# Electronic properties of graphene nanoribbon doped by boron/nitrogen pair: a first-principles study*

Xiao Jin(肖 金)[a)], Yang Zhi-Xiong(杨志雄)[a)], Xie Wei-Tao(谢伟涛)[a)], Xiao Li-Xin(肖立新)[b)], Xu Hui(徐 慧)[a)†], and OuYang Fang-Ping(欧阳方平)[a)c)‡]

[a)] *School of Physics Science and Technology, Central South University, Changsha* 410083, *China*

[b)] *School of Physics and State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, Peking University, Beijing* 100871, *China*

[c)] *State Key Laboratory of Powder Metallurgy, Central South University, Changsha* 410083, *China*

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By using the first-principles calculations, the electronic properties of graphene nanoribbon (GNR) doped by boron/nitrogen (B/N) bonded pair are investigated. It is found that B/N bonded pair tends to be doped at the edges of GNR and B/N pair doping in GNR is easier to carry out than single B doping and unbonded B/N co-doping in GNR. The electronic structure of GNR doped by B/N pair is very sensitive to doping site besides the ribbon width and chirality. Moreover, B/N pair doping can selectively adjust the energy gap of armchair GNR and can induce the semimetal–semiconductor transmission for zigzag GNR. This fact may lead to a possible method for energy band engineering of GNRs and benefit the design of graphene electronic device.

**Keywords:** graphene nanoribbons, boron/nitrogen pairs doping, electronic properties, first-principles

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## 1. Introduction

Graphene, which can be obtained by the exfoliation process[1,2] or epitaxial growth,[3,4] has attracted much attention for its remarkable electronic properties.[4,5] Graphene nanoribbon (GNR), which can be patterned from graphene by plasma etching or chemical method,[6−8] has also become a research hotspot for its prospective applications. It has been demonstrated that the electronic properties of GNR sensitively depend on the chirality and the ribbon width,[9−12] and the applications of GNR, such as gas sensor, field effect transistor, spin filter and so on,[7,8,13−15] have also been investigated theoretically and experimentally. GNR has been considered as a possible candidate material for new large scale integration electrocircuits.[4,5,16]

Adsorption, defect and substitutional doping are the important methods to adjust electronic structures of material.[17,18] For obtaining the electronics properties of GNR suitable for the electronic applications, the influences of adsorption, defect and doping on GNR have been investigated by several groups.[19−32] Boron (B) and nitrogen (N) doping is a useful way to modify the properties of GNR.[25−29] Compared with by the hydrogen (H)/oxygen (O) adsorptive doping,[29] the system is not changed from sp2 hybridized to sp3 hybridized by substitutional doping of B and N, because the properties of B and N atoms are very similar to the properties of carbon (C) atoms. Most of researches about B/N doping focus on B-doping or N-doping in GNR and B, N co-doping in which the N atoms and B atoms are unbounded to each other.[23,25,28,30] It has been demonstrated that substitutional doping of B or N in GNR can improve the ability of the chemisorption obviously and can be used as gas detector.[23,33] Moreover, B and N doping in GNR can open the energy gap of semimetallic GNR and make the nanoribbons have different electronic transmission properties.[28,30] These greatly enrich the research of graphene electronics. However, the research on the GNRs doped by the B/N bonded pair

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†Corresponding author. E-mail: xuhui@csu.edu.cn

‡Corresponding author. E-mail: oyfp04@mails.tsinghua.edu.cn

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is quite rare.

Recently, carbon nanotube (CNT) doped by B/N bonded pair has been discovered in experiment.[33] It was found that B and N atoms have a strong preference to bond with each other and B/N bonded pair doping can open the energy gap of metallic CNTs.[33,34] As the unzipping CNTs[13] and the GNRs have similar physics properties to those of CNTs and thus the GNRs doped by B/N bonded pair must have some unique electronic properties. In this paper, the electronic properties of GNRs doped by B/N bonded pair are investigated by first principles and some interesting and important results are found.

