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Modulation of the electron transport properties in graphene nanoribbons doped with BN chains

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Using density-functional theory and the non-equilibrium Green’s function method, the electron transport properties of zigzag graphene nanoribbons (ZGNRs) doped with BN chains are studied by systematically calculating the energy band structure, density of states and the transmission spectra for the systems. The BN chains destroyed the electronic transport properties of the ZGNRs, and an energy gap appeared for the ZGNRs, and displayed variations from a metal to a wide-gap semiconductor. With an increase in the number of BN chains, the band gap increased gradually in the band structure and the transmission coefficient decreased near the Fermi surface. Additionally, the doping position had a significant effect on the electronic properties of the ZGNRs.

I. INTRODUCTION

Graphene, a single-layer of a hexagonal lattice of carbon atoms, was discovered in 2004.¹ Graphene has a high specific surface area structure² and excellent thermal, mechanical and electrical properties.³–⁵ Nano-sized graphene nanoribbons (GNRs) have been cut out of graphene sheets with two basic shapes for the edges: armchair and zigzag, which have distinct electronic transport properties.⁶–⁸

Defects and impurities are inevitable in GNRs because it is difficult to experimentally obtain perfect graphene sheets. Therefore, the electronic transport properties will be affected to varying degrees. It is believed that doping carbon nano-systems with elements such as B and N can modulate their electrical properties.⁹–¹⁵ Although accurately doping graphene is difficult to achieve, there are still efforts towards achieving this goal. Lijie Ci et al.¹⁵ successfully synthesized a large area h-BNC film and found that the electrical and optical properties of the h-BNC film were different between the BN film and the graphene sheet. This indicated that GNRs may be useful in band gap engineering. Peng et al.¹⁶ calculated the elastic properties and the electronic structure of carbon nanotubes and BN nanotubes with an ab initio package. They found that metal-semiconducting carbon nanotubes could be converted by introducing uniaxial stress. This phenomenon does not exist in BN nanotubes. Latil et al.¹⁷ used an ab initio tight-binding method to calculate the transport properties of carbon nanotubes, modeled by incorporating B and N atoms into the nanotubes. They found that even small amounts of B and N atoms could significantly alter the electron transport properties of the carbon nanotubes. The mean free path and the doping rate of the electrons at the Fermi level both had a reciprocal relationship. Du et al.¹⁸ studied the energy gap of a complete BN nanobelt and the

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electronic structure by incorporating C atoms by using a first-principles method. Spin magnetization behavior was observed in the system. H. Milani Moghaddam\(^{19}\) calculated the transport properties of metallic zigzag nanotubes/BCN quantum dots/carbon nanotubes using a Green’s function, where the BCN quantum dots shielded the majority of the electronic transmission and a great transmission state appeared at some bands. The current-voltage curves were approximated to have a stepped shape. This inferred that the system could be useful in nano switching devices.

From this series of studies, incorporation of BN into carbon nanotubes significantly altered their electronic transport behavior. Xu et al.\(^{20}\) analyzed the electronic and magnetic properties of a superlattice of graphene doped with BN using first-principles calculations. They pointed out that the shape of the arrangement of the BN doping atoms had an important influence on the electrical and magnetic properties of the system. Liu et al.\(^{21}\) studied the electronic structural and magnetic properties of hybrid armchair BCN nanobelts and showed that the BN doped system produced magnetization behavior at the edges of the nanobelts. Khalfoun et al.\(^{22}\) and Wang et al.\(^{23}\) conducted studies on the electronic properties of a pair of BN atoms that were incorporated into graphene. They determined the distance between the BN atoms that played a major role in the transport properties of the system. Wei et al.\(^{24}\) found that δ-doped N atoms had a significant impact on the band structure of armchair graphene. There are few doping regulation studies on metallic zigzag graphene nanoribbons (ZGNRs). In this paper, the impact of the electronic transport in ZGNRs that had BN atom chains incorporated along the width direction is studied for different numbers of BN chains doped at either the position of a sawtooth peak or a sawtooth valley. Similar to the model of BN doped graphene\(^{25,26}\) have been reported. So we believe that our model can be realized experimentally in recent future. Doping with BN atom chains could controllably modulate the band gap of the ZGNRs. Atom chain doping is an effective method to control the transport in nanodevices, which provides a viable physical model and technical ideas for designing and implementing nano-electronic devices with excellent performance.

