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Structure and electronic properties of single-walled zigzag BN and B₃C₂N₃ nanotubes using first-principles methods

ABSTRACT

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The structure and the electronic properties of single-walled zigzag BN and B₃C₂N₃ nanotubes (n, 0; n=4–10) were investigated using first-principles calculations based on a density functional theory. A plane-wave basis set with periodic boundary conditions in conjunction with Vanderbilt ultrasoft pseudo-potential was employed. The energy gap of ZB₃C₂N₃NTs was calculated and compared with the corresponding value for BNNTs. It was found that in both types of nanotube (BNNTs and B₃C₂N₃NTs), the band gap energy is increased as the diameter of the tubes becomes larger and also these nanotubes are semiconductors with direct band gap. Although the band gap energy of the BN tubes are much larger than that of B₃C₂N₃ ones, they have similar dependence on the diameter of the tubes and a semiconducting characteristic is maintained. There is a peak near the conduction band in B₃C₂N₃NT nanotubes. Thus, energy gaps are reduced. These kind of ternary BCN nanotubes are of n-type semiconductors.

Keywords: *First-principles calculations; Boron Nitride nanotube; B₃C₂N₃ nanotube; Electronic properties; Density functional theory (DFT).*

INTRODUCTION

Following the discovery of carbon nanotubes (CNTs) in 1991 [1], boron nitride nanotubes (BNNTs) have attracted considerable research interest [2, 3]. BNNTs are expected to have enormous potential applications due to their electronic properties, high thermal and chemical stability [2, 4, and 5]. BNNTs are the semiconductors that are characterized by wide band gap energy of about 5.5 eV and they are nearly independent of chirality and morphology of the tube [4]. The wide band gap energy of BNNTs is a substantial obstruct for their applications in electronic industry. Many efforts have been done to reduce the band gap energy by proposing the doping of BNNTs, especially the ones with carbons [6]. The resultant effects are pronounced that band gap energy of the system is reduced to about 1 eV as a result of substitutional carbon doping [5, 7].

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On the other hand, an interesting possibility arises from the inclusion of substitutional carbon atoms in the BN structure which leads to the formation of ternary BCN compounds ($B_xN_yC_z$) with distinct stoichiometries [8]. These nanotubes are attracting increasing interest due to their unique electronic properties [9]. One of the advantages of the $B_xN_yC_z$ nanotubes over their carbon counterparts is the relative simplicity in controlling the electronic properties of the tubes [10–14]. Theoretical calculations have predicted that the band structure of $B_xN_yC_z$ nanotubes can be controlled by changing their atomic composition and configuration [13–16].

These nanotubes are expected to have the intermediate quality between carbon and boron nitride nanotubes [17–21]. Therefore, it opens the possibility to produce materials with tunable electronic properties with potential applications in nano-device engineering [8, 22, and 23]. Some of these nanotubes have been synthesized experimentally using electric arc discharge, laser ablation, pyrolysis and laser vaporization [12, 24–28]. In spite of so many previous studies in the electronic properties of $B_xN_yC_z$ nanotubes with different atomic arrangement such as BC_2N , BCN, etc [8, 13, 16, 22, 29–36], there has been no detailed report on the electronic properties of $B_3C_2N_3$ nanotubes based on first-principles calculation. Additionally, the doping of BNNT is very important because these impurities with carbon are used to produce p and n-type semiconductors.

In this paper, a first-principles method based on density functional theory (DFT) was applied within the generalized gradient approximation to investigate the electronic structure and properties of single-walled zigzag $B_3C_2N_3$ nanotubes ($ZB_3C_2N_3NTs$). These structures were obtained from the $B_3C_2N_3$ sheets which are the most stable nanotubes [37]. The energy gap of $ZB_3C_2N_3NTs$ was calculated and compared with the corresponding values for BNNTs. There is a peak near the conduction band of these doped nanotubes. Therefore, energy gaps are decreased and the electrons are excited more easily from the donor level to the conduction one. In fact, these kind of ternary BCN nanotubes ($B_3C_2N_3$) are n-type semiconductors.