## 2. Model and computational method

Figure 1 displays the atomic models of two typical GNRs:[13] armchair graphene nanoribbons (AGNRs) (a) and zigzag graphene nanoribbons (ZGNRs) (b). The number of carbon atoms along bandwidth direction, $n$, represents the width of ribbon. The different widths of AGNR and ZGNR are designated as $n$-AGNR (Fig. 1(a): 10-AGNR) and $n$-ZGNR (Fig. 1(b): 8-ZGNR). All the edges of ribbons are terminated by hydrogen atoms and C–C bond length is 1.424 Å (1 Å=0.1 nm) before geometry optimization. The six arrows labeled by $P_1$ to $P_6$ in Figs. 1(a) and 1(b) represent six unequivalent doping sites of B/N pair in AGNR and ZGNR, respectively. The directions of the arrows are all from B to N. The AGNR or ZGNR doped by B/N pair at the six unequivalent sites were studied.

All the calculations were performed by the Vienna *Ab initio* Simulation Package[35] which is based on the density functional theory and the plane-wave pseudopotential method. The plane-wave cutoff energy was 400 eV for all calculations. The generalized gradient approximation[36] and the Perdew–Burke–Ernzerhof exchange-correlation function[37] were adopted. All geometry optimizations and electronic structure calculations were performed using periodic boundary conditions and Brillouin-zone integrations were performed using a 1×1×21 Monkhorst–Pach grid.[38] Criterion of convergence was selected as the residual forces being smaller than 0.01 eV/Å and the change of total energy being smaller than $10^{-4}$ eV. To avoid the interaction of neighbored ribbons, GNRs are separated from each other by a distance greater than 15 Å of vacuum in our calculations.

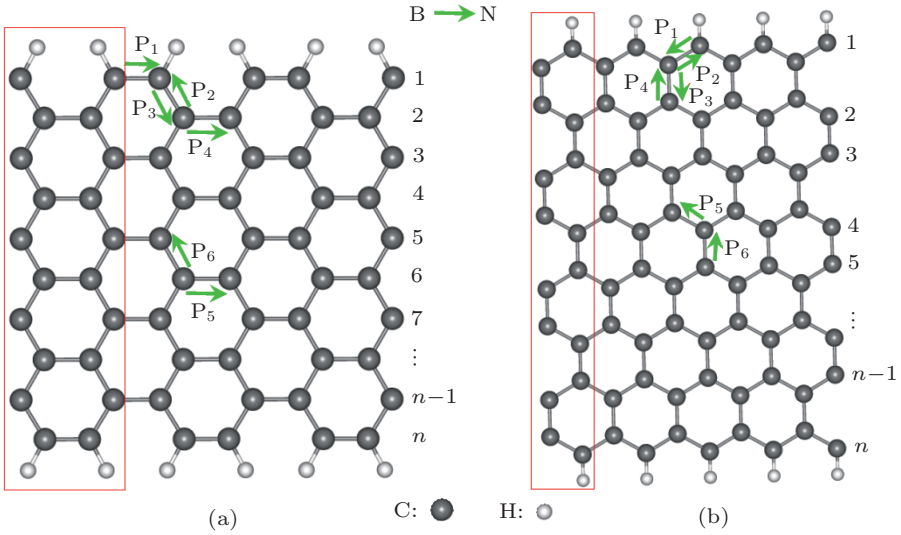



**Fig. 1.** (colour online) Atomic models of (a) AGNR and (b) ZGNR. The green arrows labeled by $P_1$–$P_6$ represent six unequivalent doping sites of B/N pair in GNR. The directions of arrows are all from B to N. The gray and white balls correspond to carbon and hydrogen atoms, respectively. The bandwidth is indicated by '$n$' , which is the number of the carbon atoms along the bandwidth direction. The prime cell of GNR is marked by the red square frame.

## 3. Results and discussion

### 3.1. Binding energies of doped GNRs

First, the binding energies of GNRs doped by B/N bonded pair were calculated and six unequivalent sites were considered as shown in Fig. 1. The calculated supercell of AGNR (ZGNR) is 3 (5) prime cells including a B/N pair and the prime cell of GNR is marked by red square frame in Fig. 1. The binding energy ($E_b$)

is defined as[27]

$$E_{\rm b} = E_{\rm B/N} + 2E_{\rm C} - (E_{\rm ribbon} + E_{\rm B} + E_{\rm N}), \quad (1)$$

where $E_{\rm B/N}$, $E_{\rm ribbon}$ and $E_{\rm C}$, $E_{\rm B}$, $E_{\rm N}$ are the total energies of GNRs doped by B/N pair, pure GNRs and free carbon, boron, nitrogen atoms, respectively.

