Electronic structure tuning and band gap opening of graphene by hole/electron codoping

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ARTICLE INFO

ABSTRACT

A pathway to open the band gap of graphene by p–n codoping is presented according to the first principles study. Two models are used: Lithium adsorbed on Boron-doped graphene (BG) and Boron–Nitrogen (B/N) codoping into graphene. The stability of Lithium adsorbed on BG is firstly analyzed, showing that the hollow site is the most stable configuration, and there is no energy barrier from some metastable configurations to a stable one. After the p–n codoping, the electronic structures of graphene are modulated to open a band gap with width from 0.0 eV to 0.49 eV, depending on the codoping configurations. The intrinsic physical mechanism responsible for the gap opening is the combination of the Boron atom acting as hole doping and Nitrogen (Lithium) as electron doping.

1. Introduction

Since the successfully experimental fabrication in 2004 [1], graphene has been under eyeball of theoreticians and experimentalists due to its novel physical and chemical properties [1–8] and its potential applications in many fields such as gas sensing [9–13] and electronic devices [5,14–16]. Graphene behaves as a semimetal, whose band gap is zero. In order to widely apply graphene to the field of electronics in the present Si-based semiconductor times, the band gap of graphene must be opened to the order of 1 eV. Up to now, there have been many methods used to open the gap of graphene. Thereinto, chemical doping and molecular adsorption are the well-known methods of manipulating the electronic properties of graphene [17–21] and graphene nanoribbons [22]. Ohta et al. controlled the electronic structure of the bilayer graphene on SiC substrate by the potassium adsorption [23], whose intrinsic physical mechanism in the experiment is the combination of p-type doping of the substrate [24,25] and n-type doping of K atoms. Furthermore, it is found that p-type and n-type doping can be induced into graphene with Boron or Nitrogen atom substituting Carbon atom [12,13,26], respectively, and the B/N codoping can change the electronic properties of graphene nanoribbons (GNRs) from semiconductor to half-metal behavior [27]. The single open shell NO_2 molecule is shown to be an electron acceptor when it rests on graphene [11], which indicates the NO_2 molecule can be

n-type doping for the graphene and partly explains the recently observed NO_2 single molecule detection on graphene [8]. Besides, the adsorption of the single atom (including non-metal and metal) on graphene can also transfer charges to graphene or obtain charge from graphene, which is dependent on the type of adsorbates. For example, the adsorption of Nitrogen atom can be p-type doping for the host graphene [28], in contrast to the n-type doping of Nitrogen by substituting C atom [26]. All these phenomenons remind us that the electronic structures can be modulated by p-type or n-type doping, or codoping.

In this Letter, we focus on the gap opening of graphene and propose a method to achieve this goal. Generally speaking, our method is based on p–n codoping, and two ways are given and verified. One path is using Lithium atom adsorbed on Boron-doped graphene (BG), the other one is using Boron–Nitrogen (B/N) codoping into graphene. In the two ways, Boron atom plays a role of p-type doping, while Nitrogen and Lithium atoms n-type doping. The first principles calculation is adopted to obtain the lowest-energy geometries of doped graphene and its electronic structures. The results show that both Lithium adsorbed on BG and codoping of B/N atoms are efficient to open the band gap of graphene.

2. Models

All the calculations are performed using QUANTUM-ESPRESSO code [29]. The generalized gradient approximation (GGA) proposed by Perdew et al. [30] is used as the exchange-correlation functional. The kinetic energy cutoff is set 30 Ry for the wave function

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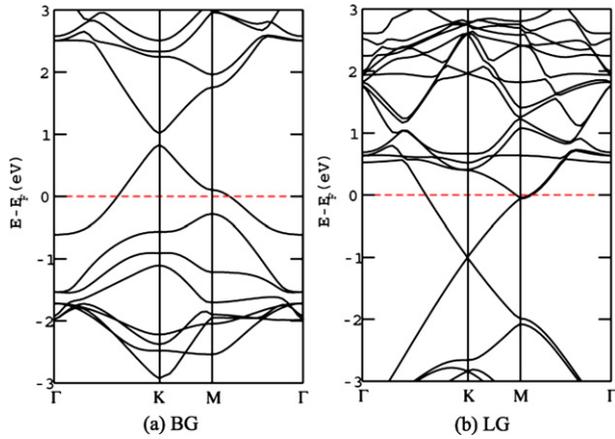*E-mail address:* jydai@nudt.edu.cn (J. Dai).