II. MODELS AND METHODS

The model in Figures 1(a)–1(d) show the widths of six ZGNR chains. The left and right electrodes were semi-infinite electrodes. The intermediate region of the system was the scattering region. To prevent edge effects caused by dangling bonds, the nanoribbons were passivated with hydrogen atoms. e (i) shows a sawtooth peak position (a sawtooth valley position) for the zigzag graphene nanoribbons in Figures 1(a) and 1(b), respectively. In Figure 1, en (in) indicates where \(n (n = 0, 1, 2, 3, 4, 5)\) BN chains were substituted at the sawtooth peak positions (sawtooth valley positions), which is marked as ZGNRs@en (ZGNRs@in). The geometry was optimized using the density functional theory plane-wave pseudopotential VASP\(^{27,28}\) software package. GGA-PBE (Perdew–Burke–Ernzerhof approximation)\(^{29}\) was applied to describe the exchange-correlation potential. The cutoff energy for the plane-waves was chosen to be 450 eV and a Monkhorst–Pack mesh of \(k\)-points \((1 \times 1 \times 9)\) was used for sampling the one-dimensional Brillouin zone. The atomic forces were less than 0.001 eV/nm. For the convergence criteria, the energy change was set less than 0.0001 eV. After testing, the vacuum layer was 1 nm, which was large enough to disallow interactions between the periodic images. For the electronic transport properties, density functional theory and the non-equilibrium Green’s function calculation package, Atomistix ToolKit(ATK),\(^{30,31}\) were used to determine the band structure, the density of states and the transmission spectra. GGA-PBE\(^{29}\) was employed as the exchange-correlation function. A Monkhorst–Pack grid of \(1 \times 1 \times 500\) was used for all structures. A double-\(\zeta\) polarized basis set was employed and the cutoff value that defined the real space grid was 150 Ry, to achieve a balance between the calculation efficiency and precision.

III. RESULTS AND DISCUSSION

The energy band gap was calculated as the number of BN chains incorporated into the ZGNRs was increased, as shown in Figures 1 and 2. “\(n = 0, 1, 2, 3, 4, 5\)” indicates the number of BN chains that were incorporated into the ZGNRs. From Figures 2(a) and 2(b), no BN chains had been incorporated into the ZGNRs when \(n = 0\), the nanoribbon was pure zigzag graphene, its band gap was zero and it
FIG. 1. The zigzag graphene nanoribbon transport systems were doped with BN chains and passivated with hydrogen. (a) Non-doped zigzag graphene nanoribbons (ZGNRs), where e (i) indicates the position of a sawtooth peak (the position of a sawtooth valley). (b) The position of a sawtooth peak was replaced by one BN chain (ZGNRs@e1). (c) The positions of the sawtooth peaks were replaced by five BN chains (ZGNRs@e5). (d) The sawtooth valley positions were replaced by five BN chains (ZGNRs@i5). The pink, blue, gray and white balls represent boron, nitrogen, carbon and hydrogen atoms, respectively.

FIG. 2. Band structures for the incorporation of BN chains (number \( n = 0, 1, 2, 3, 4, 5 \)) into the ZGNRs near the Fermi surface. ZGNRs@e\( n \) represents the position of a sawtooth peak and ZGNRs@i\( n \) represents the position of a sawtooth valley. The Fermi level is located at \( E = 0 \) eV.
FIG. 3. Energy band gap for the incorporation of BN chains into the ZGNRs. ZGNRs@en is the position of a sawtooth peak and ZGNRs@in is the position of a sawtooth valley ($n = 0, 1, 2, 3, 4, 5$).