The binding energies of B/N pair doping in AGNR and ZGNR are shown with solid lines in Figs. 2(a) and 2(c). It is very clear that B/N pair doping site $P_1$ is the most stable site in AGNR. For ZGNR, the most stable doping site is site $P_2$. Site $P_1$ in AGNR and site $P_2$ in ZGNR are both at the edge of ribbons. That means B/N pair doping in GNR tends to happen at the edge of ribbons.

Then, single B or single N doping and unbonded B/N co-doping at the ribbon edge were investigated also. In Figs. 2(a) and 2(c), the red, the blue and the black dotted lines are, respectively, the binding energy of unbonded B/N co-doping, single B doping and single N doping at the edges of 8-AGNR and 7-ZGNR and the corresponding atomic models are shown in Figs. 2(b) and 2(d) respectively. Listed in Table 1 are the binding energies of 8-AGNR and 7-ZGNR doped at the ribbon edge. It can be found that for both of 8-AGNRs and 7-ZGNRs, the binding energies of B/N bonded pair doping are smaller than those of single B doping and unbonded B/N co-doping. It demonstrates that B and N atoms prefer to bond into B/N pair, just like their doping in CNTs.[30] So, B/N bonded pair doping in GNR is realizable in theory.

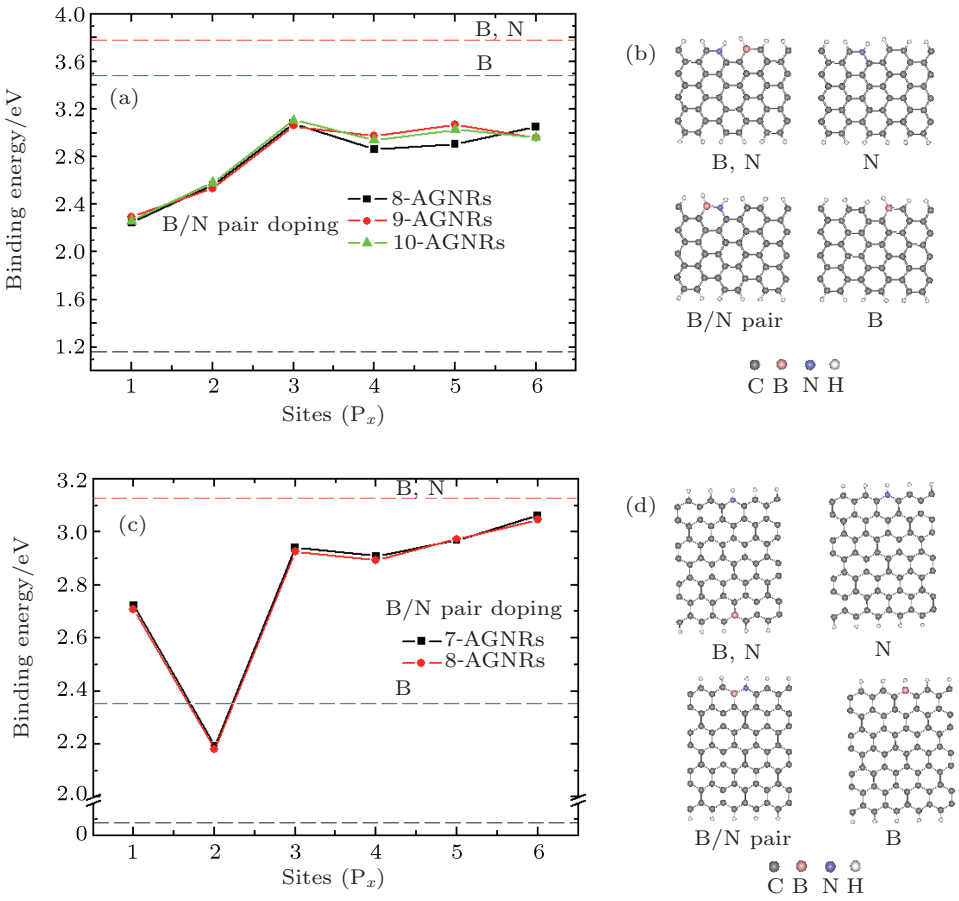



**Fig. 2.** (colour online) (a) The binding energies of B/N pair doping in 8, 9, 10-AGNRs at six unequivalent doping sites; (b) the computational model of 8-AGNR doping at the ribbon edge; (c) the binding energies of B/N pair doping in 7, 8-ZGNRs at six unequivalent doping sites; (d) the computational model of 7-ZGNR doping at the ribbon edge. The gray, pink, blue and white balls correspond to carbon, boron, nitrogen, and hydrogen atoms, respectively. Red, blue and black dotted lines in panels (a) and (c) are the binding energies of B, N co-doping, B doping and N doping at the edges of 8-AGNR and 7-ZGNR, respectively.

**Table 1.** Binding energies of 8-AGNR and 7-ZGNR doped at the ribbon edges.

| | N doping | B doping | B, N co-doping (unbonded) | B/N pair doping (bonded) |
|---|---|---|---|---|
| 8-AGNRs | 1.1693 | 3.4815 | 3.7834 | 2.2465 (at $P_1$) |
| 7-ZGNRs | 0.0702 | 2.3522 | 3.1215 | 2.1912 (at $P_2$) |

### 3.2. Electronic structures of AGNR doped by B/N pair at the ribbon edge

Considering that the edge of GNR plays an important role in the electronic structure, the electronic structure of AGNR doped by B/N bonded pair at four unequivalent doping sites ($P_1$, $P_2$, $P_3$, and $P_4$ in Fig. 1(a)) of the ribbon edges were investigated. The supercell selected in the present research is 3 prime cells of 8-AGNRs including a B/N pair. The energy gap ($E_{gap}$), the top of valance band (VB) and the bottom of conduction band (CB) of pure GNR and GNR