COMPUTATIONAL METHODS

Computational details

The calculations have been performed by the quantum espresso code [38], in which the spin polarized density functional theory method is implemented using the generalized gradient approximation (GGA) within the Perdew and Wang exchange correlation function. A plane-wave basis set with periodic boundary conditions in conjunction with Vanderbilt ultrasoft pseudo-potential was employed [39]. Kinetic energy cutoff was determined by performing appropriate convergence test 40 and 165 Ry for the wave function and the charge density, respectively. All the geometries were fully relaxed with residual forces smaller than $0.01\text{eV}/\text{\AA}$. One dimensional periodic boundary condition was applied along the tube axis. It means that a periodically repeating tetragonal unit cell with lattice constants of a, b and c was used. Both a and b were chosen to ensure negligible interaction between the tube and its periodic images (vacuum space of at least 10\AA), while c is relaxed during the optimization ($c=8.46\text{\AA}$). The zigzag single-walled $B_3C_2N_3$ nanotubes ($n, 0; n=4-10$) was studied and these structures were obtained from most stable sheets of $B_3C_2N_3$ according to ref. [37]. The unit cell of BN and $B_3C_2N_3$ nanotubes are shown in Figure 1(a-d).

The number of atoms in unit cell ($B_3C_2N_3NTs$) was 32, 40, 48, 56, 64, 72 and 80. Monkhorst-pack mesh of k-points ($1\times 1\times 6$) is used for sampling the one-dimensional Brillouin zone during geometry optimization. The number of k-points was determined from convergence tests.

RESULTS AND DISCUSSION

Similar to CNTs, achieved by rolling graphene, BNNTs can be produced by rolling up the hexagonal BN sheet into a tube. In this work, different possibilities arise from the inclusion substitutional carbon atoms into the BN sheets and rolling the sheets leads to the formation of ternary zigzag $B_3C_2N_3$ nanotubes ($n, 0; n = 4-10$) with specified stoichiometries. The structural parameters and average bond length for each nanotube after relaxation are listed in Table 1.

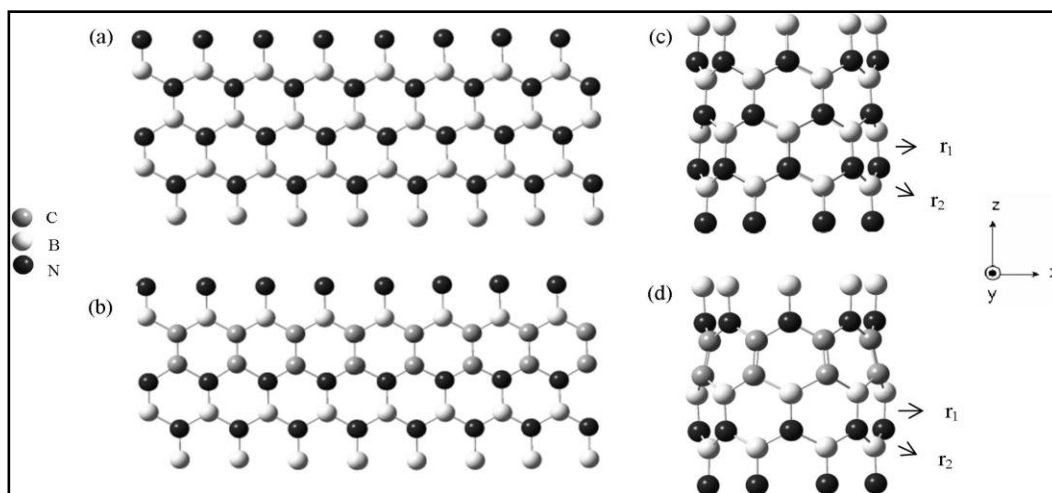


Fig.1. Illustration of (a) BN, (b) $B_3C_2N_3$ monolayer, (c) and (d) are the corresponding nanotube obtained by the similar procedure in ref. [31]. The atoms are represented by different colors as shown in the inset.

Table 1. B–N bonds length (r_1 and r_2) (Å) and average bond length (Å) of zigzag BN and $B_3C_2N_3$ nanotubes.

