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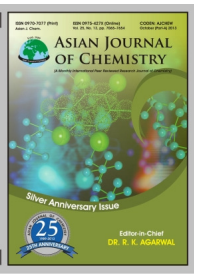

Stability and Electronic Properties of O_N-Doped Zigzag BC_2N Nanotubes

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The geometry, stability and electronic properties of O_N-doped zigzag (6,0), (7,0) and (8,0) BC_2N nanotubes are investigated by first-principles calculations based on the density functional theory (DFT). The structures for O_N-doped zigzag BC_2N nanotubes remain practically the same with negligible deformations. The results show that the O_N-doped (6,0) BC_2N nanotubes has the lowest formation energies, especially for the B-rich environment. With the tube diameter increasing, the relative stabilities of O_N-doped zigzag BC_2N nanotubes are significantly weakened. For the O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes, the Fermi levels are located inside the conduction band defining metallic characters. Moreover, O_N-doped (6,0) and (8,0) BC_2N nanotubes are direct gap semiconductors, while O_N-doped (7,0) BC_2N nanotubes is an indirect gap semiconductor.

Key Words: BC_2N Nanotubes, O_N-doped, Density functional theory, Stability and electronic properties.

INTRODUCTION

The discovery of carbon nanotubes (CNTs) by Iijima[1] has triggered great scientific interests in the structural, mechanical and electronic properties of tubular nanomaterials. However, the variations in their amazing electronic properties are related to the capability of synthesizing tubes with specific chiralities and tube diameters. The boron nitride nanotubes (BNNTs) which were non-carbon-layered structures were predicted to form. However, the boron nitride nanotubes showed a much stabilized electronic properties independently of their geometry, presenting an almost constant wide band gap of 5.5 eV[2]. They have weak conductivity and display insulators' characteristic, which limit their application severely. To some extent, the BCN compounds can be suitably engineered by compositions and arrangements of the B, C and N atoms in their structures based on the electronic and structure similarity between the B-N and C-C bonds.

For the hexagonal compound $B_xC_yN_z$ nanostructures, the BC_2N was believed to be one of the most stable stoichiometries, which the synthesis of BC_2N was first reported in 1995[3]. Analogously to carbon nanotubes, three stable ternary compounds which are labeled as type I, type II and type III can be obtained by rolling a hexagonal BC_2N sheet[4]. Theoretical calculations[5,6] predicted that the type II possessed the higher stability as compared to type II and type III due to the larger number of C-C and B-N bonds. The $B_xC_yN_z$ nanotubes can be synthesized by using several different techniques, such as chemical vapor deposition (CVD)[7-9], arch discharge[3,10,11] and pyrolysis[12]. These developments open up the possibility of producing materials with tunable electronic properties between graphite and boron nitride, suitable to the needs of a specific technological application. Recently, the optical and electronic properties of BC_2N nanotubes have been studied using first-principles calculation by Pan *et al.*[13,14]. They found that the optical and electronic properties of BC_2N nanotubes were closely related to both the diameter and chirality of the tubes. But the strain energy of the BC_2N nanotubes only depended on the diameter of the tubes. Kaschny *et al.*[15] recently studied the structural stability of BC_2N nanotubes using first-principles method based on density functional theory. The report by Turner *et al.*[16] showed that the energy associated with the BN/C interfaces can be minimized by the segregation of BN and C parts of the nanotube. A recent work on carbon and boron nitride nanotube heterojunctions carried out by Machado *et al.*[17], which they employed first-principle density functional theory to study the configurational variability of BC_2N nanotubes by varying the BN and C stripes' arrangements in order to form the nanotubes. Moreover, the tailoring of BC_2N nanotubes' electronic properties can be achieved by doping the tube as predicted in recent calculations[18]. The theoretical results demonstrate the Si impurities have lower formation energy for BC_2N nanotubes, as compared to Si in carbon nanotubes and boron nitride nanotubes. Even though important, the doped BC_2N nanotubes studies are in an early stage of development, requiring further works exploring aspects.

