

Tuning electronic properties of carbon nanotubes by Boron and Nitrogen doping



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ABSTRACT

The electronic properties of pure and doped carbon nanotubes and NC_3^- , BC_3^- , NC- and BC-nanotubes are investigated by using tight binding theory. It was found that applying the external fields and doping change the band gap. The energy gap is reduced by B/N-doping and the reduction value is sensitive to the several parameters such as nanotube diameter and chirality, external field strength, electric field direction, impurity type and concentration. The direct N (B) substitution creates a new band above (below) the Fermi level and leads to creation of n-type (p-type) semiconductor. The external fields modify the band structure and convert the doped nanotube into metal. For both XC and XC_3 nanotubes ($X=\text{B/N}$), the gap energy reduction shows identical dependence to electric field and the XC_3 nanotubes show more sensitive behavior to electric field rather than XC nanotubes.

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1. Introduction

Carbon nanotubes (CNTs) have attracted many studies according to their unique potential applications that can be controlled by geometric structure. A single wall carbon nanotube (SWNT) can be constructed by rolling up a graphene sheet and its electronic structure is characterized by a pair of non-negative integer numbers (n,m) [1]. The (n,n) armchair CNTs are metal and the $(n,0)$ zigzag CNTs are narrow-gap semiconductors [for $n=3l$] and moderate-gap semiconductors [for $n\neq 3l$] [2]. The nanotubes with other elements such as BN, AlN and SiC has been predicted and observed [3–6]. Unlike to CNTs, these nanotubes are semiconductors with direct and indirect band gaps for zigzag and armchair tubes [7–9]. Calculation of the electronic band structure of CNTs is needed to calculate some physical properties of CNTs such as optical and transport properties. Controlling the electrical properties of CNTs can be achieved by different ways such as applying an electric field, strain, doping and introducing defects [10–19]. The adsorption of different atoms and molecules such as CO_2 , SO_2 , O_2 , CO on CNTs have been investigated based on the density functional theory. It has been shown that the B and N doped CNT systems are energetically stable [20–24] and for B/N doped CNTs several properties such as optical properties [16], field emission [25,26], transport [19,27] and conductivity [28,29] have been investigated. Czerw et al. have demonstrated that N-doping of carbon nanotubes leads to the conduction band modifications, including a large electron donor state which this state lies

approximately 0.2 eV above the Fermi level [30]. B and N atoms are good dopant in CNTs because they have approximately the same radius with carbon and have one electron less and more than carbon, respectively. Nitrogen (N) doping is particularly attractive because the extra electrons from the N dopants are expected to make semiconducting nanotubes metallic [20]. It is shown that the N dopants enriched the π electrons, lowered the work function, and consequently enhanced its ultrafast saturable absorption in multiwalled CNTs [31]. By investigation the N doping of CNTs in a periodic supercell, it is shown that the most stable isomer is different for different chiralities of the tube [32]. By investigation the effects of N doping on the transport properties of CNTs, it is found that the changes from the semiconducting to the quasi-metallic state occurs and the transport properties of the doped nanotubes are sensitive to the distribution and concentration of N atoms [27]. Also it is found that Boron (B) doping affects the transport properties of CNTs which the semiconducting CNT transits to the quasi-metallic state with nonlinear current voltage curve after B doping and the transport properties of the doped tubes are affected remarkably by the impurity states [33]. For zigzag semiconducting CNTs, N-impurity increases current flow, narrows the current gap and generates a metallic transport behavior [34]. The Si-doped CNTs was investigated using first-principles calculations and it is found that for the doped metallic nanotube case a resonant state appears above the Fermi level, whereas for the semiconductor tube an empty level appears above the top of the valence band [35]. In addition to doping, it is shown that the band-gap modulation of CNTs can be easily achieved by applying a transverse electric field and parallel magnetic field [11,13,36]. These studies shown that the external fields strongly affect energy dispersions

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and energy gap. Also the semiconducting CNTs exhibit the semiconductor-metal transitions. In this study we have shown that it is possible to control the band gap by applying combined electric and magnetic fields and doping.