Fig. 1. (Color online.) The electronic band structures of (a) the BG and (b) the LG (above the center of the hexagon). Red dashed line represents Fermi level.

and 300 Ry for the charge density. A 32-atom supercell is used to simulate a 4×4 supercell of graphene. The periodical boundary condition (PBC) is employed and adjacent layers are separated by a vacuum region of 15 Å. The Brillouin Zone is sampled by using a $5 \times 5 \times 1$ Monkhorst–Pack [31] grid and Methfessel–Paxton [32] smearing of 0.01 Ry in geometries relaxations. Increasing the energy cutoff up to 35 Ry and $12 \times 12 \times 1$ k-point sampling gives the similar results of structure and total energy. To obtain accurate band structures, denser k-points of $11 \times 11 \times 1$ are chosen. We have optimized all geometries studied here by reducing the Hellman–Feynman forces down to 0.001 a.u.

3. Results and discussion

3.1. Li atom adsorbed on BG

First of all, the electronic structures of BG and Li-adsorbed on pristine graphene (LG) are calculated after careful minimization of force and energy. The band structure dispersion for BG and LG with the most stable configuration are shown in Fig. 1(a) and (b), respectively. In Fig. 1(a), the Fermi level E_F is shifted below the Dirac point, indicating that Boron doping can be regarded as hole doping. On the contrary, the Fermi level E_F is shifted above the Dirac point (Fig. 1(b)), indicating Lithium doping as electron doping. It is very interesting to notice that there is a band gap above the Fermi level in the band structure at K point, which gives us a possibility to induce a metal-to-semiconductor transition. The band structure of N-doped graphene (NG) is similar to that of BG, whose Fermi level shifts above the Dirac point. Boron atom possesses three valance electrons, less than those of Carbon atom (four valance electrons). The lack of one electron makes the graphene p-type conductor. For LG, Li will bound with graphene layer when Li rests on the pristine graphene, whose most stable adsorbed site is Lithium atom on the center of the hexagon. The transferred charge number c_e from Li to pristine graphene is 0.15 e^- by the Löwdin charge analysis, which supports that Li atom behaves as electron doping.

As the above discussions, Boron doping and Lithium adsorption (or Nitrogen doping) can shift the E_F below and above the Dirac point, respectively. Therefore, it is interesting and meaningful to know whether the Fermi level can return to the original site, and whether the band of graphene can be opened. To reach this goal, we investigate the cases of Li adsorbed on BG and B/N codoping. For the adsorption of Li atom on BG, nine positions for Li atom are considered. They are the top site (T, above the B atom), the hollow site (H, above the center of the hexagon), the bridge site (B, above the middle of Boron–Carbon bond), the random site (R, above the center of the hexagon, but far away from the hexagon containing
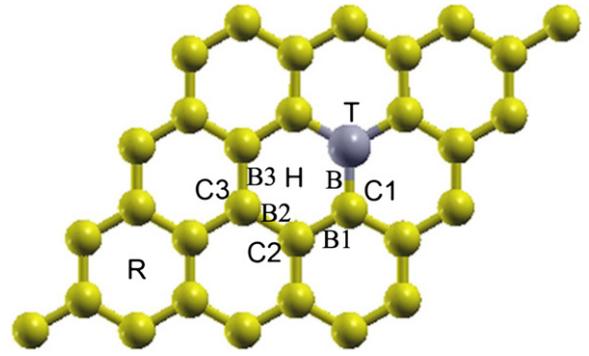

Fig. 2. (Color online.) Adsorbed sites of Lithium atom on BG.

Table 1
The adsorption energy (E_b, eV), the distance between Lithium and graphene plane (d_{Li}, Å) and the width of band gap (E_w, eV), for different sites of Lithium atom adsorbed on BG.

Sites	T	H	R	B
E_b	−1.38	−1.56	−1.15	−1.35
d_{Li}	2.14	1.83	1.86	2.15
E_w	0.139	0.128	0.166	0.142

the Boron atom), and three near top sites C1, C2, C3, three near bridge sites B1, B2, B3, as shown in Fig. 2. The adsorption energy, defined as $E_a = E_{BGL} - E_{BG} - E_L$, is used to evaluate the ability of the adsorption of Lithium on BG, where E_{BGL} is the total energy of Boron–Lithium-graphene system, E_{BG} is the energy of BG and E_L is the energy of isolated Lithium.

