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Effect of Impurity on Electronic Properties of Carbon Nanotubes

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We have studied the effect of impurity on electronic properties of single-walled carbon nanotubes using Density Functional Theory. Electronic band structures and density of states of (4, 4) and (7, 0) carbon nanotubes in the presence of different amount of B and N impurities were calculated. It was found that these impurities have significant effect on the conductivity of carbon nanotubes. The metallic (4, 4) nanotube remains to be metallic after doping with B and N. The electronic properties of small gap semiconducting (7, 0) tube can extensively change in the presence of impurity. Our results indicate that B-doped and N-doped (7, 0) carbon nanotubes can be *p*-type and *n*-type semiconductors, respectively.

Keywords: Carbon nanotube, Density Functional Theory, Impurity, Semiconductors

INTRODUCTION

Carbon nanotubes (CNTs) have attracted great interest since their discovery by Iijima in multiwall form in 1991 [1], and as a single-walled tube two years latter [2]. A single-walled carbon nanotube (SWNT) is formed when a graphene sheet is rolled into cylinder, and is characterized by two integers (n, m). The diameter of CNTs is of nanometer size and the length of the CNT can be more than 1 μm [3]. Thus CNTs are quasi-one dimensional materials and can exhibit different electronic structures depending on their chirality and radius [3].

Recently, many theoretical and experimental research groups have focused on the electronic properties of CNTs due to promising applications including nano electronic devices, gas sensors, biosensors, *etc.* [4]. It was found that the electronic properties of CNTs are extremely sensitive to their chemical environment, especially to gas exposure [5].

On the other hand, study of the electronic properties of both pure and doped CNTs is one of the most interesting issues. The latter has special importance because impurities may be easily doped in nanotube *via* mechanical [6] and chemical means [7]. Some studies indicated that, the doped-CNT systems have been found quite useful in industry. For example, Li-doped graphite and CNT systems were considered theoretically [8] and experimentally [9,10] for battery applications. In addition, chemical doping of carbon nanotubes enhances their already outstanding properties and allows the fabrication of diodes and transistors with this material, since these devices require *n*-doping and *p*-doping. By introducing new levels close to the Fermi level, doping with chemical elements such as B and N can also change the sensibility of carbon nanotubes to different kinds of molecules, making possible the fabrication of sensors [11,12].

To the best of our knowledge, there is no systematic theoretical study to determine the electronic properties of SWNT in the presence of B and N impurities. In this paper, the electronic structure of CNTs in the presence of boron and nitrogen impurities has been investigated using Density Functional Theory (DFT). For each type of impurity,

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electronic band structure and density of states were calculated.

METHOD

The DFT based calculations were performed using OpenMX 2.3. package [13]. Local density approximation (LDA) to the exchange-correlation potential was used. We considered armchair (4, 4) and zigzag (7, 0) carbon nanotubes, which contain 16 and 25 carbon atoms per unit cell, respectively. For (4, 4) CNT, the size of the unit cell is chosen as $10 \times 10 \times 2.24$ Å^3, while it is $10 \times 10 \times 4.27$ Å^3 for (7, 0) CNT. The geometry structure of (4, 4) and (7, 0) CNTs with two unit cells along the tube axis are shown in Fig. 1. Three-dimensional periodic boundary conditions are applied around one unit cell. The simulation cell consists of a unit cell of CNT which is replicated in the three spatial dimensions. In the direction perpendicular to the tube axis, CNTs are separated by a vacuum gap large enough to eliminate tube-tube interactions. On the other words the dimensions of the unit cell is such that the interaction between nearest neighbor tubes is negligible.

To understand the effect of B or N impurity on electronic properties of CNTs, electronic band structure and density of states (DOSs) of $C_{1-x}M_x$ were calculated, where M is boron or nitrogen atoms and x is amount of impurity. The amount of impurity has been expressed in terms of M impurity to atomic carbon ratio. We chose x = 0.0625, 0.125, 0.1875, 0.25 for (4, 4) CNT and x = 0.036, 0.071, 0.107, 0.143 for (7, 0). For simulation impurity in CNT, first one B or N impurity replaces one of the carbon atoms and then the amount of impurity is increased by replacing other carbon atoms with the impurity. We should notice that the B and N atoms have such regular geometry that there is a maximum distance between B-B or N-N atoms. A schematic view of B-doped (4, 4) CNTs for x = 0.0625, 0.125, 0.1875, 0.25 is shown in Fig. 2. The obtained results will be discussed in the next section.

