PRAMANA
— journal of
physics

Vol. 76, No. 6
June 2011
pp. 965–972

The effect of C atom concentration on the electronic properties of boron carbonitride alloy nanotube in zig-zag form

H MILANI MOGHADDAM[1,2,3,4]

[1]Department of Physics, University of Mazandaran, Babolsar, Iran
[2]Molecular Electronics Lab., University of Mazandaran, Babolsar, Iran
[3]Nano and Biotechnology Research Group, University of Mazandaran, Babolsar, Iran
[4]Nanotechnology group, Hariri Scientific Foundation, Babol, Iran
E-mail: milani@umz.ac.ir; hossainmilani@yahoo.com

MS received 22 April 2010; revised 4 December 2010; accepted 29 December 2010

Abstract. Electronic properties of single-walled boron nitride nanotube in zig-zag form are numerically investigated by replacing B atoms with C atoms. Using a tight-binding Hamiltonian, the methods based on Green's function theory, Landauer formalism and Dyson equation, the electronic density of states and electronic conductance in boron nitride nanotube and boron carbonitride nanotube are calculated. Our calculations indicate that in a boron nitride nanotube, the localized states associated with C impurities appear as the concentration of C atoms increases. The boron carbonitride nanotube thus behaves like a semiconductor. Also, by increasing the C atom concentration, the voltage in the first step on the *I*–*V* characteristics decreases, whereas the corresponding current increases.

Keywords. Molecular wire; boron carbonitride nanotube; electronic transport; Green's function.

PACS Nos 73.63.Fg; 73.22.-f; 73.63.-b

1. Introduction

The nanotubes have been attracting considerable interest in molecular electronics. Carbon nanotubes (CNTs) and heteromaterials including B and N have been attracting much attention in fundamental science and also because of their applications to nanotechnology devices [1–4]. Though CNTs have many applications in a broad range of potential nanodevices because of their unique structural and electronic properties [5,6], other nanotubes such as boron carbonitride (BCN) alloy nanotubes are interesting in their own right and may be able to offer different possibilities for technological applications that CNTs cannot provide [7]. It is demonstrated that heterojunctions of B–C–N nanotubes are largely independent of the radius, helicity, multiplicity, or degree of perfection of the constituting nanotubes [7]. But depending on their chirality, CNTs can be metallic or semiconducting [8].

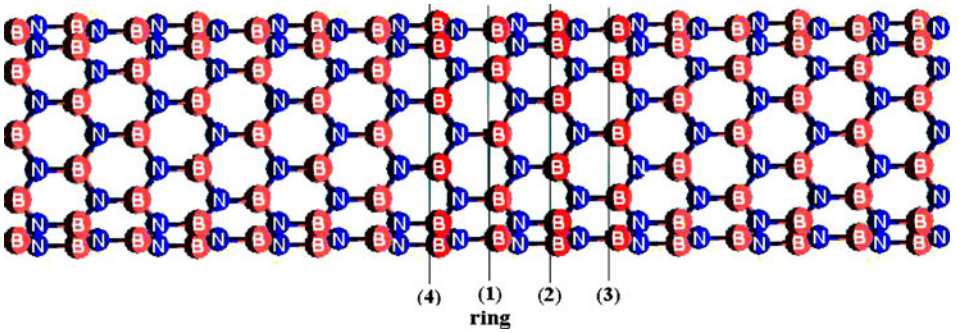

Figure 1. A typical representation of the BN nanotube.

BCN alloy nanotubes have been successfully synthesized by electrical arc discharge [9–13], pyrolysis [14,15] and laser ablation [16] methods. BCN alloy nanotubes are especially good in nanodevice applications.