doped by B/N bonded pair at four unequivalent sites, respectively, are listed in Table 2. It is obvious that the $E_{gap}$ of 8-AGNR doped by B/N pair is sensitive to doping site. For 8-AGNR with B/N pair doping at $P_1$ and $P_4$ sites, the $E_{gap}$ is bigger than that of pure 8-AGNR, because the doping shifts the top of VB down and the bottom of CB up respectively. For 8-AGNR with B/N pair doping at $P_2$ site, the top of VB and the bottom of CB are both shifted up, but the change range of VB is greater than that of CB, so the $E_{gap}$ turns small compared with that of pure AGNRs. For the B/N pair doping at $P_3$ site in 8-AGNR, the top of VB and the bottom of CB are both shifted down, but the change range of VB is smaller than that of CB, thus the $E_{gap}$ turns small also.

**Table 2.** Energy gaps, energies at the top of valance band (VB) and the bottom of conduction band (CB) of 8-AGNR doped by B/N pair at four unequivalent sites.

| | pure | $P_1$ | $P_2$ | $P_3$ | $P_4$ |
|---|---|---|---|---|---|
| Energy gap/eV | 0.3228 | 0.5016 | 0.1756 | 0.1896 | 0.6230 |
| Top of VB/eV | –3.3398 | –3.4273 | –3.1605 | –3.3548 | –3.4843 |
| Bottom of CB/eV | –3.0172 | –2.9257 | –2.9849 | –3.1652 | –2.8612 |

In order to clarify the influence of B/N bonded pair, the total density of states (TDOS) and partial density of states (PDOS) of 8-AGNR doped by B/N pair at $P_1$, $P_2$, $P_3$, and $P_4$ sites are shown in Figs. 3(a), 3(d), 3(e) and 3(f) respectively. When the doping sites are $P_1$ and $P_4$ (Figs. 3(a) and 3(f)), there are a peak at the bottom of CB in PDOS of B atoms and also a peak at the top of VB in PDOS of N atoms, which means that the B atoms mainly affect the bottom of CB and the N atoms mainly affect the top of VB for both $P_1$ and $P_4$ sites. For the doping sites $P_2$ and $P_3$, it can be found from Figs. 3(d) and 3(e) that the top of VB and the bottom of CB are influenced by both B and N atoms. In periodic table of elements, the atomic numbers of B, C, and N increase by one in turn. The 2s- and the 2p-electronic orbit energies of B (N) atom are higher (lower) than those of C atom.[1)] So, B (N) atom doping will move the corresponding band levels of GNR up (down). For AGNR doped by B/N pair at $P_1$ or $P_4$ site, the $E_{gap}$ increases because the top of VB is influenced by N atom and the bottom of CB is influenced by B atom. But for AGNR doped by B/N pair at $P_2$ or $P_3$ site, the $E_{gap}$ decreases because the top of VB and the bottom of CB are influenced by both B and N. All the results mentioned above indicate that the $E_{gap}$ of AGNRs doped by B/N pair is sensitive to the doping site, which arises from the different influences of B and N atoms on energy band.