2. Tight binding formalism

For (n,m) CNTs the chiral vector and radius are defined by $\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$ and $R = b_0/2\pi\sqrt{3(n^2 + m^2 + nm)}$ where \mathbf{a}_1 and \mathbf{a}_2 are the primitive lattice vectors of a graphene sheet and $b_0 = 1.42 \text{ \AA}$ is the C–C bond length [1]. In the present work, we use a nearest-neighbor tight binding (TB) model to calculate the band structure of a single-walled CNTs. The band structure of a CNT is obtained from the Slater–Koster tight-binding model with curvature effects [37,38]. The Hamiltonian matrix, is sufficient in describing band structure in the absence of a magnetic field. To calculate the electronic properties of doped CNTs, we use a nanotube unit cell as a cylindrical segment of length \mathbf{T} , where \mathbf{T} is the nanotube transition vector. The unit cell indicated by the indexes i and j [see Fig. 1], where each unit cell consists $2n$ A-type and $2n$ B-type atoms for $(n,0)$ zigzag and (n,n) armchair CNTs. With the existence the external electric field, all atoms should be included in the primitive unit cell to construct the Hamiltonian matrix as:

$$\mathbf{H} = \begin{pmatrix} H^{A_1, A_1} & H^{A_1, B_1} & H^{A_1, A_2} & H^{A_1, B_2} & \dots & H^{A_1, A_{2n}} & H^{A_1, B_{2n}} \\ H^{B_1, A_1} & H^{B_1, B_1} & H^{B_1, A_2} & H^{B_1, B_2} & \dots & H^{B_1, A_{2n}} & H^{B_1, B_{2n}} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ H^{A_{2n}, A_1} & H^{A_{2n}, B_1} & H^{A_{2n}, A_2} & H^{A_{2n}, B_2} & \dots & H^{A_{2n}, A_{2n}} & H^{A_{2n}, B_{2n}} \\ H^{B_{2n}, A_1} & H^{B_{2n}, B_1} & H^{B_{2n}, A_2} & H^{B_{2n}, B_2} & \dots & H^{B_{2n}, A_{2n}} & H^{B_{2n}, B_{2n}} \end{pmatrix}_{4n \times 4n} \quad (1)$$

The Hamiltonian matrix elements a given by,

$$[\mathbf{H}]^{(\alpha_p, \beta_q)} = \sum_i \left[\Sigma_i^{(1)}(\alpha_p) + \Sigma_i^{(2)}(\alpha_p, \mathbf{F}) \right] |\alpha_p, i\rangle \langle \alpha_p, i| + \sum_{ij} \sum_{p,q=1}^{2n} t_{ij}^{(\alpha_p, \beta_q)}(\Phi) |\alpha_p, i\rangle \langle \beta_q, j| \quad (2)$$

where α and β refer to both carbon atoms, $|\alpha_p, i\rangle$ is the p -th α -type atom in unit cell i , $\Sigma_i^{(1)}(\alpha_p)$ ($\Sigma_i^{(2)}(\alpha_p, \mathbf{F})$) is the on-site energy for α_p atom at the unit cell i in the absence (presence) of the electric field. The atoms in the unit cell indicate by $(\alpha_p, \beta_q) = (A_1, B_1, A_2, B_2, \dots, A_{2n}, B_{2n})$.

Several previous studies used the $4n \times 4n$ Hamiltonian matrix within the tight-binding model [10,13,39–41]. The energy dispersions $E^{C,V}(J_0, k)$ are obtained by diagonalizing the Hamiltonian matrix. ν (c) corresponds to the occupied valence band (the unoccupied conduction band). The electronic states $E^{C,V}(J_0, k)$ are characterized by the angular momentum ($j_0 = 1, 2, \dots, 2n$) and the longitudinal wave vector \mathbf{k} ($-\pi < kT < \pi$), where \mathbf{T} is the nanotube transition vector [37,38].

