Electronic structures and transport properties of armchair graphene nanoribbons by ordered doping

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ABSTRACT

Based on the first-principles method, the electronic structures and transport properties of armchair graphene nanoribbons (AGNRs) with ordered doping of B atoms or N atoms or BN molecules are studied systematically. It shows that the AGNRs may be a metal or a semiconductor depending on B or N atom-doping positions, and the calculated atom-projected density of states (atom-PDOS) indicates that B or N impurity atoms can induce the new lowest conduction band (LCB) or the highest valence band (HVB). More interestingly, as compared with the intrinsic AGNR device, the current in the B- or N-doped AGNR device with the most energetically favorable state is extremely small, completely different from a macroscopic Si semiconductor with p-type or n-type doping, which always leads to a significant increase in current. Also shown is that the doping with BN molecules generally increases the bandgap of the AGNR regardless of the doping position, but the size of these bandgaps depends on the doping positions. The current in the BN-doped AGNR device is also decreased greatly in comparison with that for the intrinsic AGNR device.

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1. Introduction

Since graphene, a two-dimensional (2D) network of sp^2-hybridized carbon atoms packed into hexagonal structure with a single-atom thickness, was successfully fabricated in 2004, it has led to a new round of research boom in condensed matter physics and material science due to its unique properties [1–8]. So far, not only graphene can be obtained and characterized by various experimental methods, but also its nature and potential applications are widely explored by theoretical calculations and analysis. Due to the carrier mobility of graphene up to 2×10^5 cm^2/(V S), it has an outstanding electrical conductivity. Meanwhile, studies also show that the effective modulation of the electronic properties of graphene can be achieved by lots of pathways, such as edge modifi-

cations [1], hetero-atom doping [2], introducing the topological defects [3], applying external electric field [9] and magnetic field [10].

With the continuous improvement of the control technology, the general tendency for doping graphene with hetero-atoms is more versatile and more ordered. Among various doping hetero-atoms, because the physical and chemical properties of nitrogen (N) and boron (B) atoms are similar to carbon atoms and their binding is a quite strong covalent bond, comparable to that of host C–C bond, their doping only results in a very small geometrically structural change for graphene. Especially, the incorporation of N atoms or B atoms into the graphene will influence electronic and transport properties of graphene by introducing extra carries and altering energy band structures, so that the N or B atom or BN molecule has become the typical substitutional dopants for graphene [11,12]. Moreover, studies showed that the BN molecule itself can form a stable hexagonal-honeycomb structure, h-BN, similar to

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graphene, but it is a wide band-gap semiconductor [13], differently from graphene which is a semimetal with a zero bandgap. Recent experiments demonstrated that a large-area atomic layered thick h-BNC composite structure could be successfully fabricated [14], this indicates the possibility of B and N atom controllable doping and the formation of hybridized geometries based on graphene. For graphene composite structures related to BN-doping, the current main studies include the separate doping of B or N atoms [15], the regular doping of BN molecules [16,17], BN-chain doping [18], and the heterostructure constituted by BN nanoribbons and graphene [19], etc.

Based on the first-principles method, the electronic structures and transport properties of armchair graphene nanoribbons (AGNR) with ordered of B atoms or N atoms or BN molecules are studied systematically. It shows that electrical behaviors of the AGNR are very sensitive to these doping, especially depending on its doping positions. More interestingly, we find that the current in the B- or N-doped AGNR device with the most energetically favorable state is greatly decreased as compared with that for an undoped AGNR device, completely different from a macroscopic Si semiconductor with p-type or n-type doping, which always leads to a significant increase in current.