BNNTs	r_1	r_2	r_2-r_1	D_B	D_N	B–C	C–N	C–C
(4,0)	1.4157	1.4889	0.0732	3.2749	3.5778	-	-	-
(5,0)	1.4283	1.4686	0.0403	3.8579	4.0865	-	-	-
(6,0)	1.4327	1.4607	0.0280	4.8573	5.0536	-	-	-
(7,0)	1.4349	1.4551	0.0202	5.5156	5.6781	-	-	-
(8,0)	1.4351	1.4513	0.0162	6.4567	6.6019	-	-	-
(9,0)	1.4362	1.4494	0.0132	7.1511	7.2773	-	-	-
(10,0)	1.4371	1.4474	0.0103	8.0631	8.1783	-	-	-
$B_3C_2N_3$ NTs	r_1	r_2	r_2-r_1	D_B	D_N	B–C	C–N	C–C
(4,0)	1.4387	1.4911	0.0524	3.2333	3.5979	1.5770	1.4528	1.3538
(5,0)	1.4422	1.4708	0.0286	3.9500	4.1091	1.5560	1.4333	1.3543
(6,0)	1.4445	1.4621	0.0176	4.7544	5.0656	1.5423	1.4223	1.3551
(7,0)	1.4453	1.4592	0.0139	5.3898	5.6774	1.5336	1.4168	1.3559
(8,0)	1.4469	1.4569	0.0100	6.2959	6.5909	1.5266	1.4134	1.3581
(9,0)	1.4488	1.4564	0.0075	6.9573	7.2463	1.5209	1.4114	1.3594
(10,0)	1.4499	1.4570	0.0070	7.8399	8.1413	1.5170	1.4110	1.3604

It can be seen in Figure 1, there are two kinds of B–N bonds length (r_1 and r_2) in zigzag $B_3C_2N_3$ nanotubes similar to BN ones, which are representative of the bond length along and around the tube axis (z -direction), respectively. As shown in Table 1, the value of r_2 is larger than r_1 for both types of nanotube (BNNTs and $B_3C_2N_3$ NTs), and the difference between them (r_2-r_1) becomes smaller as the diameter of nanotube increases.

The changes in r_1 and r_2 are mainly affected by the bond strain on the curvature surface. The large curvature (in small diameter of nanotube) causes strong bond strain and therefore the value of r_2 is larger than r_1 . The boron and nitrogen atoms in both types of nanotubes form homocentric cylinders with different diameters of D_B and D_N , respectively. The diameter of nitrogen cylinder (D_N) is larger than that of boron one (D_B). As the curvature increases, the energy gap decreases due

to the larger orbital overlap in more curved structures. Higher curvature leads to a lower energy gap because of a lower orbital overlap and higher strain. The appearance of some sp^3 hybridization due to the curvature of the BN ribbons causes a decrease in ionicity of the bonding and in the band gap. This hybridization induces a downward shift of π^* , leads to a decrease of band gaps during the rolling of BN ribbons.

In $B_3C_2N_3$ NT structure, the bond lengths of C–N and C–B decrease systematically while the bond length of C–C increases slightly with the diameter of tube. For the zigzag BN and $B_3C_2N_3$ nanotubes ($n, 0; n=4-10$), the electronic band structures were studied along the ΓZ direction. The band structures of BNNTs {a; (4, 0), b; (7, 0), c; (10, 0)}, and $B_3C_2N_3$ NTs {d; (4, 0), e; (7, 0), f; (10, 0)} are shown in Figure 2 (a-f).

The Fermi energy (E_f) and the band gap energy (E_g) are listed in Table 2. In both types of nanotubes (BNNTs and $B_3C_2N_3$ NTs), the value of band gap energy becomes higher by increasing the tube diameter. Also, both of the nanotubes are

semiconductors with direct band gap. The calculated E_g of zigzag BNNTs is in good agreement with previous prediction [40].

Figure 3 shows the values of band gap energy as a function of the tube diameter. Although the band gap energy of the pristine tubes is much larger (about 1.5–1.8 eV) than that of $B_3C_2N_3$ ones, they have similar dependence on the tube diameter and the semiconducting characteristic nevertheless remains. It means that the effect of tube diameter on the electronic property of BNNT structures of this atomic arrangement is independent of carbon doping. The BN nanotube doped with a single carbon atom has a localized bound state in the band gap near the bottom of conduction band. But, when boron or a nitrogen atom is replaced by a carbon one, the localized bound state is near the top of the valence band [41]. As shown in Figure 2, the $B_3C_2N_3$ nanotubes of equal number of B and N atoms doped with carbon atoms (Figure 1) have an extra valence electron and provide an occupied level in the band gap.

