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,
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 $10 \times 10 \times 2.24 \text{ Å}^3$, while it is $10 \times 10 \times 4.27 \text{ Å}^3$ 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 $\Gamma$-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 $\Gamma$ 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].