Simple tight-binding [17] and density functional theory [18] calculations predict a direct band gap for zig-zag (n,0) BN nanotubes and an indirect gap for armchair (n,n) nanotubes (n is an integer). BN nanotubes in chiral or zig-zag symmetric structures are intrinsically polar and therefore piezoelectric effect can be used to develop structural actuators. Minimal lattice energy calculations suggest that zig-zag is the most favourable chirality for BN nanotubes. In addition, the zig-zag BN nanotubes were repeatedly observed by Terauchi *et al* [19], Ma *et al* [20,21], Demczyk *et al* [22] and Lee *et al* [23], prepared by different synthetic routes.

In this paper, keeping all these in mind, we use a model for a zig-zag single-walled BCN nanotube. In this model, B atoms are substituted by C atoms in the unit cell of the middle part of the BN nanotube (UMN). Then, the concentration of C atoms gradually increases so that B atoms are replaced by C atoms in the B rings of both sides of UMN. For example, all B atoms of the 1, 2, 3 and 4 rings in figure 1 are replaced by the concentration of 20% of C atoms and to be continued for the rest of the concentration of C atoms similarly.

We numerically investigate the electronic properties and I–V characteristics of (10,0) zig-zag BCN alloy nanotube. The model and description of the methods for investigating the electronic properties of this nanotube is introduced in §2. The results are presented in §3 followed by a conclusion in §4.

2. Methodology

The most commonly used computational schemes for calculating the (coherent) conductance, g, are the Landauer theory [24], the Green's function formalism [25–27] and Dyson equation.

The conductance g at zero temperature is proportional to the transmission coefficient, $T(E)$, for injected electrons

$$g = g_0 T(E), \qquad g_0 = \frac{2e^2}{h}. \tag{1}$$

It can be shown that the Landauer transmission at a certain energy can be expressed in the Green's function formalism by the Caroli expression [28]

$$T(E) = \mathrm{Tr}[\Gamma_1(E)G^+(E)\Gamma_2(E)G(E)]. \tag{2}$$

The coupling matrices $\Gamma_1(E) = \Gamma_2(E) = \Gamma(E)$ are minus the imaginary part of the nanotube self-energy

$$\Gamma(E) = i(\Sigma(E) = \Sigma^+(E)). \tag{3}$$

Here, E and $G(E)$ are the electron energy and the modified Green's function of the nanotube, respectively.

$G(E)$ can be calculated using the following equation:

$$G(E) = (EI - H - \Sigma_1(E) - \Sigma_2(E))^{-1}. \tag{4}$$

In this relation, I, H and $\Sigma_1(E) = \Sigma_2(E) = \Sigma(E)$ are respectively the unit matrix, the nanotube's Hamiltonian and the nanotube's self-energy. The nanotube's self-energy can be calculated via the Dyson's equation as follows:

$$\Sigma = V(EI - H_0 - \Sigma)^{-1}\, V^+, \tag{5}$$

where H_0 and V are respectively the Hamiltonian of the nanotube supercell and the interaction between two adjacent supercell in the nanotube.

$\Sigma(E)$ in relation (5) is calculated self-consistently to 10^{-8} precision. In our calculation, a unit cell of the nanotube is chosen as a nanotube supercell.

The electronic density of states (DOS) is also given as [28]

$$\mathrm{DOS}(E) = -\frac{1}{\pi}\,\mathrm{Im}\{\mathrm{Tr}[G(E)]\}. \tag{6}$$

The BCN alloy nanotube is modelled within the tight-binding Hamiltonian with only one π-orbital per atom based on orthogonal basis sets [29,30]. This Hamiltonian can describe reasonably well the band structure of a nanotube especially near the Fermi level, ε_{F}, which is zero in this case.

$$H = \sum_j \varepsilon_j c_j^+ c_j + \sum_j t_{j+1,j}(c_{j+1}^+ c_j + c_j^+ c_{j+1}), \tag{7}$$

where c_j (c_j^+) is the annihilation(creation) operator of an electron at the j site. ε_j and $t_{j+1,j}$, respectively, represent the on-site energy and the nearest-neighbour hopping integral.