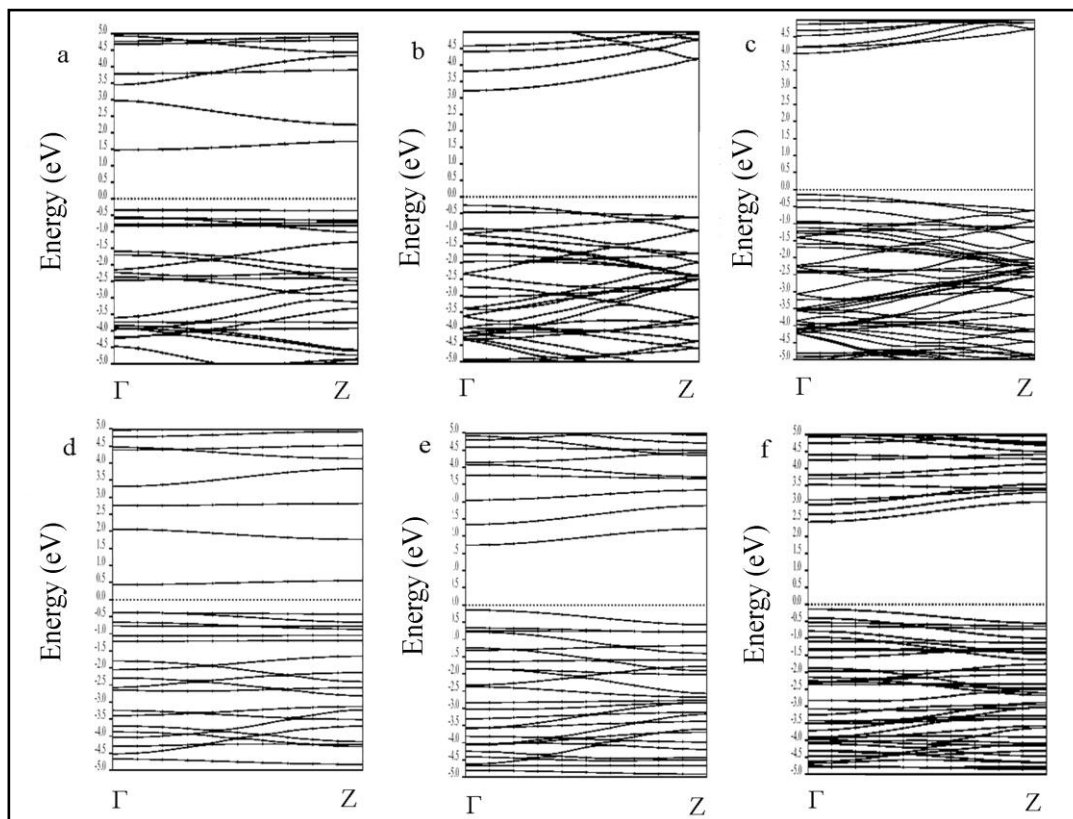


Fig. 2. The calculated band structures of BNNTs {a; (4,0), b; (7,0), c; (10,0)}, and of $B_3C_2N_3$ NTs {d; (4,0), e; (7,0), f; (10,0)}. The electronic band structures along the ΓZ direction are shown. The Fermi level is at 0 eV.

Table 2. Calculated Fermi energy (eV) and band gap energy (eV) of BN and B₃C₂N₃ nanotubes. (Direct band gap is denoted by 'D'.)

BNNTs	(4,0)	(5,0)	(6,0)	(7,0)	(8,0)	(9,0)	(10,0)
E _f	-3.68	-3.47	-3/36	-3.24	-3.07	-3.17	-3.02
E _g	2.4 (D)	3.0 (D)	3.3 (D)	3.9 (D)	4.2 (D)	4.5 (D)	4.8 (D)
B ₃ C ₂ N ₃ NTs							
E _f	-3.57	-3.23	-2.78	-2.85	-2.61	-2.72	-2.58
E _g	0.9 (D)	1.3 (D)	1.8 (D)	2.1 (D)	2.4 (D)	2.7 (D)	3.0 (D)

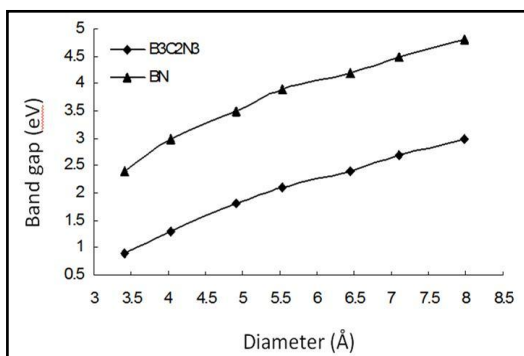


Fig. 3. The band gap energies of BN and B₃C₂N₃ nanotubes as a function of tube diameter.

investigated from density of states (DOS) viewpoint and the results are in agreement with those obtained from energy band structure. The DOS of BNNTs {a; (4, 0), b; (7, 0), c; (10, 0)} and of B₃C₂N₃NTs {d; (4, 0), e; (7, 0), f; (10, 0)} are shown in Figure 4(a-f). As it can be seen, the DOS for spins with orientation up and down are completely equal. The DOS near Fermi level is very small in BNNTs. It means that a few of valence electrons occupy the highest level. The electrons in valence band can rarely transit to conduction band and the conductivity of pure BNNTs is very low [41]. So, there is a peak near conduction band for these doped nanotubes.