### 3.3. Electronic structures of NB/N pair doped AGNRs with different widths

Then, the electronic structures of $n$-AGNRs ($n$ = 8, 9 and 10) doped by B/N pair at $P_1$ site, the most stable site, were investigated. The values of $E_{gap}$ of 8, 9, 10-AGNRs doped by B/N pair are listed in Table 3. Compared with the $E_{gap}$ of pure AGNR, the $E_{gap}$ of AGNR doped by B/N pair is increased for 8-AGNR, decreased for 9-AGNR and not obvious changed for 10-AGNR. Their TDOS and PDOS spectra are shown in Figs. 3(a), 3(b), and 3(c). For 8-AGNR, the top of VB is affected mainly by N atom and the bottom of CB is affected mainly by B atom, so the top of VB is shifted down and the bottom of CB is shifted up: the $E_{gap}$ of 8-AGNR doped by B/N pair is increased. For 9-AGNR, the top of VB is affected mainly by B atom and the bottom of CB is affected mainly by N atom. So the top of VB is shifted up and the bottom of CB is shifted down: the $E_{gap}$ of 9-AGNR doped by B/N pair is decreased. For 10-AGNR, because the influences of B and N on the top of VB and the bottom of CB is almost equal, the $E_{gap}$ of 10-AGNR doped by B/N pair is almost unchanged.

[1)] The atomic energy levels of free N, C and B atoms calculated by VASP are listed below: the 2s orbit of N, C and B atoms are –18.6085, –13.7815, and –9.4599 eV respectively; the 2p orbit of N, C and B atoms are –7.1340, –5.3217, and –3.6212 eV respectively.