After the relaxation of the forces on atoms, the analyses of the total energies and structures are performed to understand the stability of the adsorption. The results are shown in Table 1, which show that the adsorption of energy for the most stable configuration (the hollow site is the lowest-energy site) is $E_b = -1.56$ eV. In this case, Boron atom still remains in the plane almost, and the distance between the graphene plane and Li (d_{Li}) is 1.83 Å. It is very interesting that when Li atom is located on the sites of C1, C2 and C3 at the beginning, it will diffuse to B site from C1, and at the same time to H site from C2, C3 sites, respectively. Furthermore, the Li atom will also diffuse from B1, B2, B3 sites to H sites spontaneously. That is to say, the top sites and bridge sites near Boron atom are not stable for the adsorption of Li, indicating more reactivity of Boron than Carbon in BG. This can be verified by the Climbing-Image Nudged Elastic Band (CI-NEB) calculation, which shows there is no any barrier from CX and BX (X = 1, 2, 3) sites to B or H sites. The top sites and the bridge sites have very similar reactivity for Li atom, which are the second most stable positions. Its d_{Li} and E_a are about 2.1 Å and −1.3 eV, respectively, as shown in Table 1. For the random site adsorption of Li on the BG, the obtained d_{Li} and E_a are 1.86 Å and −1.15 eV, respectively, almost the same as those without Boron doping into graphene. Therefore, we can safely conclude that Boron doping can improve the adsorption of Li on graphene. The short distance d_{Li} and the large adsorption ability support the existence of the tight bound between Li and BG. In other words, Li can be chemisorbed on the BG. Furthermore, we analyze the possible transition from T site to H site, from B site to H site, from B site to T site, using 7 images to perform CI-NEB calculation for each case. It is found that there is also no barrier from T to H, and from B to H, as shown in Fig. 3(a) and (b), respectively, indicating the T site is also a metal stable configuration. Further, the barrier from B to T is about 0.09 eV, as shown in Fig. 3(c), indicating the diffusion from B to T site should not happen spontaneously, but it is still not very difficult.
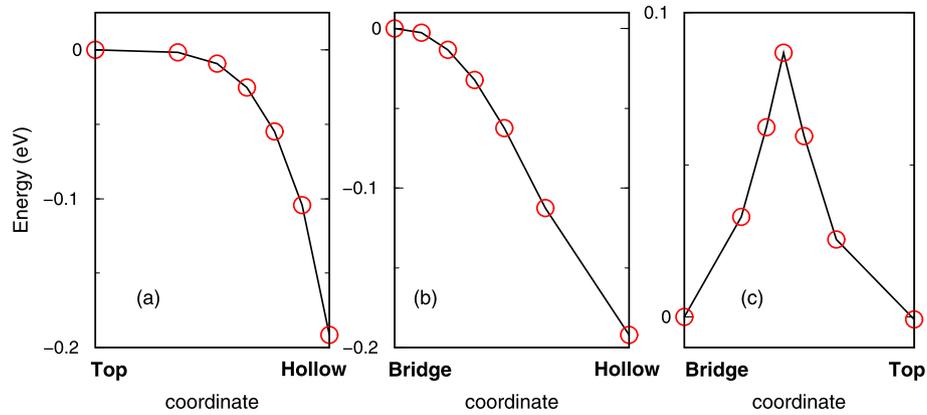
Fig. 3. (Color online.) The minimum path of Lithium atom adsorbed on BG from T to H site (a), B to H site (b), and B to T site (c), respectively.
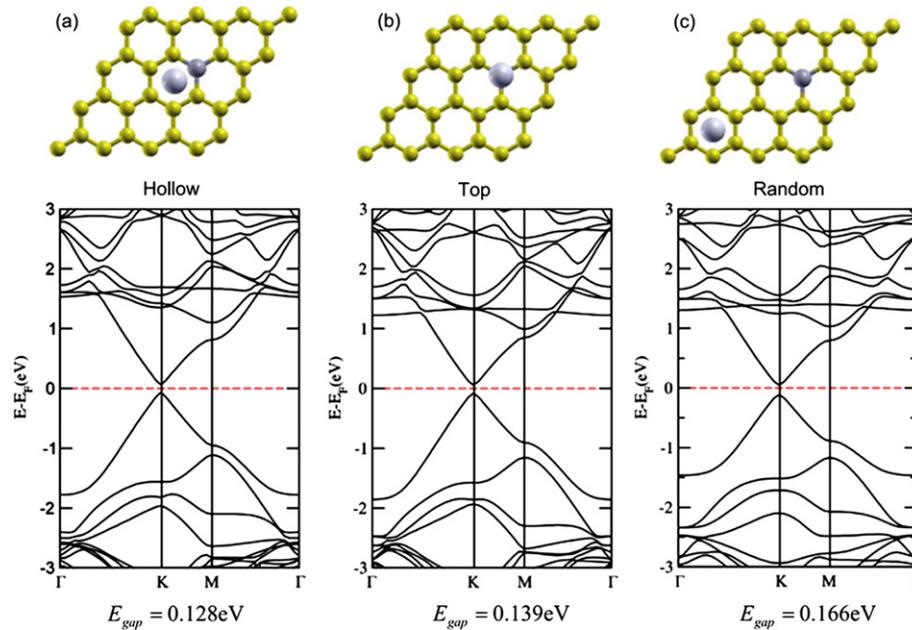