The conductivity of BNNTs doped with carbon atoms (B and N substituted) was also

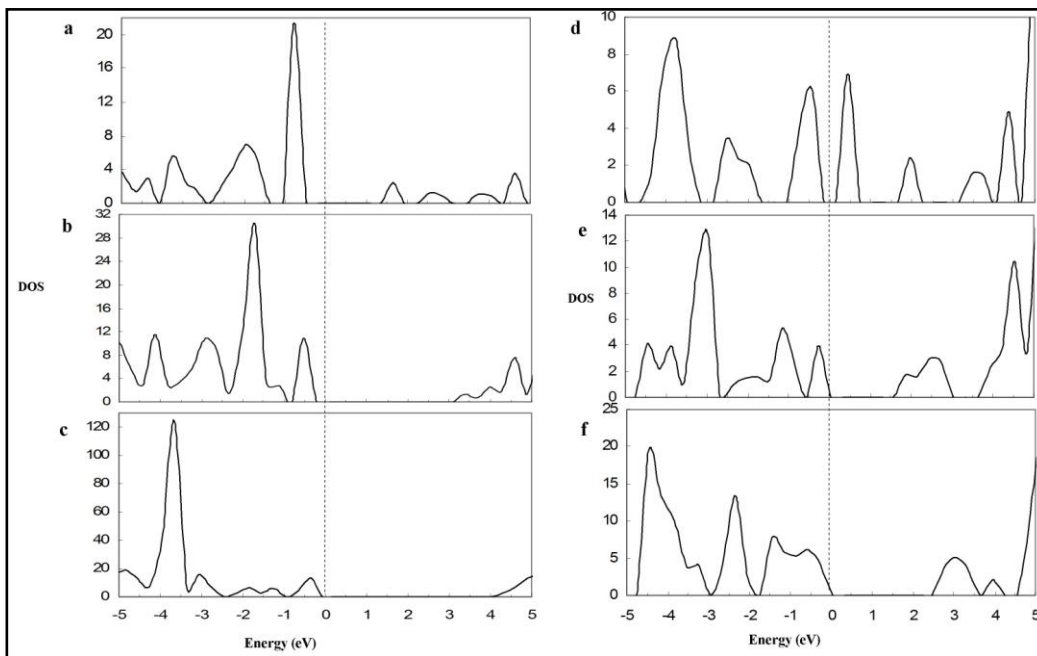


Fig. 4. DOS of BNNTs {a; (4, 0), b; (7, 0), c; (10, 0)} and of B₃C₂N₃NTs {d; (4, 0), e; (7, 0), f; (10, 0)}. The Fermi level is at 0 eV and shown with dotted line.

Partial density of states (PDOS) were calculated for B and N atoms in BN and B, N and C atoms in $B_3C_2N_3$ nanotubes, respectively. The PDOS of BNNTs {a; (4, 0), b; (10, 0)} and of $B_3C_2N_3$ NTs {(c) (4, 0), d; (10, 0)} were illustrated in Figure 5(a-d). As it can be seen, the occupied and unoccupied states are mainly contributed by 2p orbitals of N and B atoms near the Fermi level in BNNTs, respectively. While 2s and 2p orbitals of B and N atoms strongly mix together in lower and

higher energy regions far from the Fermi level. The significant contribution of C-2p was seen in both occupied and unoccupied levels of $B_3C_2N_3$ NT because the numbers of B and N atoms are still equal after doping the carbon atoms. The 2p orbitals of C atoms near the boron atoms contributed to the top of the valence band, while the 2p orbitals of C atoms near the nitrogen atoms contributed to the bottom of conduction band (Figure 1).