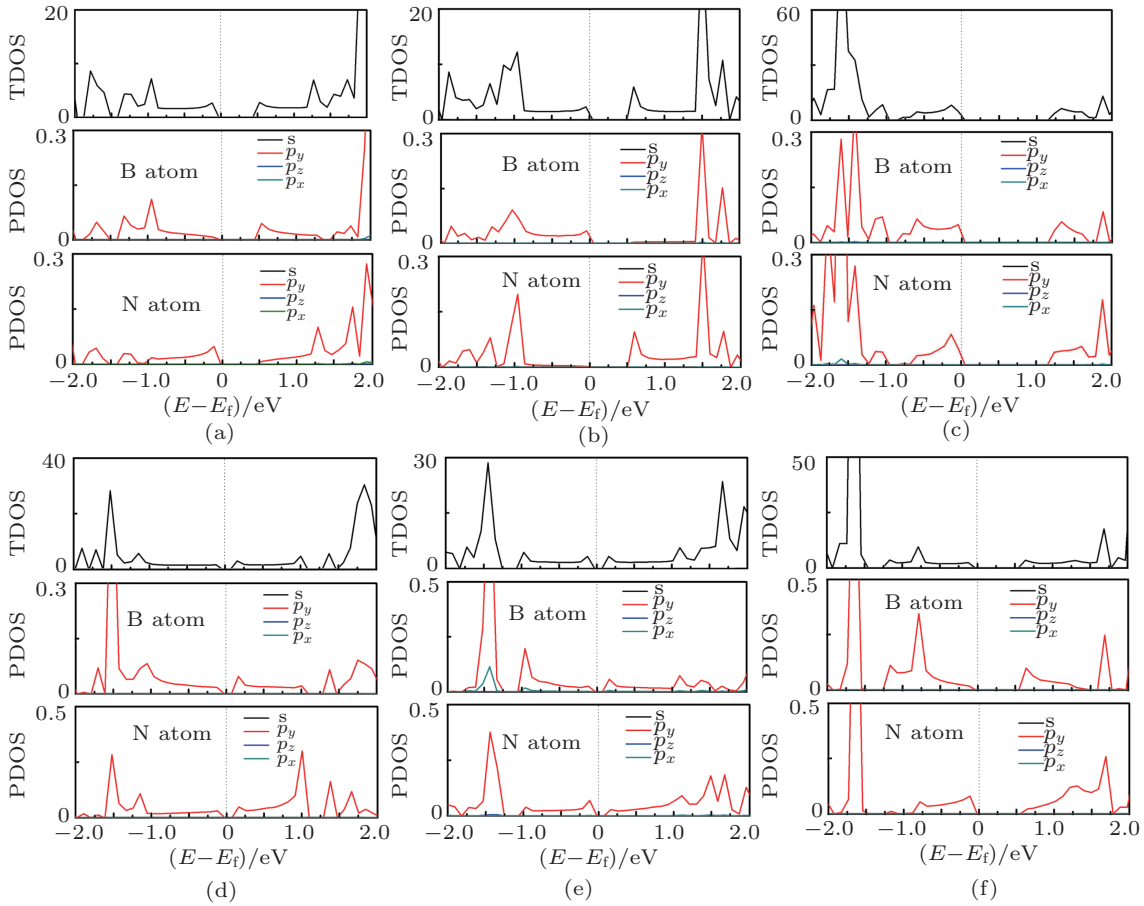



**Fig. 3.** (colour online) (a)–(c) TDOS and PDOS of 8, 9, 10-AGNRS doped by B/N pair at $P_1$ site respectively. (d)–(f) TDOS and PDOs of 8-AGNR doped by B/N pair at $P_2$, $P_3$ and $P_4$ sites respectively.

**Table 3.** Energy gaps of pure AGNR and doped AGNR (eV).

| | Pure | B/N pair doping at $P_1$site |
|---|---|---|
| 8-AGNRs | 0.3228 | 0.5016 |
| 9-AGNRs | 0.7292 | 0.5799 |
| 10-AGNRs | 1.1724 | 1.1821 |

It has been demonstrated that the $E_{gap}$ of pure AGNR is a periodic oscillation function of ribbon width ($n$), whose period is three and AGNR can be divided into three classes,[14,19] whose ribbon widths are respectively $3p$, $3p+1$, and $3p+2$ ($p = 1, 2, 3, 4, \ldots$). Considering that, the electronic properties of AGNRs with different widths, doped by B/N pairs at $P_1$ site, were investigated further. Figure 4 shows the $E_{gap}$ values of pure AGNR and AGNR doped by B/N pair at $P_1$ site each as a function of the ribbon width ($n$). Compared with the $E_{gap}$ value of pure AGNR, the $E_{gap}$ value of $n$-AGNR doped by B/N pair is decreased for $n = 3p$, almost unchanged for $n = 3p+1$ and increased for $n = 3p+2$ and the oscillation range of energy gap tends to ease up, which indicates that the energy gap of AGNR can be selectively adjusted by B/N pair substitutional doping and that the doping is a feasible way for energy band engineering of GNRs.

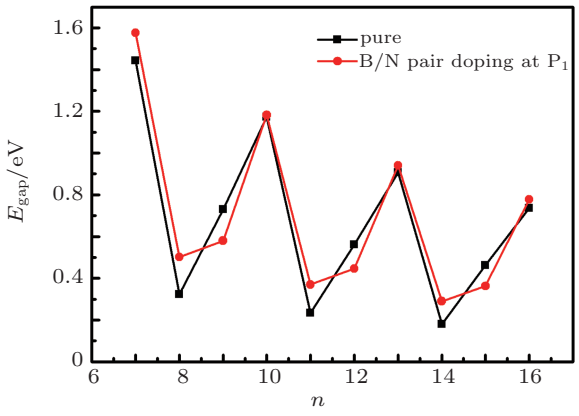



**Fig. 4.** (colour online) Values of energy gap ($E_{gap}$) of pure AGNR (black) and AGNR doped by B/N pair (red) at $P_1$ site each as a function of ribbon width ($n$).