3. Results

Based on the formalism described in §2, we have investigated the electronic properties for (10,0) BCN alloy nanotube (figure 1). In our calculations, the on-site energies at B atoms and that at N atoms are assumed to be $+2.33$ and -2.50 eV, respectively, if measured from the C on-site energy ($\varepsilon_{\mathrm{c}} = 0$) [31].

We also assume $t_{\mathrm{C-N}} = -3.14$ eV and $t_{\mathrm{B-N}} = -2.81$ eV (t stands for the hopping integral) [32]. Our calculations are done for (10,0) zig-zag single-walled nanotube to nearly 5.92 nm length (equivalent to the length of ten unit cells). Similar results are obtained for other zig-zag nanotubes.

Figure 2a shows the DOS and the electronic conductance of (10,0) BN nanotube. The pure BN nanotube is a wide band gap semiconductor with a band gap of nearly 5 eV and behaves similar to an insulator as reported in [1,9].

We now replace B atoms with C atoms in the UMN. Then, the concentration of C atoms gradually increases so that B atoms are substituted by C atoms in the B rings of both sides of UMN. For example, all B atoms of the 1, 2, 3 and 4 rings in figure 1 are substituted by the concentration of 20% of C atoms and to be continued for the rest of the concentration of C atoms similarly. The plots in figures 2b–f show that the presence of C atoms in BCN alloy nanotube induces electronic states within the band gap. Our calculations demonstrate that as the concentration of C atoms increases, the localized states associated with carbon

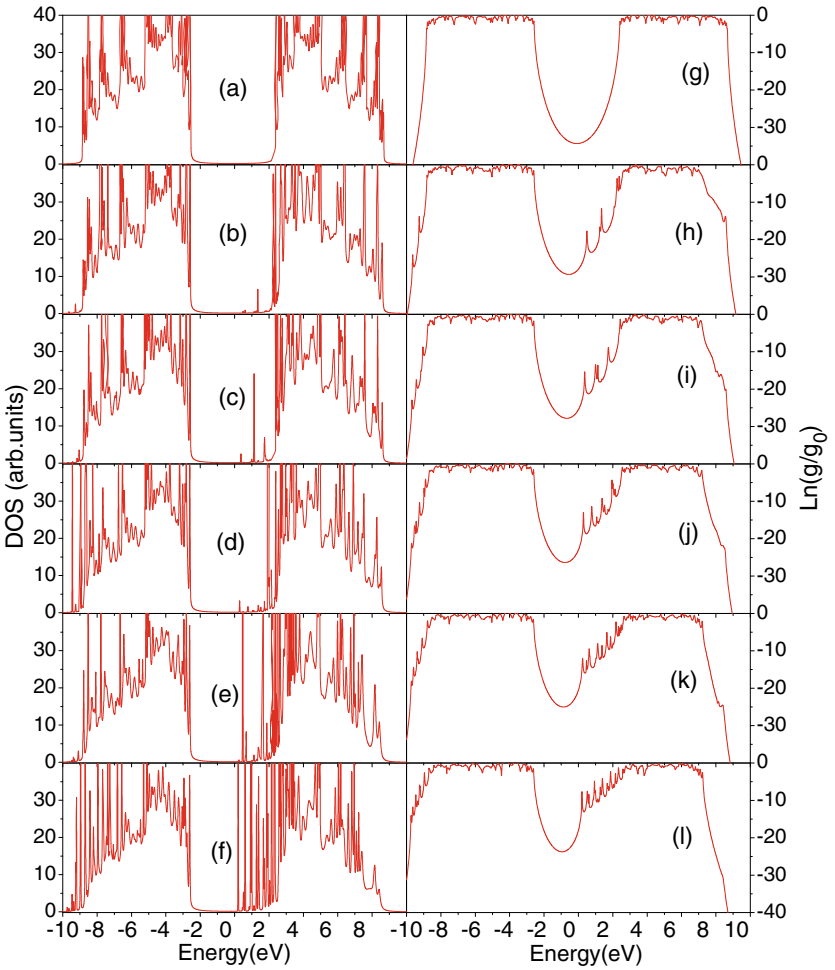

Figure 2. (**a**)–(**f**) panels show the DOS vs. energy for the BN and BCN nanotubes with 30, 40, 50, 60 and 70% concentration of C atoms, respectively. The nanotube is from (10,0) zig-zag type to the nearly 5.92 nm length. (**g**)–(**l**) panels show the conductance logarithm vs. energy that correspond to the (**a**)–(**f**) panels.