In this work, we apply a first-principle calculations method, based on the density functional theory (DFT) to investigate the stability and electronic properties of the oxygen atom substituted in the type II BC_2N nanotubes. We calculate the formation energies, band gap, density of states (DOS) of O_N - doped (6,0), (7,0) and (8,0) BC_2N nanotubes, which correspond the diameters of 4.7, 5.5 and 6.3 Å.

EXPERIMENTAL

Model and methods of calculation: In the present work, a 1 × 1 × 2 supercell of zigzag BC_2N nanotubes was constructed. The carbon and boron nitride nanotubes selected were (6,0), (7,0) and (8,0) zigzag-nanotubes with 48, 56 and 64 atoms, respectively. The optimized structure for pristine BC_2N nanotubes was show in Fig. 1(a). Periodic boundary conductions and the supercell approximation were considered. The oxygen atom was then incorporated as a substitutional atom in nitride site of zigzag BC_2N nanotube, as show in Fig. 1(b). In present study, the structure optimizations were performed by CASTEP[19,20] package, which used the density functional theory to obtain high accuracy systems. The atomic positions of the structure were relaxed up to the point of obtaining all force components smaller than 0.05 eV/Å.

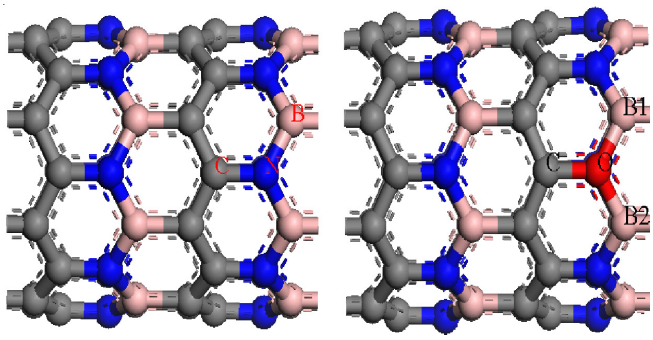

Fig. 1. Optimized structure: (a) pristine BC_2N nanotubes, (b) O_N-doped BC_2N nanotubes and the B, N, C and O atom are labeled by B, N, C and O, respectively

In order to investigate structural and electronic properties of the oxygen-doped BC_2N nanotubes, the first-principle calculations are performed based on the density functional theory (DFT)[21]. We employed the plane-wave pseudo-pontential (PWP) approach implemented in CASTEP, with a plane-wave kinetic cutoff of 380 eV. For the exchange and correlations terms the generalized gradients approximation (GGA) with the parametrization of Perdew-Wang generalized-gradient approximation (PW91) was used[22]. The interaction between ionic cores and valence electrons is modulated by Vandberbilt-type ultrasoft pseudo-potentials in the Kleinman-Bylander form[23]. Summation over the Brillouin zone was sampled by (1 × 1 × 5) mesh points in the k space using the Monkhorst-Pack scheme[24], resulting in three special k points along the tube axis.

RESULTS AND DISCUSSION

Geometric structure: Firstly, structural optimizations were obtained both for pristine BC_2N nanotubes and for oxygen atom substitute for nitride atom (O_N) in zigzag BC_2N nanotubes. From the fully relaxed structure (Fig. 1(b)), we can find that the O atom is incorporated on the BC_2N nanotubes with negligible local deformation. Typically, the bond angles of the hexagonal rings including the O atom change hardly, which are 120º presenting the same with the pristine nanotubes. The corresponding inter- atomic distances in O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes between substitution impurity and its adjacent atoms are given in Table-1. The values listed in this table are closed to the typical inter-atomic distances found in organic compounds. These values suggest a negligible interaction between O atom and other atoms in zigzag BC_2N nanotubes due to their similar electro negativity between N atom and O atom.