### 3.4. Electronic structures of ZGNR doped by B/N pair at the ribbon edge

Finally, the electronic structures of 7-ZGNR doped by B/N pair at $P_2$ site, the most stable site, were investigated. The supercell in this calculation is shown in Fig. 5(a), including four prime cells of 7-ZGNR and a B/N pair doped at $P_2$ site and the energy band structures of pure 7-ZGNR and B/N pair doping 7-ZGNR are shown in Figs. 5(b) and 5(c). For pure 7-ZGNRs, due to the effect of ribbon edges, $\pi$ and $\pi^*$ subbands are degenerate around the Fermi level and there are level bands around $\Gamma$ point.[15] But at $K$ point, the $\pi$ ($\pi^*$) subband is degenerate with the next subband of VB (CB),[28] which are marked by red circles in Fig. 5(b). However, the degeneracies at $\Gamma$ and $K$ points are removed by B/N pair doping at $P_2$ site, which is similar to that of single B or single N doping.[28] As the consequence of removing degeneracy, the gap of 7-ZGNR is opened by B/N pair doping and 7-ZGNR is converted into semiconducor from original semimetal.

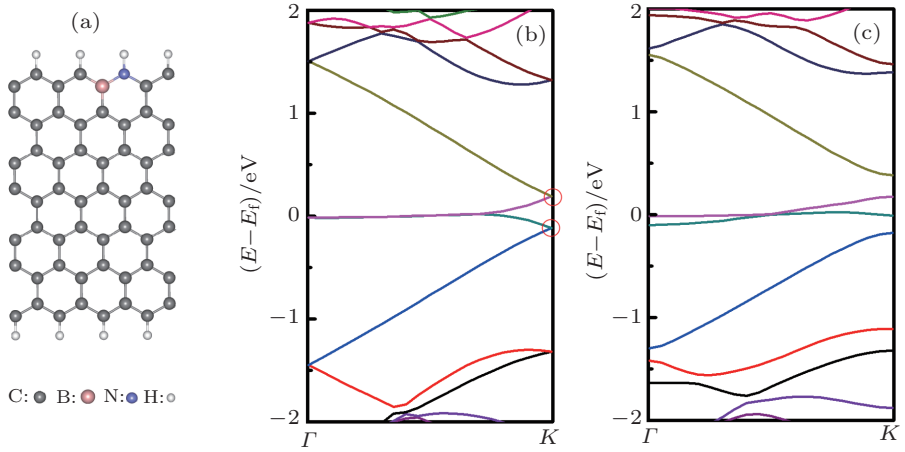



**Fig. 5.** (colour online) (a) the calculated model of 7-ZGNR, the energy band structures of (b) pure 7-ZGNR and (c) 7-ZGNR doped by B/N pair at $P_2$ site.

## 4. Conclusions

The electronic structure of GNR doped by B/N bonded pair is investigated by first principles. It is found that B/N bonded pair doping in GNR tends to happen at the edge of ribbons and is more stable than B doping and unbonded B/N co-doping. Moreover, the electronic structure of AGNR doped by B/N pair is very sensitive to doping site and the energy gaps of AGNRs with different widths can be selectively adjusted by B/N pair doping. For AGNR doped by B/N pair at $P_1$ site, the most stable doping site, the energy gap is shifted down for $3p$-AGNRs, shifted up for $(3p+2)$-AGNRs and almost unchanged for $(3p+1)$-AGNR. For 7-ZGNR doped by B/N pair at $P_2$ site, also the most stable doping site, the energy gap is opened. Unlike the semimetallic 7-ZGNR, the doped 7-ZGNR behaves as a semiconductor, which arises from the symmetry breaking induced by B/N pair doping. Our results bring forward a possible method for energy band engineering of GNRs and are beneficial to the design of graphene electronic device.

## References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y and Dubonos S V 2004 *Science* **306** 666

[2] Özyilmaz B, Herrero P J, Efetov D, Abanin D A, Levitov L S and Kim P 2007 *Phys. Rev. Lett.* **99** 166804

[3] Siegel D A, Zhou S Y, Gabaly F E, Fedorov A V, Schmid A K and Lanzara A 2008 *Appl. Phys. Lett.* **93** 243119

[4] Berger C, Song Z, Li X, Wu X, Brown N, N aud C, Mayou D, Li T, Hass J, Marchenkov A N, Conrad E N, First P N and de Heer W A 2006 *Science* **312** 1191