impurities appear in a BN nanotube. Therefore, by replacing B atoms with C atoms, the BCN alloy nanotube behaves like a semiconductor. The electronic transmission probability through such a BCN structure is shown in figures 2h–l which corresponds to figures 2b–f, respectively. This is because the substituted carbon atom can contribute an extra electron to the system. In this case, the unpaired $2p$ electrons tend to form a local π orbital for reducing the total energy of the system. Doping with C was also found to be an effective way to reduce the band gap of the tubes to nearly 1 eV [33].

In all the above calculations no voltage drop is considered across the BCN structure. To study the structural behaviour in the presence of an applied voltage, we use

$$I(V) = (2e/h) \int_{\mu_L}^{\mu_R} \mathrm{d}\varepsilon\, T(\varepsilon)\,[f_L(\varepsilon) - f_R(\varepsilon)], \tag{8}$$

where $I(V)$, $T(\varepsilon)$, $f_{L/R}(\varepsilon) = (\exp[\beta(\varepsilon - \mu_{L/R})] + 1)^{-1}$ and $\mu_{L/R} = \varepsilon_{\mathrm{F}} \pm eV/2$, respectively, represent the total current through the device in the V bias voltage, the transmission coefficient, the Fermi–Dirac distribution function and the chemical potential. β is equal to $1/k_{\mathrm{B}}T$ (k_{B} and $T = 4$ K are Boltzmann constant and temperature of the reservoir responsible for injecting the electrons into the contacts, respectively). e and h correspond to the electron charge and Planck's constant, respectively.

Figure 3 shows the I–V characteristics of (10,0) BCN nanotube when the concentration of C atoms are 20%, 50% and 80%. The current jumps are determined by the position of the reservoir Fermi level and the details of the molecular structure. The appearance of jumps in the molecular eigenvalue staircase is a conspicuous feature of the molecular wire I–V curve. We explain the origin of the staircase shape of the I–V curve as follows. For

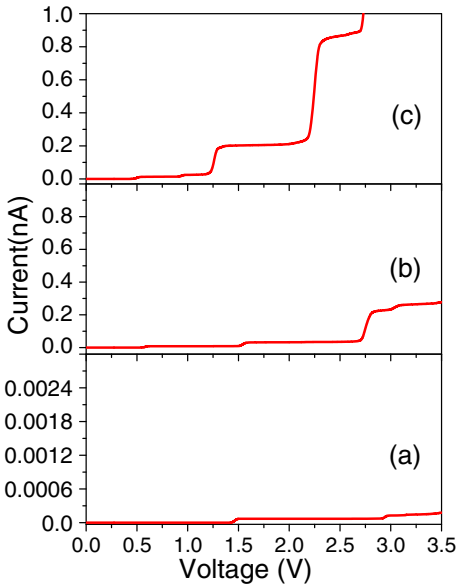

Figure 3. (**a**)–(**c**) panels show the I–V characteristics of (10,0) BCN alloy nanotube for 20, 50 and 80% concentration of C atoms, respectively.