Fig. 4. (Color online.) The atomic structure maps (top panel) and the electronic band structures (bottom panel) of BG with Lithium atom adsorbed on its surface. (a) is Li on the hollow site, (b) Li on the top site and, (c) Li on the random site. Yellow ball expresses Carbon atom, small grey Boron atom, and big grey Lithium atom. It is noticed that the electronic structure of Lithium atom on B site is very similar to that of top site.

The electronic band structures for the different sites of Lithium are shown in Fig. 4, and the corresponding width of band gap is shown in Table 1. After Lithium is adsorbed on BG, the Dirac point, shifted above Fermi level E_F by Boron doping, is depressed to E_F and a gap with about 0.1 eV width is opened. As the discussions regarded to Fig. 1, the combination of the pull from Boron and the push from Lithium makes the "Dirac point" come back to the original site. Furthermore, the behavior opening band gap depends on the adsorbed sites of Lithium on BG, as shown in Fig. 4 and Table 1. The maximum gap occurs in random site with a width of 0.166 eV. It can be expected that if we add the number of adsorbed Li atoms, the gap should be closed and the Fermi level should also shift away from the Dirac point, which has been verified in the previous experiment [23]. The intrinsic physical mechanism for the opening band gap should also be responsible for the broken of π bond of graphene by Boron doping, spreading the valence bond and conduction bond of graphene at the Dirac point.

3.2. B/N codoping

The electronic structures of the graphene with Boron and Nitrogen codoping at different sites are finally investigated. There have been a lot of results published to analyze the structures of BG or NG. Therefore, we focus on the electronic structures of B/N codoping graphene in this work. Three codoping cases, i.e., adjacent site case, opposite site case and random site case, are considered, as shown in Fig. 5. Here, the random site case means that the two sites of B and N atoms substituting are chosen randomly in the graphene plane. After the substitution of Carbon using Boron and Nitrogen atoms simultaneously to graphene, the Boron and Nitrogen atoms remain in the graphene plane for all three cases. This should be responsible for the size effects, i.e., Boron or Nitrogen atom has an atomic radius comparable to Carbon atom, as discussed in Ref. [12]. In order to analyze the stability and possible synthesization of these structures, the formation energy is defined as $E_f = E_{bn} + N * E_c - E_g - E_b - E_n$, where E_{bn} is the total energy of B/N codoping system, E_c is the energy of carbon atom in intrinsic graphene, N is the number of carbon atom substituted by dopants, E_g is the total energy of intrinsic graphene, E_b and E_n the energies of single Boron atom in solid state and single Nitrogen atom in molecular state. By this definition, we find that the formation energies of three sites shown in Fig. 5 are −0.73 eV, 0.54 eV and 0.72 eV, respectively. These small energies indicate that it should not be difficult to synthesize them in experiments comparing with
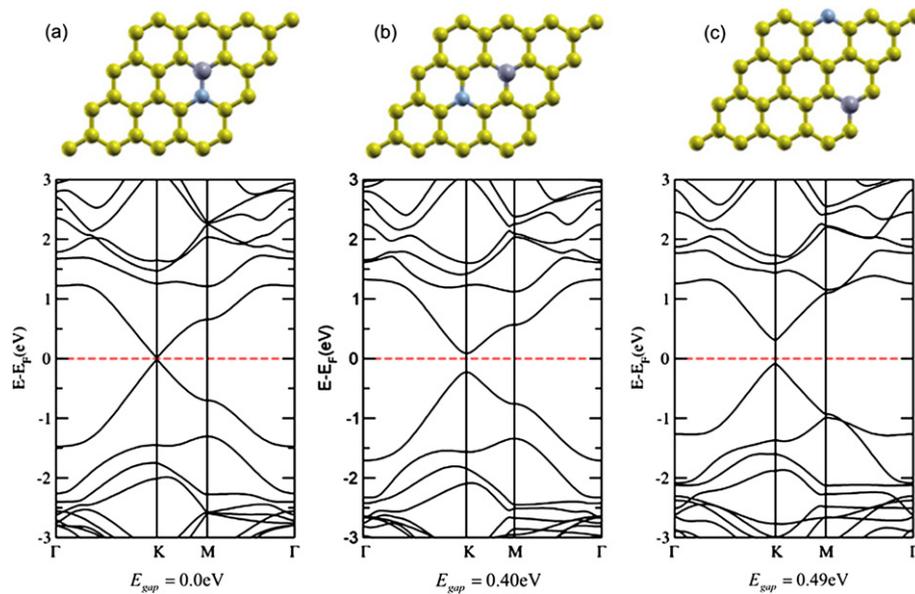
Fig. 5. (Color online.) The atomic structure map (top panel) and the electronic band structures (bottom panel) of B/N codoped graphene. (a) is adjacent site, (b) the opposite site and, (c) the random site. Yellow ball expresses Carbon atom, grey Boron atom, and blue Nitrogen atom.