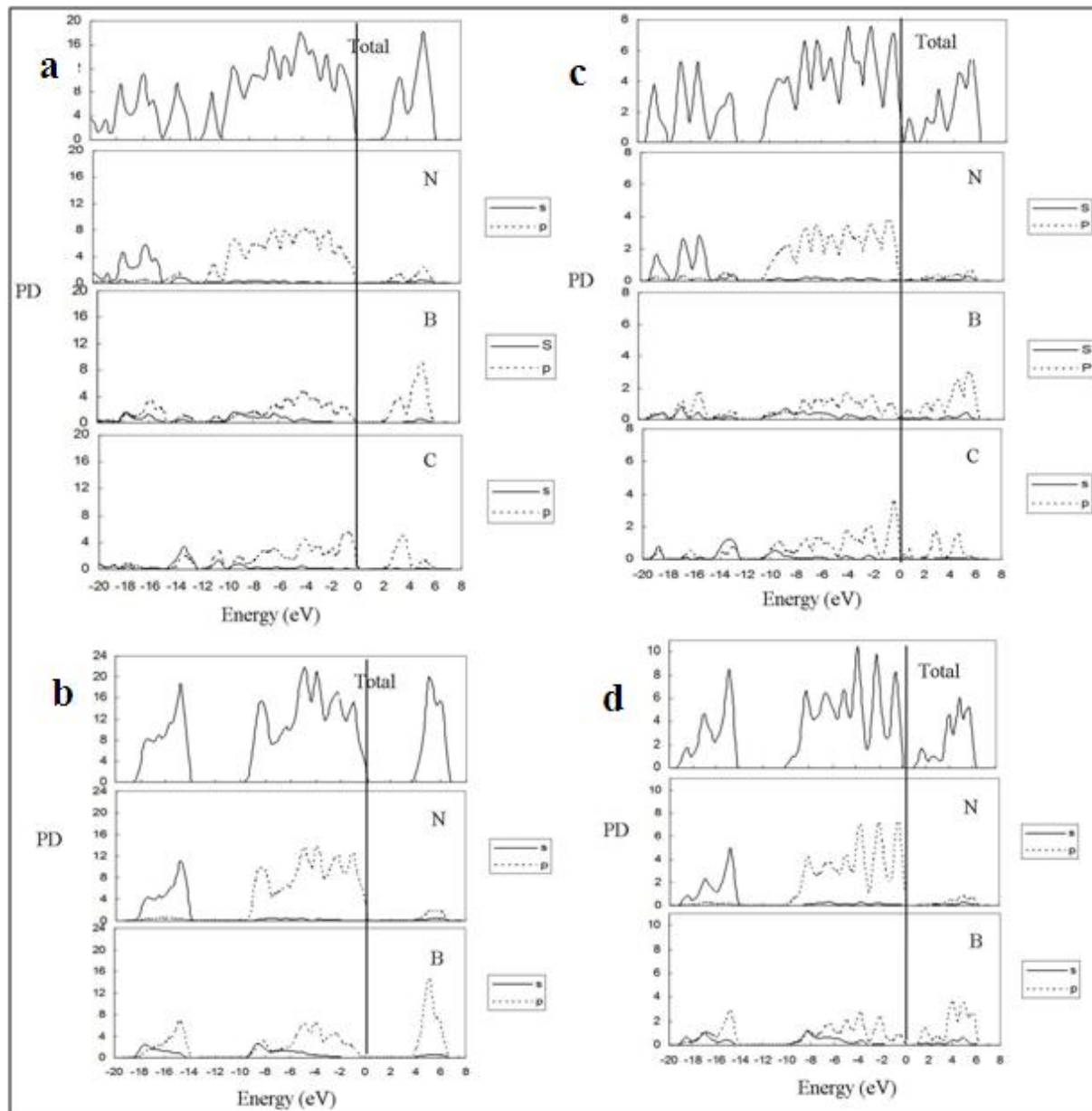


Fig. 5. LDOS of BNNTs {a; (4, 0), b; (10, 0)} and of $B_3C_2N_3$ NTs {(c) (4, 0), d; (10, 0)}. The Fermi level is at 0 eV and shown with dotted line.

CONCLUSIONS

The structural and electronic properties of zigzag BN and $B_3C_2N_3$ nanotubes ($n, 0; n=4-10$) were investigated by first-principles spin polarized total energy calculations. It was found that the value of band gap energy becomes higher in both types of nanotubes (BNNTs and $B_3C_2N_3$ NTs) by increasing the tube diameter. Also, both nanotubes are semiconductors with direct band gap. Although the band gap energy of the BN tubes are much larger than that of $B_3C_2N_3$ ones, they have similar dependence on the tube diameter and semiconducting character nevertheless remains. It means that the effect of the tube diameter on its electronic property is independent of carbon doping in BNNTs. There is a peak near the conduction band in $B_3C_2N_3$ NTs nanotubes. Therefore, energy gaps are decreased and the electrons are exited more easily from donor level to conduction one. In fact, these kind of ternary BCN nanotubes ($B_3C_2N_3$) are n-type semiconductors. The significant contribution of C-2p was seen in both occupied and unoccupied levels of $B_3C_2N_3$ NTs because the numbers of B and N atoms are still equal after doping the carbon atoms. The 2p orbital of C atoms near the boron and nitrogen atoms contributed to the top of the valence band and the bottom of conduction one, respectively.