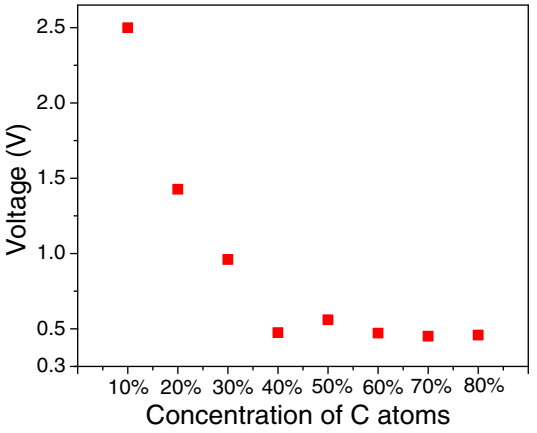

Figure 4. The corresponding voltage in the first step of the I–V characteristics. The horizontal axis corresponds to 10, 20, 30, 40, 50, 60, 70 and 80% concentration of C atoms respectively for (10,0) BCN alloy nanotube.

small V, there are no molecular resonances between the Fermi levels of the two electrodes, and the current is small. As V increases, the energies of the wire orbitals decrease and eventually one of the molecular resonances crosses one of the Fermi levels. This opens a current channel, and shows as a jump in the I–V curve. This behaviour is similar to the phenomenon of resonant tunnelling observed in quantum well devices. One important difference, however, is the fact that in quantum wells, application of a voltage above the resonant voltage shuts down the current channel because the resonance lies in the energy gap of the reservoirs. With molecular wires, once a channel is activated, it remains open since the reservoirs are metallic and occupied states that align with the molecular resonance can always be found.

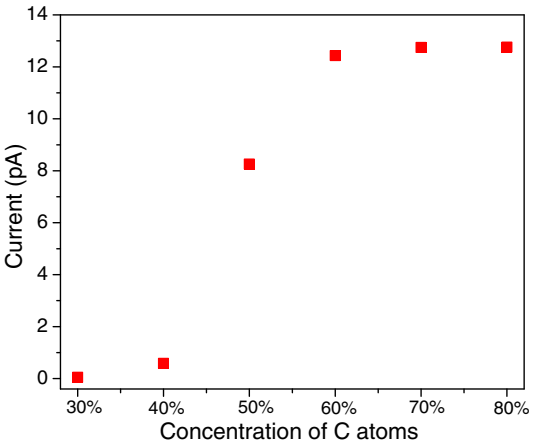

Figure 5. The corresponding current in the first step of the I–V characteristics. The horizontal axis corresponds to 30, 40, 50, 60, 70 and 80% concentration of C atoms respectively for (10,0) BCN alloy nanotube.

The effect of C atom concentration

By increasing the concentration of C atoms, the voltage in the first step decreases whereas the corresponding current increases (see figures 4 and 5) because the voltage drop makes the molecular orbital wider, and thus electron tunnelling from site to site will be easier.

Therefore, the effect of concentration of C atoms on the electronic properties of BCN alloy nanotube is remarkable. According to our results, the BCN alloy nanotube can be a possible candidate for a nanoelectronics element.

4. Conclusions

To summarize, we numerically investigated the electronic properties of (10,0) zig-zag single-walled BCN alloy nanotube. We have carried out some well-known approaches and methods based on Green's function theory, Dyson equation and Landauer formalism as well as tight-binding Hamiltonian model to study the electron conductance and I–V characteristics through the BCN nanotube structure.

The work showed that the presence of C atoms in BCN alloy nanotube induced electronic states within the band gap. We found that any increase in the concentration of C atoms gave rise to an increase of the number of induced electronic states within the BCN band gap. The electronic conductance and I–V characteristics are highly sensitive to the concentration of C atoms. We also found that by increasing the concentration of C atoms, there was a decrease in the voltage in the first step on the I–V characteristics, whereas there was an increase in the corresponding current. This is an important finding. Our results could be used to model some nanoelectronic elements and to develop manufacturing technologies of the considered structures.

Our future work includes the study of the effect of other structural defects as well as electron–phonon interaction on the I–V characteristics of BCN alloy nanotube.

