 demonstrates that the MPSH eigenstates and their orbit space distribution are remarkably affected by the molecular configuration. Under zero bias, the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) for M1 and M2 devices are completely delocalized, whereas they are localized for the M3 device bias. Thus, the tunneling current of M3 is much smaller than those of M2 and M1, as shown in Fig. 2.

We present the MPSHs of M1, M2, and M3 under different biases in Fig. 4. Fig. 4(a) shows that for the M1 junction, the HOMO is obviously delocalized in the bias range of 1.3 V

to 1.5 V, and the LUMO and LUMO+1 are also delocalized on most atoms, except a little on the left S atom for the LUMO and the right S atom for the LUMO+1. The energy gap between the HOMO and LUMO+1 is larger than the bias, which implies that both the HOMO and LUMO can but the LUMO+1 cannot contribute to the electron tunneling the junction. The HOMO is mainly responsible for the large current in the range of 1.3 V to 1.5 V. In the bias range of 1.9 V, the delocalized behavior of the HOMO disappears. By contrast, the weak delocalized behavior of the LUMO and LUMO+1 remains, the gap between the HOMO and LUMO+1 is smaller than the bias, and the energy gaps between the HOMO and LUMO and LUMO+1 are smaller than the bias; these phenomena result in small current in the M1 junction [21, 22]. The HOMO, LUMO, and LUMO+1 jointly lead to the strong NDR behavior of M1.

Fig. 4(b) demonstrates the MPSHs for the M2 junction. No obvious delocalization for the HOMO, but an obvious delocalization for the LUMO is identified when the bias is larger than 0.1 V. The negative bias shows similar behavior, which is omitted in the Figure for brevity. The energy gaps between the HOMO and LUMO are smaller than the corresponding bias. Therefore, the LUMO is the main contributor to the charge transport of M2 junction.

The MPSHs for M3 junction are presented in Fig. 4(c). The HOMOs exhibit obvious delocalization under -0.7 and -0.9 V and weak delocalization under -1.2 and $+1.8$ V, whereas no obvious delocalization is observed for all the LUMOs. Hence, the small currents that occur from -1.2 V to -0.7 V and near $+1.8$ V biases were caused by the HOMOs.

3.3 Transmission spectrum and projected density of states (PDOS)

We further calculated and analyzed the transmission spectrum and PDOS to fully understand the I - V characteristics of the molecular junctions. The results are presented in Fig. 5. For the M1 junction, we focus on the origin of the NDR behavior. The transmission spectrum in the left panel of Fig. 5(a) for the M1 junction shows that the magnitude of the peak in the bias window determines the strength of the current [12, 23]. For example, at the $+1.3$ V bias, the entire peak is in the bias window, which results in the largest current. We calculate the PDOS for the two parts of M1 junction, i.e., the left hexagonal BN (M1-L) and the right hexagonal BN (M1-R), under each bias to analyze the mechanism of the electron transport. The PDOSs of M1-L and M1-R are obviously different, and the transmission

spectrum is determined by the common part of the M1-L and the M1-R in the bias windows [24]. For example, at the +1.3 V, the PDOSs of the M1-L and the M1-R present similar magnitude and shape in the bias window. Therefore, the transmission spectrum is large. At +1.7 V, the PDOS of the M1-L is approximately the same as that at +1.3 V. However, the PDOS of the M1-R in the bias window is small, which results in a small transmission spectrum.

Fig. 5(b) demonstrates the transmission spectrum and the PDOS of M2 junction. The peak of the transmission spectrum approximately keeps the magnitude and shape in the bias window in the bias range from +0.1 V to +1.8 V. As a result, the current is large in the bias range, as shown in Fig. 1. Unlike the M1 junction, the PDOSs of M2-L and M2-R are almost the same, which are responsible for the large peak of the transmission spectrum in the bias window.

The transmission spectrum and the PDOS of M3 junction in Fig. 5(c) indicate that the peak begins entering the bias window at -0.3 V, and the height of the peak heightens along with the increase in the bias. Some of the peaks are beyond the bias window at +1.8 V and completely stay out of the window at +2.0 V. These changes are in good agreement with the I - V curve of M1 junction in Fig. 1. The results are presented in the left panel of Fig. 5(c). The right panel of Fig. 5(c) shows that the PDOSs of M3-L and M3-R are obviously different. The differences in the bias windows determine the transmission spectrum of the junction. For example, at +0.4 V, approximately half of the PDOS peak of M3-L was in the bias window, but the two peaks of M3-R are almost out of the window, thereby resulting in a small transmission spectrum. The smaller one of the PDOSs of the two components of the junctions determines their electron transport properties.

4. CONCLUSIONS

We calculate the electronic transport properties in orthogonal interlocking hexagonal BN molecular junction based on first-principle DFT and NEGF. The electronic transmission spectrum and I - V characteristics of three different junctions are obtained. The I - V curve of M1 junction shows strong NDR behavior, whereas a low bias switch effect is identified in the I - V curve of M2 junction. Only small and irregular I - V characteristics are obtained for the M3 junction. Therefore, M1 and M2 junctions are promising candidates for NDR or sensitive

switch devices. The transmission spectra of the junctions support the characteristics of I - V for all three junctions. Comparison of the transmission spectrum with PDOS indicates that the different PDOSs of the left and right components of the junctions are responsible for the various characteristics of the I - V curves.

Acknowledgments

This work was supported by the National Science Foundation of China (NSFC) under Grant Nos. NSFC-11374132 and NSFC-11574125, as well as the Taishan Scholars project of Shandong Province (ts201511055).

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Fig.1 Structures of the molecular junctions of T-B_xN_y ($x, y = 5, 6, 11$). The H-passivated structures are omitted.

(a)

(b)

Fig.2 Calculated I - V curves for $T-B_xN_y$ and $T-B_xN_y$ -H molecular junctions. (a) $T-B_xN_y$ (b) $T-B_xN_y$ -H.

Fig.3 MPSHs for M1, M2 and M3 molecular junctions at zero bias.

Fig.4 MPSHs for the considered molecular junctions. (a) M1; (b) M2 and (c) M3.

Fig.5 Transmission spectra and PDOSs of the left and the right components for the junctions. (a) M1; (b) M2 and (c) M3. The region between the red dashed vertical lines for each panel represents the bias windows at the corresponding bias voltage.