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REFERENCES

- [1] Iijima S., (1991), Helical microtubules of graphitic carbon. *Nature*. 354: 56-58.
- [2] Rubio A., Corkill J. L., Cohen M. L., (1994), Theory of graphitic boron nitride nanotubes. *Phys. Rev. B*. 49: 5081-5084.
- [3] Chopra N. G., Luyken R. J., Cherrey K., Crespi V. H., Cohen M. L., Louie S. G., Zettl A., (1995), Boron nitride nanotubes. *Science*. 269: 966-967.
- [4] Blasé X., Rubio A. S., Louie G., Cohen M. L., (1994), Stability and band gap constancy of boron nitride nanotubes. *Europhys. Lett*. 28: 335-340.
- [5] Chen Y., Zou J., Campbell S. J., Caer G. L., (2004), Boron nitride nanotubes: Pronounced resistance to oxidation. *Appl. Phys. Lett*. 84: 2430-2433.
- [6] Golberg D., Bando Y. C., Tang C., Zhi C. Y., (2007), Boron nitride nanotubes. *Adv. Mater*. 19: 2413-2432.
- [7] Li J., Zhou G., Chen Y., Gu B. L., Duan W., (2009), Magnetism of C atoms on BN nanostructures: Implications for functional nanodevices. *J. Am. Chem. Soc*. 131: 1796-1801.
- [8] Matos M., Azevedo S., Kaschny J. R., (2009), On the structural properties of B-C-N nanotubes. *Solid State Commun*. 149: 222-226.
- [9] Yang Y., Zhang Z. F., Kan K., Ge Y. L., Sun Y. L., Shi K. Y., (2012), Preparation and characterization of BCN nanotubes and their sensitivity to NO_x at room temperature. *Adv. Mater. Research*. 616: 1778-1782.
- [10] Stephan O., Ajayan P. M., Colliex C., Redlich Ph., Lambert J. M., Bernier P., Lefin P., (1994), Doping graphitic and carbon nanotube structures with boron and nitrogen. *Science*. 266: 1683-1685.
- [11] Wengsieh A., Cherrey K., Chopra N. G., Blasé X., Miyamoto Y., Rubio A., Cohen M. L., Louie S. G., Zettl A., Gronsky A. R., (1995), Synthesis of $B_xC_yN_z$ nanotubules. *Phys. Rev. B*. 51: 11229-11232.
- [12] Redlich P., Loeffler J., Ajayan P. M., Bill J., Aldinger F., Ruhle M., (1996), B.C.N nanotubes and boron doping of carbon nanotubes. *Chem. Phys. Lett*. 260: 465-470.
- [13] Miyamoto Y., Rubio A., Cohen M. L., Louie S. G., (1994), Chiral tubules of hexagonal BC_2N . *Phys. Rev. B*. 50: 4976-4979.