References

[1] K Harigaya, *Physica* **E29**, 628 (2005)

[2] R Saito, G Dresselhaus and M S Dresselhaus, *Physical properties of carbon nanotubes* (Imperial College Press, London, 1998)

[3] J Otsuka, K Hirose and T Ono, *Phys. Rev.* **B78**, 035426 (2008)

[4] S Roy *et al*, *Nanolett.* **8**, 26 (2008)

[5] C T White, D H Robertson and J W Mintmire, *Phys. Rev.* **B47**, 5485 (1993)

[6] J W C Wilder, L C Venema, A G Rinzler, R E Smalley and C Dekker, *Nature* **391**, 59 (1998)

[7] J Yu, X D Bai, J Ahn, S F Yoon and E G Wang, *Chem. Phys. Lett.* **323**, 529 (2000) and references therein

[8] G Y Guo, K C Chu, D Wang and C Duan, *Phys. Rev.* **B69**, 205416 (2004)

[9] F Piazza *et al*, *Diamond Relat. Mater.* **14**, 965 (2005)

[10] O Stephan *et al*, *Science* **266**, 1683 (1994)

[11] Z Weng-Sieh *et al*, *Phys. Rev.* **B51**, 11229 (1995)

[12] P Redlich, J Loeffler, P M Ajayan, J Bill, F Aldinger and M Ruhle, *Chem. Phys. Lett.* **260**, 465 (1996)

[13] K Suenaga, C Colliex, N Demoncy, A Loiseau, H Pascard and F Willaime, *Science* **278**, 653 (1997)

[14] M Terrones *et al*, *Chem. Phys. Lett.* **257**, 576 (1996)
[15] R Sen *et al*, *Chem. Phys. Lett.* **287**, 671 (1998)
[16] Y Zhang, H Gu, K Suenaga and S Iijima, *Chem. Phys. Lett.* **279**, 264 (1997)
[17] A Rubio, J L Corkill and M Cohen, *Phys. Rev*. **B49**, 5081 (1994)
[18] M S Si and D S Xue, *Europhys. Lett.* **76**, 664 (2006)
[19] M Terauchi, M Tanaka, K Suzuki, A Ogino and K Kimura, *Chem. Phys. Lett.* **324**, 359 (2000)
[20] R Z Ma, Y Bando, T Sato and K Kurashima, *Chem. Mater.* **13**, 2965 (2001)
[21] R Z Ma, Y Bando and T Sato, *Chem. Phys. Lett.* **337**, 61 (2001)
[22] B G Demczyk, J Cumings, A Zettl and R O Ritchie, *Appl. Phys. Lett.* **78**, 2772 (2001)
[23] R S Lee *et al*, *Phys. Rev*. **B64**, 1405 (2001)
[24] M Buttiker, Y Imry, R Landauer and S Pinhas, *Phys. Rev*. **B31**, 6207 (1985)
[25] V Mujica, M Kemp and M A Ratner, *J. Chem. Phys.* **101**, 6849 (1994)
[26] B Larade and A M Bratkovsky, *Phys. Rev*. **B68**, 235305 (2003)
[27] Y Calev, H Cohen, G Cuniberti, A Nitzan and D Porath, *Israel J. Chem.* **44**, 133 (2004)
[28] P A Khomyakov, G Brocks, V Karpan, M Zwierzycki and P J Kelly, *Phys. Rev*. **B72**, 035450 (2005)
[29] W Fa, J Chen, H Liu and J Dong, *Phys. Rev*. **B69**, 235413 (2004)
[30] X Yang and J Dong, *Phys. Lett.* **A330**, 238 (2004)
[31] T Yoshioka, H Suzuura and T Ando, *J. Phys. Soc. Jpn* **72**, 2656 (2003)
[32] C Delerue and M Lannoo, *Nanostructures – theory and modeling* (Springer-Verlag, Berlin, 2004)
[33] D Golberg, Y Bando, C Tang and C Zhi, *Adv. Mater.* **19**, 2413 (2007)