TABLE-1
BOND LENGTH (Å) AND FORMATION ENERGIES (E_{form}) (eV) CALCULATED FOR O_N-DOPED (6,0), (7,0) AND (8,0) BC_2N NANOTUBES

Type	Bond length (Å)			Formation energy (E_{form}) (eV)	
	O-B1	O-B2	O-C	B-rich	N-Rich
(6,0)	1.476	1.472	1.438	-8.872	-1.886
(7,0)	1.472	1.477	1.433	-7.889	-0.903
(8,0)	1.471	1.463	1.442	-7.608	-0.622

Relative stability: In this part, we now proceed to a comparative analysis of energetic stability of O_N-doped zigzag BC_2N nanotubes. The formation energies (E_{form}) of the oxygen substitution impurities (O_N, the O atom occupying the site of the N atom) are determined according to the equation

$$E_{form}[O_N] = E_t[NT + O_N] - E_t[NT] - \mu_O + \mu_N \quad (1)$$

where E_{form} and E_t is the formation and total energies of the systems. $E_t[NT]$ is the total energies of the pristine nanotubes. μ are the atomic chemical potentials (μ_O, μ_B, μ_N and μ_C), which are calculated as the total energy per atom of the most stable configurations: the O_2 molecule, α-boron bulk, N_2 molecule and graphitic carbon, respectively. Following the previous studies[6,25], only the B and N chemical potentials are constrained by the thermodynamic equilibrium condition in which μ_{BN} is calculated as the chemical potential for a BN pairs in the hexagonal boron nitride.

$$\mu_B + \mu_N = \mu_{BN} \quad (2)$$

Based in the equilibrium requirement, two extreme conditions can be specified defining the foreign species as either an N-rich or a B-rich environment. For the B-rich condition, the μ_N is calculated through (2) by taking μ_B as a fixed parameter; then, in this case, $\mu_B = \mu_B^{bulk}$. Similarly, for the N-rich condition $\mu_N = \mu_N^{molecule}$, the remaining chemical potential μ_B is calculated through (2). Considering these extreme conditions, we can simulate the most favorable environment which doping pattern could be form.

In Table-1, the calculated values for the formation energies (E_{form}) of O_N doped in (6,0), (7,0) and (8,0) BC_2N nanotubes in both B-rich and N-rich conditions are also listed. Obviously, E_{form} values for O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes in both B-rich and N-rich environments are negative, which indicate that additional stable phases for the BC_2N nanotubes can occur. For the N-rich growth condition, O_N-doped (6,0) BC_2N nanotubes is most likely defect, which

possesses the lowest formation energy. Along with the increase of tube diameter, the formation energies increase gradually in O_N-doped zigzag BC_2N nanotubes, which should be suggestive that O_N-doped zigzag BC_2N nanotubes with smaller diameter presents better stability under N-rich condition. In B-rich environments, it is noted that the formation energy value for O_N-doped (6, 0) BC_2N nanotubes is the least, -8.872 eV, even highly less than that in N-rich condition. That illustrate O_N-doped (6, 0) BC_2N nanotubes is most favorable, especially for the B-rich condition. We could also reach a conclusion that the stabilities of O_N-doped zigzag BC_2N nanotubes are lowered with increase of tube diameter. The formation energies are by far higher in the N-rich condition, indicating a great probability for O_N-doped zigzag BC_2N nanotubes under B-rich condition than N-rich condition.

Electronic structure: To elucidate in more detail the electronic properties, we study the electronic band structures near the Femi level and the corresponding density of states (DOS) for O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes, respectively. The band structures for pristine zigzag BC_2N nanotubes are also considered. The obtained results for the energy gap of pristine and O_N-doped zigzag BC_2N nanotubes are displayed in Fig. 2. It can be observed that the energy gaps found for pristine (6,0), (7 0) and (8 0) BC_2N nanotubes are 0.485, 0.344 and 0.853 eV, respectively. Our results show that pristine zigzag tubes behave as direct gap semiconductors. The energy gaps in the band are 0.171, 0.137 and 0.687 eV for O_N-doped (6, 0), (7, 0) and (8, 0) BC_2N nanotubes, respectively. We can see clearly that these values are all smaller than those corresponding pristine zigzag BC_2N nanotubes from Fig. 2. It suggests that energy gaps all have different rate reduced by substitution of nitride atom for oxygen atom O_N in the zigzag BC_2N nanotubes.