The brillouin zone of CNTs was constructed after determining their unit cell. We studied the electronic band structures of CNT along the high symmetry Γ-M direction, which is in the direction of the tube axis. In this direction, the reciprocal lattice vector k corresponds to the translational vector T with the length of $k = 2\pi/T$. The first brillouin zone in the tube axis is the interval $(-\pi/T, \pi/T)$. Therefore, the Γ has position (0,0,0) and the position of the M point is $(0,0, \pi/T)$. For more information about brillouin zone and k-points see Ref. [3].

RESULTS AND DISCUSSION

Electronic Structure of Clean SWNTs

According to the early studies by the tight-binding (TB) model, the (n, m) CNT can be a metal or a semiconductor depending on its n, m. When (n-m) is a multiple of 3, tube is metal; otherwise, it is a semiconductor. It is predicted theoretically that the energy gap of the semiconducting CNTs is inversely proportional to the CNT diameter [3].

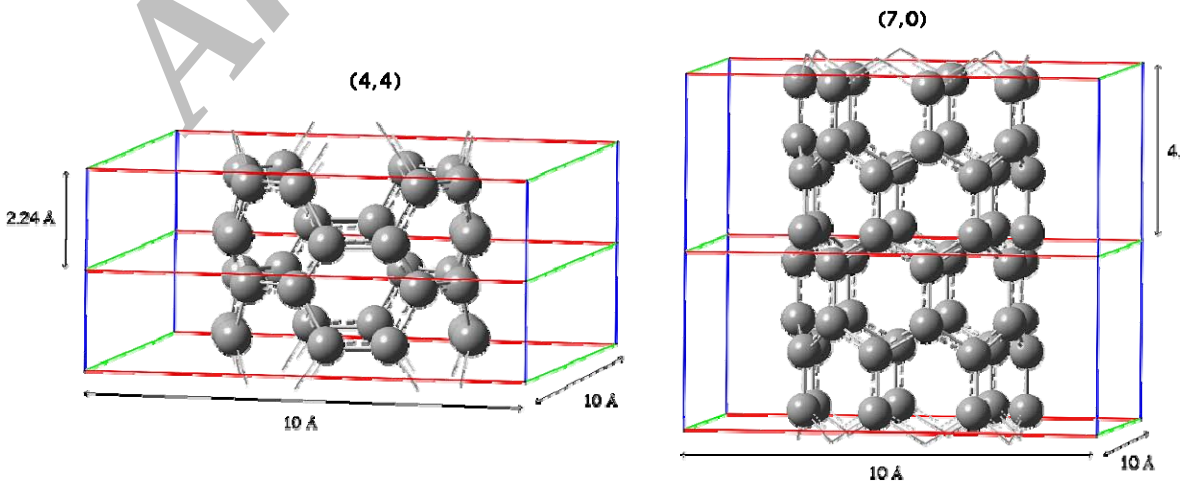

Fig. 1. Geometry structure of (4, 4) and (7, 0) CNTs.

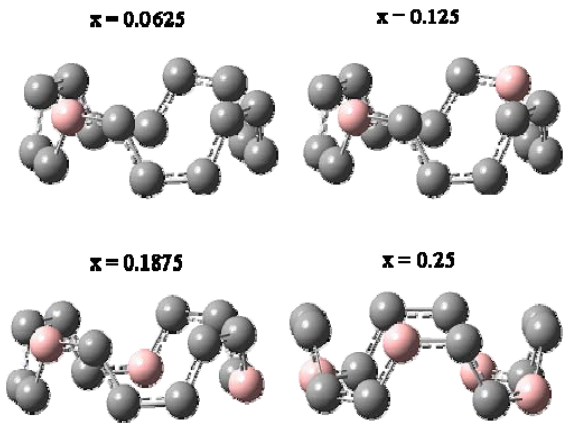

Fig. 2. Snapshot of the B-doped (4, 4) CNT for x = 0.0625, 0.125, 0.1875, 0.25.

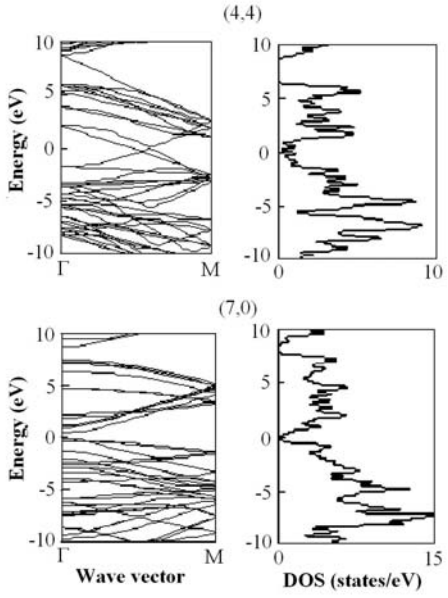

Fig. 3. Band structure and DOS of (4, 4) and (7, 0) CNTs.

