Organic Electronics 46 (2017) 150–157

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Large rectifying ratio in a nitrogen-doped armchair graphene device modulated by the gate voltage

Le Xie, Shi-Zhang Chen, Wu-Xing Zhou, Ke-Qiu Chen*

Department of Applied Physics, School of Physics and Electronics, Hunan University, Changsha, 410082, China

ARTICLE INFO

Article history:
Received 10 March 2017
Received in revised form
11 April 2017
Accepted 17 April 2017
Available online 19 April 2017

Keywords:
Electronic transport
Rectifying behaviors
Molecular device
Density-function theory
Non-equilibrium Green's function method

ABSTRACT

Using a combination of first-principles density functional theory and the non-equilibrium Green's function method, we have investigated the electronic transport properties of devices based on an orderly nitrogen-doped armchair graphene nanoribbon under gate voltages. The results show that the gate voltage strongly affects the electronic transport properties of the devices. Strong rectifying behavior is observed and it can be modulated by the gate voltage. The maximum rectifying ratio reaches the order of 10^6 at a specific gate voltage, which is two orders of magnitude higher than the device without applying a gate voltage. The mechanism for the rectifying behavior was investigated from the calculated transmission spectra, potential drop, and local device density of state. The results indicate that the devices regulated by the gate voltage can potentially be applied to high-performance rectifiers.

1. Introduction

Along with the recent progress in experimental fabrication technology, scientists have designed and built molecular devices in nanoscale. Many novel physical properties have been reported, such as field-effect characteristics [1–3], molecular rectification [4–7], negative differential resistance (NDR) [8–11], spin filtering [12,13], and magnetoresistance [14,15]. In particular, the rectifying behavior has attracted considerable attention, and it can be applied to logic circuits and molecular memory [16–18].

Graphene, as a two-dimensional (2D) carbon structure, has attracted extensive interest for applications in physics and material science owing to its unusual band structure [19–22]. In particular, graphene nanoribbons (GNRs) can be obtained by cutting graphene along a specific direction to give two types of GNRs, namely, zigzag and armchair GNRs (ZGNRs and AGNRs). All ZGNRs are metallic because of degeneration of the two edge states at the Fermi level without considering the spin freedom [20–22]. In contrast, AGNRs have no such localized state. However, it is interesting to note that the nanoribbon width determines whether AGNRs are metallic or semiconducting [23,24].

Several rectifiers based on GNRs have been reported. For example, Wang et al. [25] found that ballistic rectification can be achieved in a graphene heterojunction device constructed by connecting a ZGNR between two AGNR electrodes and applying an external gate voltage in the heterojunction region. Zeng et al. [26] investigated the electronic transport properties of AGNR systems and observed rectifying behavior by nitrogen doping the AGNR electrode. Deng et al. [27] reported the transport properties of trigonal graphenes with zigzag edges coupled to gold electrodes, where the vertex carbon atoms on the center were substituted by one nitrogen or boron atom bonded by a B–N pair. They found that the rectifying ratio can be controlled by the size of the device. Zhao et al. [28] observed obvious rectifying and negative differential resistance behaviors in nitrogen-doped AGNRs, and both behaviors were strongly dependent on the doping position. Yun et al. [29] found that the electron transport properties of ZGNR field effect transistors under bias and gate voltages and the gate potential can activate the device states, resulting in a boosted current. However, these reported molecular rectifier performances do not yet fully meet application requirements, and the rectification ratio needs to be improved. Hence, it is important to develop nanomaterials for high-performance rectifiers and determine ways to regulate the rectifying ratio.

The different properties of GNRs can be realized in various ways, such as chemical doping [30,31], chemical modification [32,33], and hybrid connection [34,35]. In particular, doping with nitrogen atoms is easy to implement in experiments by chemical vapor

* Corresponding author.
E-mail address: keqiuchen@hnu.edu.cn (K.-Q. Chen).

http://dx.doi.org/10.1016/j.orgel.2017.04.017
1566-1199/

deposition [36] or by NH_3 annealing after ion irradiation [37]. In the present work, we investigate the electronic transport properties of devices with orderly nitrogen-doped AGNR under various gate voltages using non-equilibrium Green's functions (NEGFs) in combination with density functional theory (DFT) [38]. The results indicate that rectifying behavior can be achieved in the AGNR devices by introducing an ordered nitrogen dopant chain in one of the electrodes, and the gate voltage plays an important role in the transport properties, resulting in a stronger rectifying effect. In particular, the maximum rectifying ratio can be increased from 10^4 to 10^6 by applying a specific gate voltage.

2. Models and computational methods

The molecular device based on the AGNR is shown in Fig. 1. The device is divided into three parts: the left electrode, the scattering region, and the right electrode. Each electrode is described by a supercell with two repeated carbon unit cells along the transport direction, and the scattering region is the AGNR with six unit cell length. The top-gate voltage [29], which is considered to be a local perturbation potential, is applied to the right half of the scattering region, which is perpendicular to the transport direction. Here, the edge carbon atoms of the AGNR are saturated by hydrogen atoms. The band gap of the AGNR shows three distinct width-dependent behaviors: $W = 3p$, $3p+1$, and $3p+2$ [21,24], where p is a positive integer. Several typical configurations with various ribbon widths and different nitrogen-doped positions are considered: W-AGNR-N(n, m), where W (= 6, 7, and 8) is the width of the AGNR. The right half of the device is assumed to be orderly doped with a row of nitrogen atoms, where n (= 1, 2, 3,$\cdots$, and 7) indicates the nitrogen atom doping position, and m (= 4 and 6) denotes the number of nitrogen atoms.