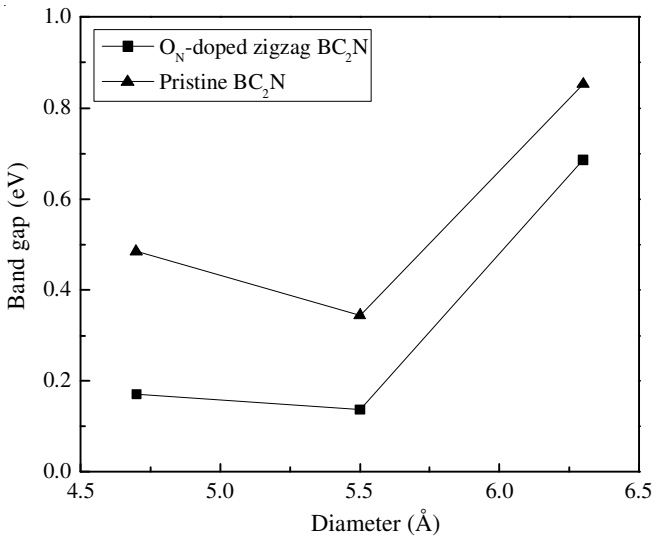

Fig. 2. Band gaps of pristine BC_2N nanotubes and O_N-doped zigzag BC_2N nanotubes as a function of the tube diameter

As show in Fig. 3(a-f), more detailed investigations have been carried out for pristine and O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes. The Fermi level is localized in zero. By O_N doped in (6,0), (7,0) and (8,0) BC_2N nanotubes, band structures change in several aspects. In these three cases, it is observed