[5] Wu Y Q, Ye P D, Capano M A, Xuan Y, Sui Y and Qi M 2008 *Appl. Phys. Lett.* **92** 092102

[6] Lemme M C, Echtermeyer T J, Baus M and Kurz H 2007 *IEEE Electron Device Lett.* **28** 282

[7] Chen Z H, Lin Y M, Rooks M J and Avouris P 2007 *Physica* E **40** 228

[8] Han M Y, Özyilmaz B, Zhang Y B and Kim P 2007 *Phys. Rev. Lett.* **98** 206805

[9] Nakada K, Fujita M, Dresselhaus G and Dresselhaus M S 1996 *Phys. Rev.* B **54** 954

[10] Wakabayashi K and Hiroshima H 2001 *Phys. Rev.* B **64** 125428

[11] Zheng H X, Wang Z F, Luo T, Shi Q W and Chen J 2007 *Phys. Rev.* B **75** 165414

[12] Sasaki K, Murakami S and Saito R 2006 *Appl. Phys. Lett.* **88** 113110

[13] Castro A H, Guinea F, Peres N M, Novoselov K S and Geim A K 2009 *Rev. Mod. Phys.* **81** 109

[14] Lu Y H, Wu R Q, Shen L, Yang M, Sha Z D and Cai Y Q 2009 *Appl. Phys. Lett.* **94** 12111

[15] Li Z Y, Qian H Y, Wu J, Gu B L and Duan W H 2008 *Phys. Rev. Lett.* **100** 206802

[16] Areshkin D A and White C T 2007 *Nano Lett.* **7** 3253

[17] Gao W, Gong S L, Zhu J Q and Ma G J 2011 *Acta Phys. Sin.* **60** 027104 (in Chinese)

[18] Lu Y, Wang P J, Zhang C W, Jiang L, Zhang G L and Song P 2011 *Acta Phys. Sin.* **60** 063103 (in Chinese)

[19] Yan Q M, Huang B, Yu J, Zheng F W, Zang J, Wu J and Duan W H 2007 *Nano Lett.* **7** 1469

[20] Zhou B H, Duan Z G, Zhou B L and Zhou G H 2010 *Chin. Phys.* B **19** 037204

[21] OuYang F P, Peng S L, Zhang H, Weng L B and Xu H 2011 *Chin. Phys.* B **20** 058504

[22] OuYang F P, Peng S L, Chen L N, Sun S Y and Xu H 2011 *Chin. Phys.* B **20** 027102

[23] Zhang Y H, Chen Y B, Zhou K G, Liu C H, Zeng J and Zhang H L 2009 *Nanotechnology* **20** 185504

[24] Biel B, Blase X, Triozon F and Roche S 2009 *Phys. Rev. Lett.* **102** 096803

[25] Wang X R, Li X L, Zhang L, Yoon Y, Weber P K and Wang H L 2009 *Sience* **324** 768

[26] Wei D C, Liu Y Q, Wang Y, Zhang H L, Huang L P and Yu G 2009 *Nano Lett.* **9** 1752

[27] Yu S S, Zheng W T, Wen Q B and Jiang Q 2008 *Carbon* **46** 537

[28] Huang B, Yan Q M, Zhou G, Wu J, Gu B L and Duan W H 2007 *Appl. Phys. Lett.* **91** 253122

[29] OuYang F P, Yang Z X, Xiao J, Wu D and Xu H 2010 *J. Phys. Chem.* C **114** 15578

[30] OuYang F P, Xiao J, Guo R, Zhang H and Xu H 2009 *Nanotechnology* **20** 055202

[31] Zhou Y G, Zu X T, Gao F, Nie J L and Xiao H Y 2009 *J. Appl. Phys.* **105** 014309

[32] Wang X M and Liu H 2011 *Acta Phys. Sin.* **60** 047102 (in Chinese)

[33] Xu Z, Lu W G, Wang W L, Gu C Z, Liu K H, Bai X D, Wang E and Dai H J 2008 *Adv. Mater.* **20** 3615

[34] Li Y T and Chen T C 2009 *Nanotechnology* **20** 375705

[35] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15

[36] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[37] Perdew J P, Burke K and Ernzerhof M 1998 *Phys. Rev. Lett.* **80** 891

[38] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188