All of the calculations were performed with the Atomistix ToolKit (ATK) program package based on DFT combined with NEGFs [36–38]. The calculations based on the local-density approximation, the devices were fully relaxed until the maximum force tolerances were less than 0.02 eV/Å. A double-ζ plus polarization basis set was used to describe the systems. The k-point sampling was $1 \times 1 \times 100$ and the cutoff energy was set to 150 Ry. When a low-bias voltage is applied to the left electrode and right electrode, the Landauer–Büttiker formula can be used to obtain the transmission coefficients $T(E)$ of the device through the Green's function technique [26]. The nonlinear current through the central scattering region is calculated by

$$I(V) = (2e/h)\int T(E,\ V_b)[f_l(E-\mu_l) - f_r(E-\mu_r)]dE \quad (1)$$

where $\mu_{l/r} = E_F \pm e\cdot V_b/2$ is the chemical potential of the left/right electrode, where V_b is the applied bias voltage. E_F is the Fermi energy, which is set to zero. The total transmission probability is

$$T(E,\ V_b) = Tr\left[\Gamma_l G^R \Gamma_r G^A\right] \quad (2)$$

where $\Gamma_{l/r}$ is the contact broadening function related to the left/right electrode and $G^{R/A}$ is the retarded/advanced Green function.

3. Results and discussions

We first calculated the current as a function of the applied bias V_{SD} for the W-AGNR-N(4, 6) devices (W = 6, 7, 8) in a bias range −1 to 1 V, as shown in Fig. 2(a). The rectifying ratio $R(V)$ is defined as $R(V) = |I(-V)/I(V)|$ [28], where $I(V)$ and $I(-V)$ represent the current under positive and negative bias, respectively. $R(V)$ as a function of V_{SD} is shown in the inset of Fig. 2(a). For the 7-AGNR-N(4,6) device, the I–V curve is highly asymmetric, and there is clearly a strong rectification effect for a large rectifying ratio. We changed the width of the nanoribbon, and the I–V curves of the other two devices (W = 6 and 8) show different characteristics from the 7-AGNR-N(4,6) device. The rectification performances in these systems are negligibly small, as shown in the inset of Fig. 2(a). Therefore, we chose the 7-AGNR for further investigation. In addition, we also investigated the influences in the transport properties for the 7-AGNR-N(n, m) device with different nitrogen-doped positions and nitrogen atom numbers, as shown in Fig. 2(b). Although all of the devices show the rectification effect, the currents of the 7-AGNR-N(4,6) device under a negative bias are larger than those of the other devices. Thus, the 7-AGNR-N(4,6) device shows a better rectifying effect than the other devices, and the rectifying ratios reach the order of 10^3 in the bias range [0.6, 0.8] V, as shown in the inset of Fig. 2(b). Therefore, it is possible to achieve a molecular rectifier owing to the large rectifying ratio of the 7-AGNR-N(4,6) device.

The local gate voltage can shift the Fermi level in the gated region [29,39], and the gate voltage can strongly affect the electronic transport properties of the C_{60} dimer and change it from semiconducting to metallic [40]. Therefore, we applied various external gate voltages (V_g = −20 to 20 V) to the right half of the scattering region of the 7-AGNR-N(4,6) device to modulate the electronic

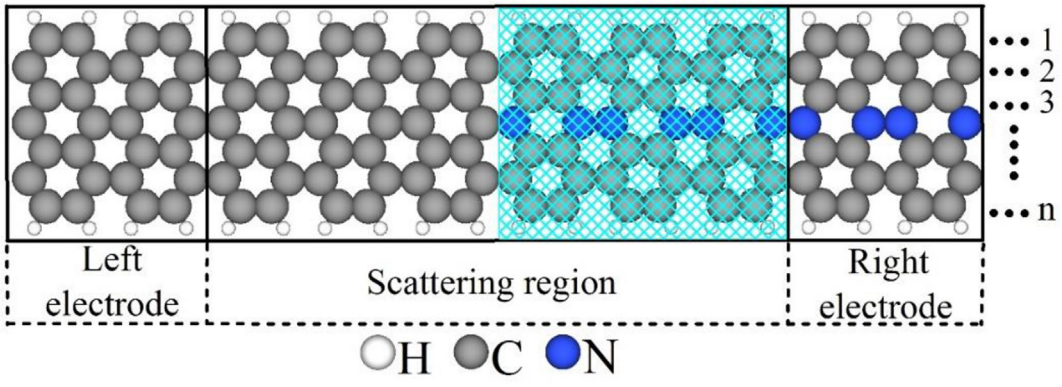

Fig. 1. Nitrogen atom orderly doped AGNR and the corresponding device. For the device, the external top-gate is applied in the right half of the scattering region (cyan grid region), which is perpendicular to the electron transmission direction. the gate region includes the metallic region and the dielectric region, the thickness of the metal region and the dielectric region is 1Å and 2.58Å, respectively. The dielectric constant is $4\varepsilon_0$. The edge carbon atoms of the AGNR are passivated by hydrogen atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)