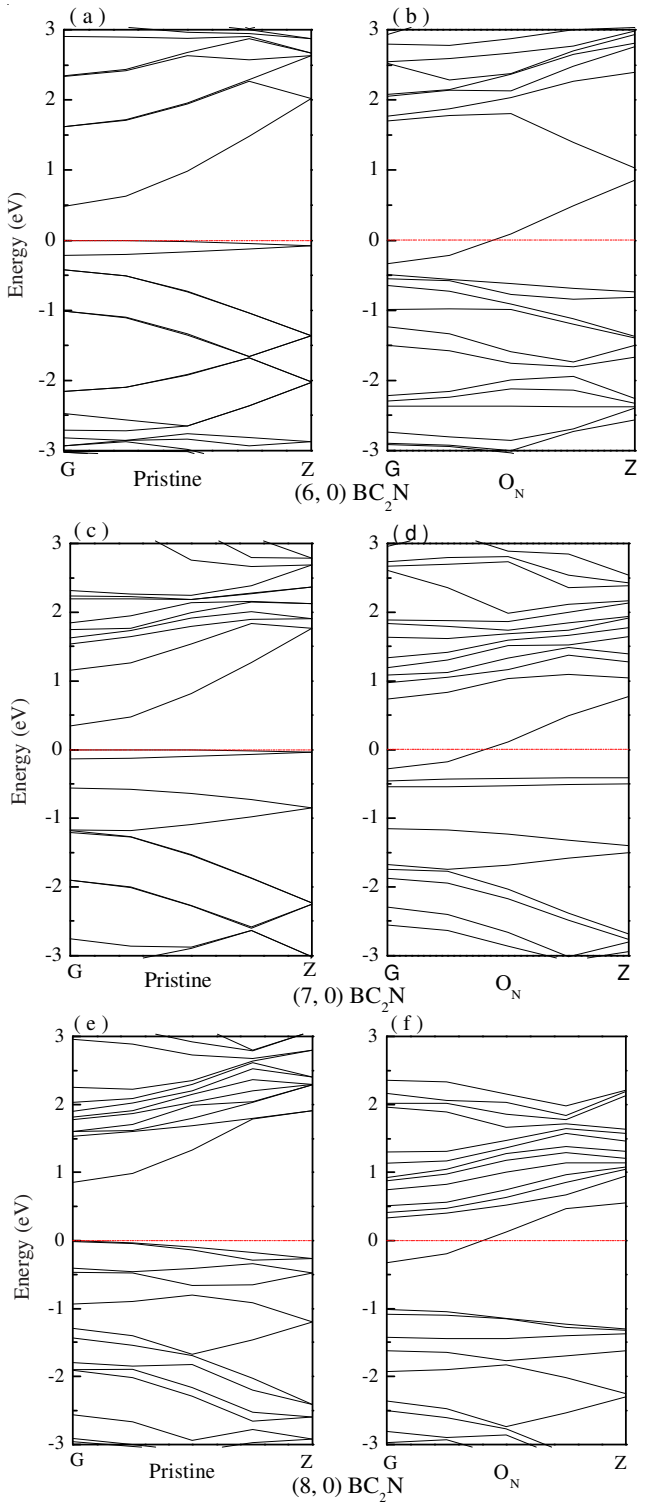

Fig. 3. Electronic band structure for: (a), (c) and (e) pristine (6,0), (7,0) and (8,0) BC_2N nanotubes, respectively; (b), (d) and (f) O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes, respectively. The Fermi energy is indicated by dotted-trace lines

that the most striking modifications are one deep level of the conduction band shift down in the Fermi level suggesting shallow like defects with donor characters. Both the conduction bands and valence bands of O_N-doped zigzag BC_2N nanotubes shift down obviously. The shifts are so drastic that they cause the energy gaps reducing as compare to those pristine BC_2N nanotubes.

Exceptionally, the drastic shifts for the case of (7,0) and (8,0) BC_2N nanotubes cause the lowest conduction band to be filled at the G point. The top of the valence band for O_N-doped (7,0) and (8,0) BC_2N nanotubes are located at the Brillouin zone boundary (Z) and (G), respectively, which imply that the nanotubes are indirect gap semiconductors and direct gap semiconductors, respectively. However, the O_N-doped (6,0) BC_2N nanotubes is direct gap semiconductor with both the bottom of the conduction level and the top of valance level are located at the Brillouin zone boundary (Z). Moreover, the bands' density of O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes are highly increased comparing to those pristine nanotubes, both in the valence and in the conduction bands. The density of states for O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes reflects all such modification, as show in Fig. 4. The density of states of O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes show that Fermi levels are located inside the conduction band defining metallic characters. The introduction of impurities induces the valence and conduction bands are broadened due to the widened distribution of energy levels.

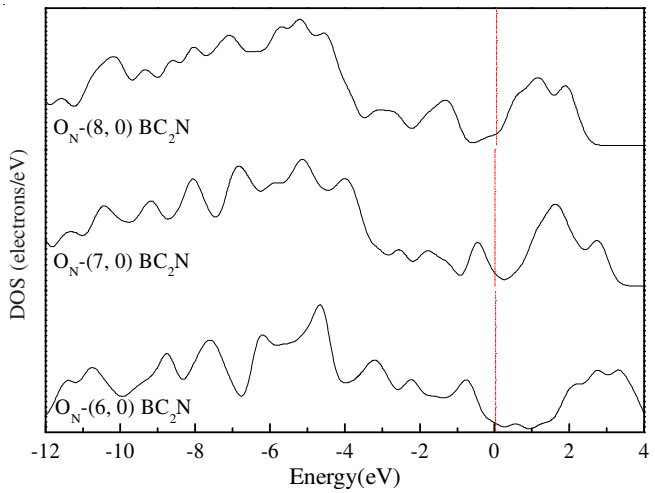

Fig. 4. Calculated density of states (DOS) for: O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes, respectively. The Fermi energy is indicated by dotted-trace lines

Conclusion

In summary, we have systematically investigated the stability and electronic properties of O_N-doped zigzag BC_2N nanotubes using a first-principles calculation based on the density functional theory (DFT). The optimized structures show that the deformations of O_N-doped zigzag BC_2N nanotubes would be negligible due to their closer electronegativity between O atom and N atom. The analysis of the formation energies shows that the O_N impurity substitute in BC_2N nanotubes with smaller tube diameter is more favorable, especially in the case of a B-rich situation. That is, relative stabilities of O_N-doped zigzag BC_2N nanotubes are reduced with the increase of the tube diameter. The electronic properties of O_N-doped (6,0), (7,0) and (8,0) BC_2N nanotubes are found to differ appreciably. Band structure and density of states results indicate that the systems of O_N doped zigzag BC_2N nanotubes behave as donor characters. Besides, O_N-doped (6,0) and (8,0) BC_2N nanotubes are direct gap semiconductors, while O_N-doped (7,0) BC_2N nanotubes is indirect gap semiconductor.