the discussions with the Sulfur-doped graphene [33], and the most stable configuration is the adjacent site.

The electronic band structures for these three cases are shown in Fig. 5. After B/N codoping, the Dirac point is depressed around the Fermi energy. As mentioned above, B doping makes the Dirac point move below the Fermi energy (Fig. 1(a)). Therefore, we can regard that Dirac point in BG moves to the Fermi level because of Nitrogen doping. As the same as Lithium atom, Nitrogen atom acts as the electronic doping. For the adjacent case (Fig. 5(a)), the band gap is zero. This should be responsible for the counteraction between the Boron and Nitrogen doping. With the distance between Boron and Nitrogen increasing, the band gap is opened from 0.0 eV to 0.49 eV (Fig. 5(b) and (c)). The physical reason of opening band gap here may also be the broken of π bond by B/N codoping. The width of band gap is increasing with the increase of the distance between Boron and Nitrogen atoms, which can be explained by the accumulation of the effects of Boron and Nitrogen separately doping into graphene, where single Boron or Nitrogen atom doping will broke the π bond with inducing a gap in the valence or conduction band, as shown in Fig. 1. Comparing with the Li/B system, which can open the band gap to the value of 0.128 eV for the most stable configuration, the B/N codoping mechanism induces 0.49 eV in a metastable state. However, it is a pity that there is no band gap for the most stable configuration of the adjacent case, and the formation energies for the other two configurations are opposite, indicating that this mechanism is not every good considering the energetic synthesization comparing with Li/B codoping.

We also find that the band gap of the doped graphene is strongly dependent on the concentration of the dopant such as the number of Boron and Nitrogen atoms, or the number of Lithium atoms. Basically, we should use the same number of Boron and (Lithium) Nitrogen atoms, promising the Fermi level located in the gap. When the concentration of one dopant (e.g., electron dopant) is more than the other type (e.g., hole dopant), the band gap should be closed again, which is in agreement with Ohta's experiment [23]. Furthermore, different concentrations of the dopants will also change the width of the band gap. For example, two Boron atoms and two Nitrogen atoms codoping with two adjacent sites in the same supercell will decrease the width of band gap to 0.08 eV. This tells us that the interaction between B/N pair also plays an important role in the formation of the band gap of

graphene because the distance of B/N pairs cannot be neglected in the small supercell.

It is also worth to point out that the calculation of GGA would underestimate the band gap of the system. Therefore, the real band gap should be wider than those shown in this Letter. Even so, the mechanism and the pathways to open the band gap of semi-metal graphene are valid and useful both in theory and practical applications of graphene.

4. Conclusion

In summary, we have performed the first-principles band structure calculations to investigate the band gap opening of graphene. The mechanism of p–n codoping is adopted and two models are used. One is Lithium adsorbed on BG, the other is Boron and Nitrogen codoping into graphene. The results show that Boron atom acts as hole doping and Lithium (Nitrogen) as electron type doping. Boron doping elevates the Dirac point above the Fermi energy, and Lithium (Nitrogen) depresses Dirac point below the Fermi energy. The combination of the pull force from Boron and the push force from Lithium (Nitrogen) makes the Dirac point return to the original position. More importantly, the band gap of graphene is finally opened. Furthermore, the broken of π bond by the dopant should be also responsible for the opening gap. The maximum gap for Lithium–Boron-graphene reaches 0.166 eV and 0.49 eV for B/N codoped graphene, respectively. This work will enrich the recent nanoscale electronics investigations about graphene and point out a way to manipulate its band gap by codoping.

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