2. Structure model and theoretical method

The structural models studied are shown in Fig. 1, where an armchair graphene nanoribbon (AGNR) with an ordered substitutional doping is considered, which is possible for the standardized fabrication. By convention, the width of the AGNR is defined as the number of dimer carbon atom chains, W, across the width direction. Here, we take $W = 11$ as representative. Fig. 1(a) displays the model of AGNR doped orderly with B atoms, and Fig. 1(b) and (c) show the unit cells of orderly doped AGNR by N atoms and BN molecules, respectively. The AGNR is assumed to be orderly doped with a row of B atoms or N atoms or BN molecules along the length direction of the AGNR each time. Therefore, various different orderly-doped AGNR prototypes can be achieved. To keep structural stability, all models are saturated with hydrogen atoms. For orderly doped AGNRs, the black dotted horizontal lines, as shown in Fig. 1(a), represent six different doping positions, marked as P1, P2, ..., P6, respectively. Thus positions P1 and P6 are just located at the outer edge and the axis of the AGNR with width $W = 11$. As example, Fig. 1(a)–(c) exhibit the B atom-doping, N atom-doping, and BN molecule-doping at position P3, respectively. Each black dotted box denotes an unit cell, namely, a smallest repeatable unit of the periodical structure along the length direction of the AGNR. The undoped AGNR is marked as P0. Fig. 1(d) demonstrates the electronic device model consisting of doped or undoped AGNRs, and the B atom-doping AGNR at position P3 is taken as representative. Each electronic device model is divided into three parts: the left electrode (LE), the scattering region (SR), and the right electrode (RE).

The structural relaxations and transport calculations for of above all models are performed by the Density Function-al Theory (DFT) combined with the non-equilibrium Green's function (NEGF) technique as implemented in the Atomistix ToolKit (ATK) [20–22]. In order to solve the Kohn–Sham equation, The Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) is used as the exchange–correlation functional. Considering the polarized effects of atoms, the single-zeta plus polarization (SZP) basis set is used for H atoms, and the double-zeta plus polarization (DZP) basis set is used for other atoms. We employ Troullier–Martins norm-conserving pseudopotentials to represent the atom core and linear combinations of local orbitals to expand the valence states of electrons. In the Brillouin zone, the k-point sampling is chosen as $1 \times 1 \times 150$, and 300 Ry is set as the cut-off energy for the grid integration, mainly controlling the size of the real space integral network partitioning and the solution of the Poisson equation, and achieving the balance of computational efficiency and precision. In all models, the geometric structure is optimized until all residual forces on each atom are smaller than 0.05 eV/Å.

Once the convergence in self-consistency calculations is achieved, the current through a device is computed by the Landauer-like formula [23]: $I = \frac{2e}{h} \int T(E, V_b) dE$, where E represents the energy, V_b is a bias, and T denotes the transmission spectrum, then the current is obtained by integrating the transmittance coefficient in the bias window.

3. Results and discussion

3.1. Electronic structures and transport properties of AGNR with ordered doping of B atoms

Band structures for the AGNR orderly doped with B at six positions, P1–P6, are shown in Fig. 2(a), denoted in turn as BP1–BP6. As comparison, the band structure of undoped (intrinsic) AGNR is also shown in Fig. 2(a), marked as P0. The Fermi level is set as zero, indicated with the dotted line. From figures, several important features are visible: (1) The intrinsic AGNR is a semiconductor with a narrowed bandgap, 0.14 eV, which is basically consistent with that shown in Ref. [4]. The doping of B atoms at positions P1 and P4 can keep its semiconductor behaviors, but it also can make AGNR be metallic if the B-doping at positions P2, P3, P5, and P6. (2) The doping leads to the additional band produced, such as, the lowest conduction band (LCB), which is particular obviously. (3) Bands move upward, resulting in the original highest valence band is closer to or passes through the Fermi level, this is because the B-doping is a p-type doping, the Fermi level moves downward, which is equivalent to the upward movement of the bands. (4) The number of valence bands increases significantly, the reasonable explanation for this issue is that impurity atoms are periodically distributed along the longitudinal direction of AGNR, as stated above, this configuration forms well-defined impurity band structures. B-doping can make AGNR be metallic or semiconductoring, which means that we can choose suitable B-doping positions in a AGNR to meet the specific requirements of the electrical properties for semiconductor technology and nano-electronic devices.