- [14] Blasé X., Charlier J. C., De Vita A., Car R., (1997), Theory of composite $B_xC_yN_z$ nanotube heterojunctions. *Appl. Phys. Lett.* 70: 197-200.
- [15] Liu A. Y., Wentzcovitch R. M., Cohen M. L., (1989), Atomic arrangement and electronic structure of BC_2N . *Phys. Rev. B.* 39: 1760-1765.
- [16] Blasé X., Charlier J-Ch., De Vita A., Car, R., (1999), Structural and electronic properties of composite $B_xC_yN_z$ nanotubes and heterojunctions. *Appl. Phys. A.* 68: 293-300.
- [17] Nozaki H., Itoh, S., (1996), Structural stability of BC_2N . *J. Phys. Chem. Solids.* 57: 41-49.
- [18] Enyashin A. N., Yu Makurin N., Ivanovskii A. L., (2004), Quantum chemical study of the electronic structure of new nanotubular systems: α -graphyne-like carbon, boron–nitrogen and boron–carbon–nitrogen nanotubes. *Carbon.* 42: 2081-2089.
- [19] Martins D. R., Chacham J H., (2011), Disorder and segregation in B–C–N graphene type layers and nanotubes: Tuning the band gap. *ACS Nano.* 5: 385-393.
- [20] Fan Y., Zhao M., He T., Wang Z., Zhang X., Xi Z., Zhang H., Hou K., Liu X., Yueyuan X., (2010), Electronic properties of BN/C nanotube heterostructures. *J. Appl. Phys.* 107: 094304-094310.
- [21] Xiao H. P., He C., Zhang C. X., Sun L. Z., Zhou P., Zhong J., Xiao H. P., (2013), Stability electronic structures and transport properties of armchair (10, 10) BN/C nanotubes. *J. SolidState Chem.* 200: 294-298.
- [22] Baei M. T, Ahmadi Peyghan A., Moghimi M., Hashemian S., (2013), Electric field effect on the zigzag (6,0) single–wall BC_2N nanotube for use in nano-electronic circuits. *J. Mol. Model.* 19: 97-107.
- [23] Bhattacharya S., Majumder C., Das G. P., (2009), 3d Transition metal decorated B–C–N composite nanostructures for efficient hydrogen storage: A first-principles study. *Bull. Mater. Sci.* 32: 353-360.
- [24] Sen R., Satishkumar B. C., Govindaraj A., Harikumar K. R., Raina G., Zhang J. P., Cheetham A. K., Rao C.N., (1998), B–C–N, C–N and B–N nanotubes produced by the pyrolysis of precursor molecules over CO catalysts. *Chem. Phys. Lett.* 287: 671-676.
- [25] Zhang Y., Gu H., Seunage K., Ijima S., (1997), Heterogeneous growth of B.C.N nanotubes by laser ablation. *Chem. Phys. Lett.* 279: 264-269.
- [26] Enouz S., Stephan O., Cochon J. L., Colliex C., Loiseau, A., (2007), C–BN patterned single-walled nanotubes synthesized by laser vaporization. *Nano Lett.* 7: 1856-1862.
- [27] Iyyamperumal E., Wang S., Dai L., (2012), Vertically aligned BCN nanotubes with high capacitance. *ACS Nano.* 6: 5259-5265.
- [28] Yin Y., Chen Y., (2011), Synthesis and growth mechanism of BCN nanowires. *Mater. Lett.* 65: 2476-2478.
- [29] Blase X., (2000), Properties of composite $B_xC_yN_z$ nanotubes and related heterojunctions. *Comput. Mater. Sci.* 17: 107-114.
- [30] Azevedo S., de Pavia R., Kaschny J. R., (2006), Stability and electronic structure of $B_xN_yC_z$ nanotubes. *J. Phys. Condens. Matter.* 18: 10871–10879.
- [31] Guo C. S., Fan W. J., Chen Z. H., Zhang R. Q., (2006), First-principles study of single-walled armchair $C_x(BN)_y$ nanotubes. *Solid State Commun.* 137: 549-552.
- [32] Pan H., Feng Y. P., Lin J., (2006), Ab initio study of single-wall BC_2N nanotubes. *Phys. Rev. B.* 74: 045409-045413.

- [33] Ahmadi Peyghan A., Noei M., (2013), Fluorination of BC_3 nanotubes: DFT studies. *J. Mol. Model.* 19: 3941-3946.
- [34] Freitas A., Azevedo S., Machado M., Kaschny J. R., (2012), First-principles calculations of BC_4N nanostructures: stability and electronic structure. *Appl. Phys. A.* 108: 185-193.
- [35] Noei M., Ahmadi Peyghan A., (2013), A DFT study on the sensing behavior of a BC_2N nanotube toward formaldehyde. *J. Mol. Model.* 19: 3843-3850.
- [36] Beheshtian J., Ahmadi Peyghan A., (2013), Theoretical study on the functionalization of BC_2N nanotube with amino groups. *J. Mol. Model.* 19: 2211-2216.
- [37] Azevedo S., de Pavia R., (2006), Structural stability and electronic properties of carbon–boron nitride compounds. *Europhys. Lett.* 75: 126-132.
- [38] <http://www.pwscf.org/>.
- [39] Vanderbilt D., (1990), Soft self-consistent pseudopotentials in generalized eigenvalue formalism. *Phys. Rev. B.* 41: 7892-7895.
- [40] Jia J. F., Wu H. S., Jiao H., (2006), The structure and electronic property of BN nanotube. *Physica B.* 381: 90-95.
- [41] Zhao J. X., Dai B. Q., (2004), DFT studies of electro-conductivity of carbon–doped boron nitride nanotube. *Mat. Chem. Phys.* 88: 244-249.

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