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REFERENCES

1. S. Iijima, *Nature*, **354**, 56 (1991).
2. P.C. Eklund, A.M. Rao, S. Bandow, A. Thess and R.E. Smalley, *Nature*, **388**, 257 (1997).
3. Z. Weng-Sieh, K. Cherrey, N. Chopra, X. Blase, Y. Miyamoto, A. Rubio, M. Cohen, S. Louie, A. Zettl and R. Gronsky, *Phys. Rev. B*, **51**, 11229 (1995).
4. A. Liu, R. Wentzcovitch and M. Cohen, *Phys. Rev. B*, **39**, 1760 (1989).
5. Y. Miyamoto, A. Rubio, M.L. Cohen and S.G. Louie, *Phys. Rev. B*, **50**, 4976 (1994).
6. J. Rossato, R.J. Baierle and W. Orellana, *Phys. Rev. B*, **75**, 235401 (2007).
7. X.D. Bai, J. Yu, S. Liu and E.G. Wang, *Chem. Phys. Lett*., **325**, 485 (2000).
8. J. Yu, X.D. Bai, J. Ahn, S.F. Yoon and E.G. Wang, *Chem. Phys. Lett*., **323**, 529 (2000).
9. L.-W. Yin, Y. Bando, D. Golberg, A. Gloter, M.-S. Li, X. Yuan and T. Sekiguchi, *J. Am. Chem. Soc*., **127**, 16354 (2005).
10. O. Stephan, P.M. Ajayan, C. Colliex, P. Redlich, J.M. Lambert, P. Bernier and P. Lefin, *Science*, **266**, 1683 (1994).
11. P. Redlich, J. Loeffler, P.M. Ajayan, J. Bill, F. Aldinger and M. Rühle, *Chem. Phys. Lett*., **260**, 465 (1996).
12. R. Sen, B.C. Satishkumar, A. Govindaraj, K.R. Harikumar, G. Raina, J.-P. Zhang, A.K. Cheetham and C.N.R. Rao, *Chem. Phys. Lett*., **287**, 671 (1998).
13. H. Pan, Y.P. Feng and J.Y. Lin, *Phys. Rev. B*, **73**, 035420 (2006).
14. H. Pan, Y.P. Feng and J.Y. Lin, *Phys. Rev. B*, **74**, 045409 (2006).
15. M. Matos, S. Azevedo and J.R. Kaschny, *Solid State Commun*., **149**, 222 (2009).
16. W. An and H. Turner, *J. Phys. Chem. Lett*., **1**, 2269 (2010).
17. M. Machado, T. Kar and P. Piquini, *Nanotechnology*, **22**, 205706 (2011).
18. C.J. Rupp, J. Rossato and R.J. Baierle, *J. Chem. Phys*., **130**, 114710 (2009).
19. M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark and M.C. Payne, *J. Phys.: Condens. Matter.*, **14**, 2717 (2002).
20. S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.I.J. Probert, K. Refson and M.C. Payne, *Z. Kristallogr*., **220**, 567 (2005).
21. P. Hohenberg and W. Kohn, *Phys. Rev*., **136**, 864 (1964).
22. J.P. Perdew and Y. Wang, *Phys. Rev. B*, **45**, 13244 (1992).
23. D. Vanderbilt, *Phys. Rev. B*, **41**, 7892 (1990).
24. H.J. Monkhorst and J.D. Pack, *Phys. Rev. B*, **13**, 5188 (1976).
25. M. Mazzoni, R. Nunes, S. Azevedo and H. Chacham, *Phys. Rev. B*, **73**, 073108 (2006).