The band structures and the DOSs of the (4, 4) and (7, 0) tubes are shown in Fig. 3. (The Fermi level is at 0 eV). The armchair (4, 4) CNT shows metallic behavior with band crossing at k = 2π/T. The value of the DOS at Fermi energy is nonzero. Thus the (4, 4) CNT is a metal as suggested by previous predictions.

We also found an energy gap of 0.6 eV at Γ point between the bottom of the conduction band and the top of the valence band, which shows the semiconducting behavior of (7, 0) CNT. The DOS at Fermi energy is zero. With *ab initio* molecular dynamics calculation, the band gap is reported 0.39 eV [5]. The band gaps of about 0.243 and 1.04 eV were reported by GGA [14] and LDA [15] calculations, respectively.

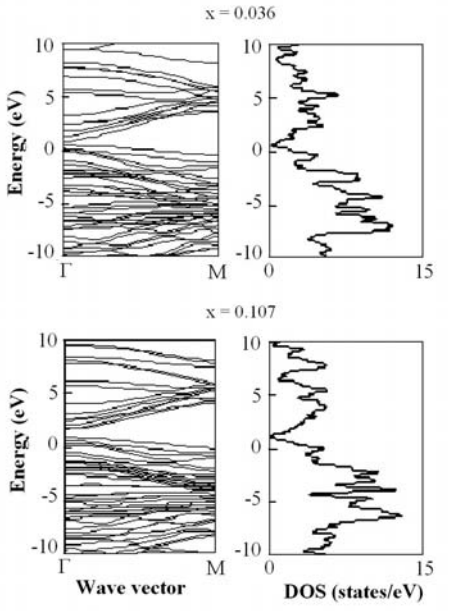

Fig. 4. Band structure and DOS of B-doped (7, 0) CNT for x = 0.036, 0.107

Electronic Structure of B-Doped and N-Doped SWNTs

First, we studied the electronic properties of small gap semiconducting (7, 0) CNT after doping with B and N. The electronic band structures and DOSs of B-doped (7, 0) SWNT for various amount of impurities (x = 0.036, 0.107) are shown in Fig. 4. Boron has one valence electron less than carbon. When one of the carbon atoms is replaced with a boron atom, one electron is removed. As shown in Fig. 4, after doping with B, several unoccupied states above the Fermi level will appear, which can easily accept electron from the valence band. Therefore, the boron impurity is called as acceptor. If an electron moves to these unoccupied states, a hole leaves in the states under the Fermi level. On the other words, acceptor levels raise the concentration of the holes by accepting

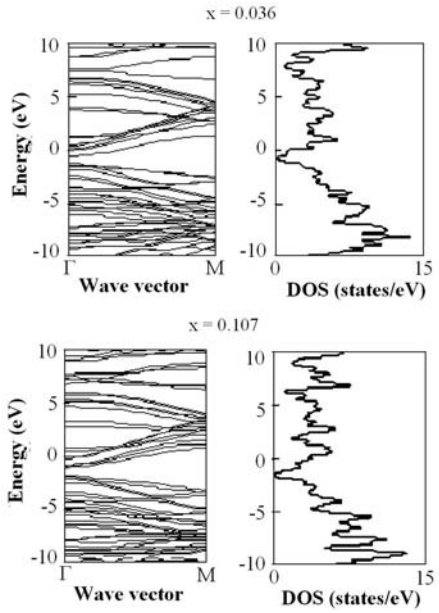

Fig. 5. Band structure and DOS of N-doped (7, 0) CNT for x = 0.036, 0.107.

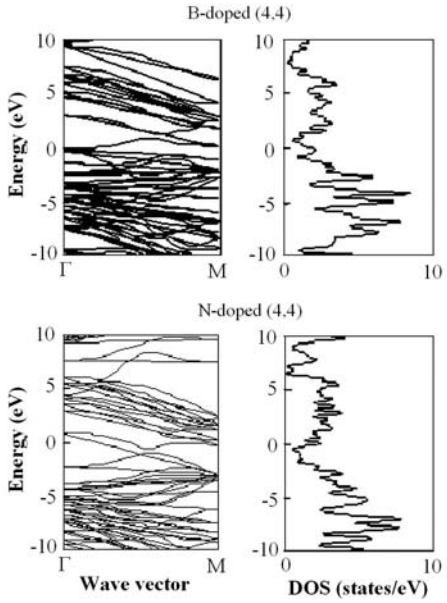

Fig. 6. Band structure and DOS of B-doped and N-doped (4, 4) CNT for x = 0.0625.

electrons from the states under the Fermi level. The (7, 0) CNT with an acceptor impurity such as B is known as *p*-type semiconductor. By Comparing the DOSs of B-doped (7, 0) CNT with pure CNT, we find that the shape of the DOS does not change clearly but the Fermi level is moved down through the valence band and, thus, number of valence electrons is decreased. The number of unoccupied states and the concentration of whole carriers are enhanced by increasing the amount of impurity.

