

Chapter 11

Effect of Diameter and Doping on Electronic Band Structure of Single-Walled Carbon Nanotubes



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Abstract Carbon nanotubes (CNTs) are basically graphene roll-up in cylindrical form that can have large value of length-to-diameter ratio. In this paper electrical property such as band-gap, density of states, and energy-dependent conductance of single walled carbon nanotubes is quantumly calculated using density functional theory (DFT). It can be seen that band-gap of different SWCNTs changes with the change in diameter. Density of states and energy dependent conductance is also calculated for different single walled CNTs. It is observed that armchair carbon nanotube band gap remain constant irrespective of the diametric size.

11.1 Introduction

In more recent history the discovery of CNTs is attributed to Iijima as the first scientist who described the multiwalled carbon nanotubes (MWCNTs) preparation process after a random event during the test of a new arc evaporation method for C₆₀ carbon molecule fabrication in 1991 [1–3]. Structurally, SWCNTs can be described as a “rolled up” one-atom-thick sheets of graphene (Fig. 11.1). The way in which the graphene sheet is wrapped gives different structures of carbon nanotubes describe by chiral vector C which is a result of a pair (n,m) of integers that correspond to graphene vectors $\sim a_1$ and $\sim a_2$ [4, 5]. The principle of SWCNT construction from a graphene sheet along the chiral vector $C = na_1 + ma_2$ is shown in Fig. 11.1. Depending on the values of n and m three types of carbon nanotubes are formed [6–8]. When n has any integer values and value of m is zero the nanotube structure thus formed is called “zigzag”. When values of $n = m$ the nanostructure thus formed is called “armchair”. The third type of CNTs construction, for which $n > m > 0$, is called as “chiral” nanotubes [9].

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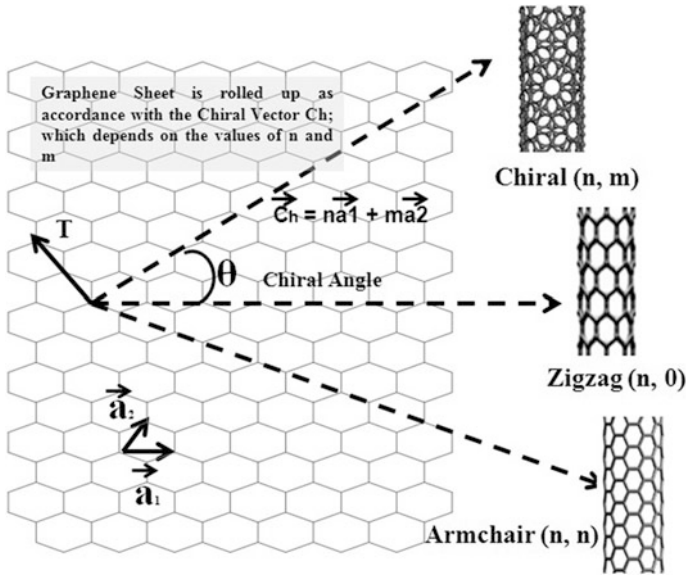


Fig. 11.1 CNT from graphene sheet along the chiral vector C_h

11.2 Method

The most common and simplest method used for determining the electronic structure of SWCNTs is the density functional theory (DFT). This model is best for the case of weak overlap of atomic wave functions in an insulating crystal and widely used in solid-state physics. According to the density functional theory (DFT), the conducting properties of different carbon nanotube structure will depend on the relationship between the coefficient n and m of the vector $C = na_1 + ma_2$, which relates two crystallographic equivalent sites as shown in Fig. 11.1. It is observed that if $\text{mod}(n - m, 3) = 0, 1, 2$, then $\text{mod}1$ and $\text{mod}2$ are semiconducting in nature and $\text{mod}0$ SWCNTs are metallic in nature at room temperature and exhibit a small chirality dependent energy-gap. The small energy-gap corresponds to quasi-metallic conduction at lower temperature. The energy gap has a minimum value of zero corresponding to $p = 2n/3$. If n is not an integer multiple of three then minimum value of $p - 2n/3$ is equal to $1/3$. This suggests that the minimum energy gap is then given by

$$E_g = \frac{\sqrt{3}at}{3} \frac{2\pi}{na} = \frac{2a_{c-ct}}{d_{\text{CNT}}} \approx \frac{0.8 \text{ eV nm}}{d_{\text{CNT}}}$$

The impact of B doping in pristine and doped CNT(8,0) is analysed using density functional theory (DFT) along with non-equilibrium green function (NEGF).

11.3 Results

The nanotube diameter, dictated through C_h , also affects the electron dispersion and it was derived in a semiconducting nanotube, $E_g = \frac{4\hbar v_F}{3d_t}$. The above translates numerically to $E_g = \frac{0.9}{d_t}$ eV, with a $v_F = 10^6$ m/s (Figs. 11.2 11.3 and 11.4).

Effect of Boron doping concentration on electronic properties

In this section the CNTs are doped with boron atoms. With variation in the number of doped atoms, there band structures are analyzed. For this work CNT(8,0) is taken and doped with one, two and four atoms of boron. The band structure of the undoped CNT(8,0) is compared with that of doped nanotubes.