The $t_{ij}^{(\alpha_p, \beta_q)}(\Phi)$ is the nearest neighbor hopping integral between α_p and β_q atoms in the unit cells i and j in the presence of magnetic field $\Phi = \Phi/\Phi_0$ where $\Phi = \pi r^2 B_0$ is the magnetic flux flow through the corresponding nanotube section, Φ_0 is the magnetic quantum flux and B_0 is the magnetic field [42]. For the B/N-doped CNTs the nearest neighbors hopping integral are 3, 2.7, 3.14 and 2.81 eV for CC, BC, NC and BN, respectively [43]. In absence of electric field, the on-site energies ($\Sigma_i^{\alpha_p}$) for B and N atoms are assumed to be +2.33 and –2.50 eV, respectively with respect to the carbon on-site energy ($\Sigma_i^C = 0$) [43,44]. Applying the electric field across the tube cross-section leads to addition of an external potential at the atom locations given by $\Sigma_i^{(2)}(\alpha_p, \mathbf{F}) = F r_i \cos(\theta_i)$ where \mathbf{r}_i is the distance of each atom from the center axis of the tube, F is the electric field strength and the azimuthal angle θ_i is defined by the electric field direction and the position of the atoms along the cylindrical surface of the tube. In the presence of uniform axial magnetic field, the transfer parameters is modified as follows [45],

$$t_{ij}^{(\alpha_p, \beta_q)}(\Phi) = t_0 e^{\frac{2i\pi}{\Phi_0} \int_{R_\alpha - d_i}^{R_\alpha} A(\vec{r}) \cdot d\vec{r}} \quad (3)$$

where $A(\vec{r})$ is the vector potential defined as in gauge $A(\vec{r}) = \frac{\vec{r} \cdot \vec{B}_0}{2}$.

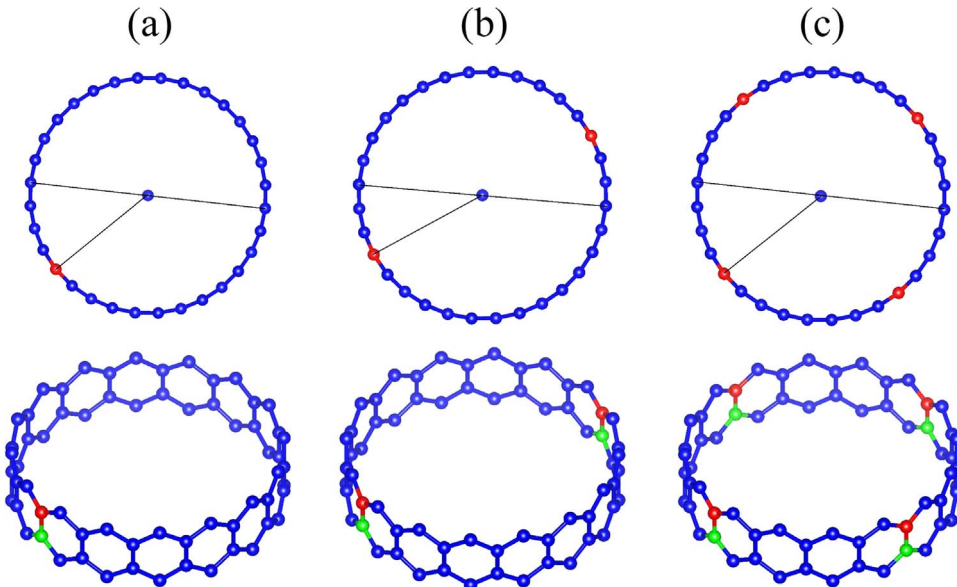


Fig. 1. Schematic picture of the carbon nanotubes with B_1N_1 , B_2N_2 and B_4N_4 configurations. θ indicates angel between electric field and dopant position.

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