Nitrogen has one valence electron more than carbon. Thus, after doping with N, the number of the valence electrons is increased and some states of the conductance band are filled and, consequently, the N impurity enhances electron carriers. Nitrogen is called donor and the N-doped (7, 0) CNT is an *n*-type semiconductor. It is also found that N impurity does not affect the shape of the conduction band of the pure (7, 0) CNT. In Fig. 5 are shown the electronic band structure and DOS of N-doped (7, 0) CNT for x = 0.036, 0.107.

We also studied the electronic properties of metallic CNT DOS, while the Fermi level moves up and locates at the in the presence of various amount of impurities. The electronic band structures and DOS of B-doped and N-doped (4, 4) CNT for x = 0.0625 are given in Fig. 6. Our results indicate that the (4, 4) tube remains metallic after doping with B and N. The difference between the DOS of (4, 4) CNT and doped CNT are very small. By increasing the number of the impurity, the size of the DOS at Fermi level will change.

For (4, 4) and (7, 0) CNTs, the size of DOSs at Fermi energy as a function of the amount of B and N impurities are shown in Fig. 7. The value of DOS at Fermi Level and conductivity of CNTs is increased by increasing number of impurity. These graphs also indicate that there is a saturation limit for impurities in nanotubes, which shows the maximum conductivity. This is possibly due to the increasing of DOS in s orbital of impurity atoms. As an example, the saturation limit for (4, 4) nanotubes with boron impurity occurs when 25% of nanotubes contain boron (4 atoms) and it occurs for (7, 0) nanotubes when there is 7% of boron impurity (2 atoms). Moreover, by increasing the amount of the nitrogen impurity, the saturation limit is observed when it contains 10.7% with 3 atoms of nitrogen. For (4, 4) nanotube the saturation limit is observed by 18.75% (3 atoms) of nitrogen impurity.

In summery, we have studied the electronic properties of single-walled carbon nanotubes in the presence of different ratios of impurities (B and N) using Density Functional Theory. The calculated band structures and density of states

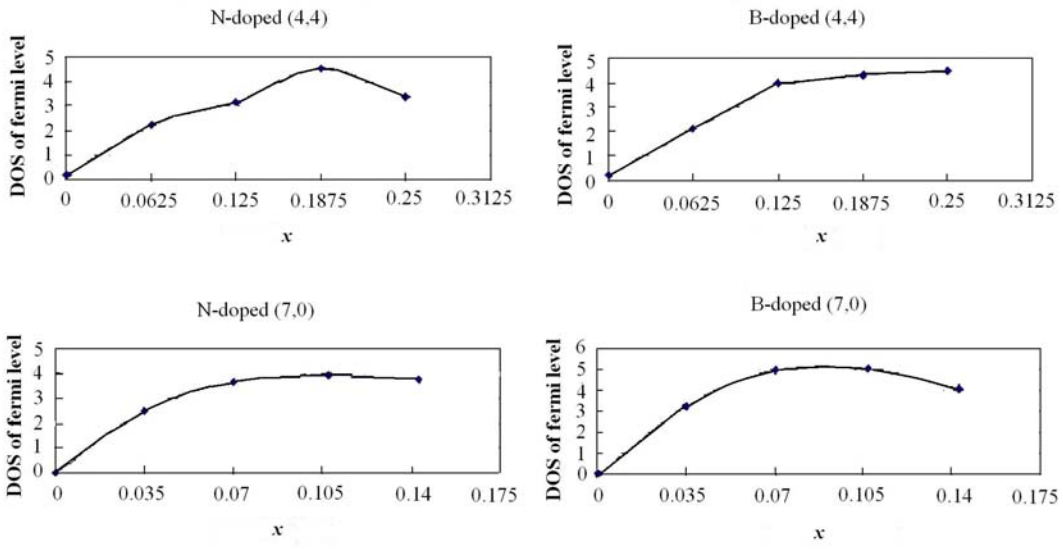

Fig. 7. DOSs of (4, 4) and (7, 0) CNTs at Fermi energy as a function of the amount of B and N impurities.

denote that impurities can impose a significant effect on the electronic properties of (7, 0) CNTs. The B-doped and N-doped (7, 0) can exhibit *p*-type and *n*-type semiconductors, respectively. On the other hand, the (4, 4) CNT remain to be metal after doping with B and N.

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