exhibited metallic properties, which is consistent with the literature\textsuperscript{32,33} for the ZGNRs@en system (ZGNRs@in system). By incorporating BN chains into the ZGNRs@en system, some localized impurity bands were introduced (Figure 2). With an increase in the number of BN chains, the band gap widened and increased. However, when $n = 2$, the band gap was reduced in comparison with $n = 1$. From Figure 2(b), replacing the incorporated BN chains in the ZGNRs@in system resulted in the introduction of some localized impurity bands. As the number of BN chains increased, the band gap became wider. However, different from the ZGNRs@en when $n = 3$, the band gap was reduced to 0.006 eV. As the number of BN chains increased, the band gap initially decreased, and then it increased. In Figure 3, the band gaps were larger in the ZGNRs@en system than in the ZGNRs@in system, illustrating the effect on the band gap in ZGNRs. For the ZGNRs@en and ZGNRs@in systems, increasing of the number of BN chains caused the B and N atom concentrations to increase in the ZGNRs. B atoms have one less electron than C atoms, while N atoms have more than one electron more than C atoms. The B and N atoms were replaced in pairs. After incorporation of BN atomic chains, the doped and non-doped ZGNRs had the same number of electrons. The atomic radius of B is relatively large in comparison with that of C. The atomic radius of N is relatively small in comparison with C, and the values of the electron binding strengths are different. Due to similar bond length for B-N and C-C, the covalent bond will be formed by sp\textsuperscript{2}-hybridized. The different electronic transitions had a significant impact on the band gaps of the doped ZGNRs. The number of BN chains incorporated into the ZGNRs opened the band gap in the ZGNRs, turning its metallic properties into semiconducting properties.

As the number of BN chains increased, the calculated density of states and transmission spectra for the ZGNRs@en and ZGNRs@in systems ($n = 1, 2, 3, 4, 5$) were calculated, as shown in Figures 4(a) and 4(b). When $n = 0$, there was a high density of electronic states at the Fermi energy $E_f = 0$ eV, because the band was electronically half-filled. Thus, it exhibited metallic behavior, which corresponds to the energy band structure in Figure 2. Simultaneously, several new peaks appeared in the ZGNRs@in system, but not in the ZGNRs@en system, near the Fermi level. In the ZGNRs@in, as the number of BN chains increased, a new peak gradually emerged. The BN atomic chains that were incorporated into the ZGNRs had a larger impact on the electronic transport properties in the ZGNRs@in system than in the ZGNRs@en system.

Figures 4(c) and 4(d) show the transmission spectra for the ZGNRs@en and ZGNRs@in systems ($n = 0, 1, 2, 3, 4, 5$), respectively. Regardless of whether the doped BN chains were at a sawtooth peak or valley, the transmission spectra had a good symmetry and when $n = 0$, the ZGNRs had a good
transmittance near the Fermi surface. As the BN chains were substituted, they introduced impurities. The scattering of electrons and impurity atoms were enhanced in the system. The scattering of impurities was enhanced as the number of BN chains increased and the transmittance of electrons near the Fermi surface became small. For the ZGNRs@en system, the transmission coefficient was almost zero near the Fermi level. When \( n = 3, 4 \) or 5, the system turned from its metallic state into a semiconducting state. For the ZGNRs@in system, a higher transmission peak arose for \( n = 3 \) near the Fermi level and the system had a high electron transmittance, which corresponds to the previous energy band structure analysis. Additionally, scattering was greater in the ZGNRs@en system than in the ZGNRs@in system. The transmission spectra in particular are quite different in a sawtooth peak or valley. When the doped BN chains were at a sawtooth peak, as the number of BN chains increased, the edge transport channel was limited. And when the doped BN chains were at a sawtooth valley, the edge channel of electron transport appears. The edge transport channel resulted in transmission spectra having a significant difference between the sawtooth peak and valley position, as can be seen from Figure 4(c) and 4(d). Doping the ZGNRs with BN chains had a significant impact on the transport properties of the ZGNRs. 34, 35

IV. CONCLUSIONS

In this paper, a first-principles study on the band structure, the density of states and the transmission spectra of ZGNRs doped with BN chains was carried out. The ZGNRs were six zigzag chains wide. The pure ZGNRs were metallic, but when the ZGNRs were doped with BN chains a band gap emerged in the band structure and the system turned from a metallic state to a semiconducting state. Further calculations on the transport properties obtained the transmission spectra and density of states, which confirmed the above. Doping the ZGNRs with BN chains inhibited the transmission of electrons in the ZGNRs. As the number of BN chains was increased, the electronic transmission rate was reduced near the Fermi surface. Different doping positions had a significant impact on the electron transport properties. Regulation of the doping concentration and the doping position of the electronic transport properties contribute to the design and performance of nano-electronic devices based on ZGNRs.

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