Our results clearly indicates that CNT(8,0) is semimetallic in nature (Fig. 11.5a1). The corresponding density of states (DOS) plot shown in Fig. 11.5a2 completely agrees with the band structure of CNT(8,0). There is a band gap of 0.6 eV between the valence and conduction band. Carbon nanotubes electronic properties can be altered by doping with various impurities. In this work, boron is

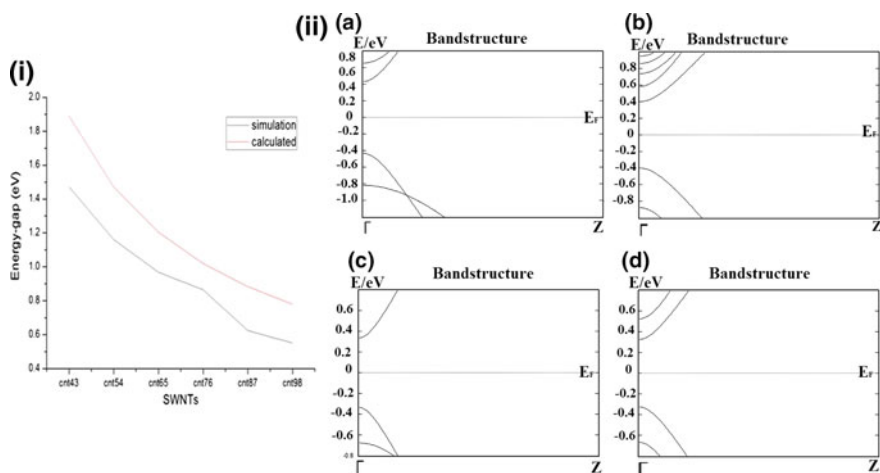


Fig. 11.2 i Energy band-gap plot for different chiral SWCNTs. ii Figure shows band structure of different $(n,0)$ zig-zag carbon nanotubes (a) (10,0) (b) (11,0) (c) (13,0) (d) (14,0). From the figure it can be shown that the band-gap is inversely proportional to diameter of the nanotubes which is dependent on the values of n . As value of n increases, the band-gap decreases

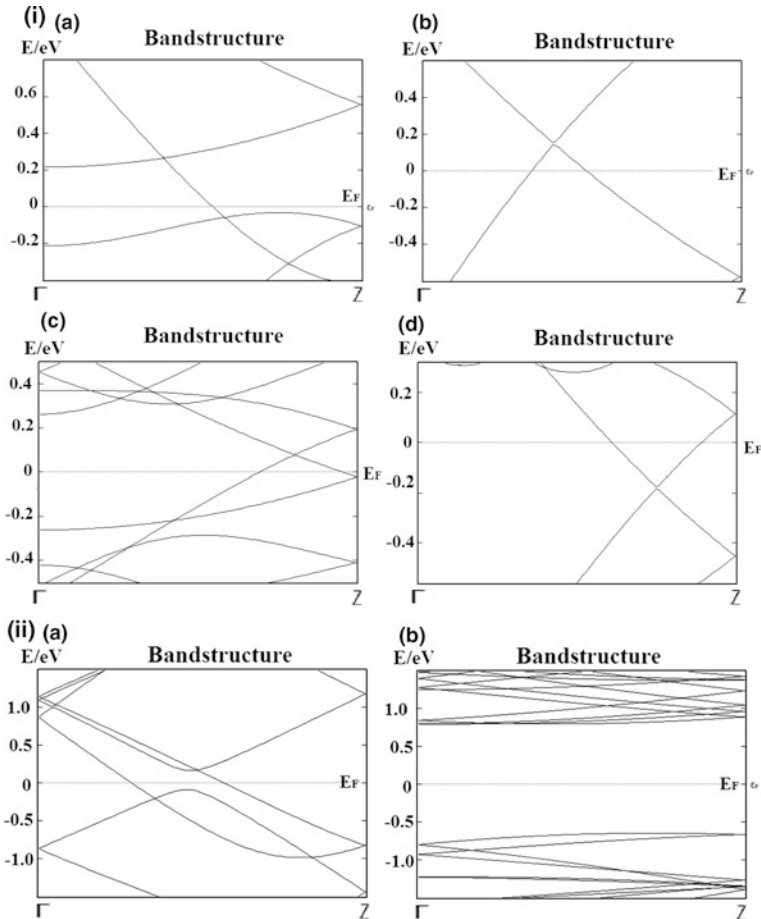


Fig. 11.3 i Figure shows band structure of different (n,n) arm-chair nanotubes (a) (2,2) (b) (3,3) (c) (4,4) (d) (5,5). So, from the above figure it can be concluded that arm-chair nanotubes are always metallic nanotubes. (ii) Figure shows band structure of different (n,m) chiral nanotubes for which values of $n \neq m$, (a) for (4,1) and (b) for (4,3). So, those nanotubes for which $\text{mod}((n - m), 3) = 0$ are metallic nanotubes. And band-gap for which $\text{mod}((n - m), 3) = 1, 2$ i.e. case (b) are semiconducting nanotubes

taken for doping of CNT. It was clearly observed from Fig. 11.5 that Fermi level of doped CNT(8,0) shifts downward resulting in p-type semiconducting behavior. The energy band gap is decreased with the increase in doping atoms as evident from band structure of undoped and doped CNT(8,0). The incorporation of boron atoms adds additional electronic states around the Fermi level, E_F . With the increase in doping concentration number of electronic states near the Fermi level increases.

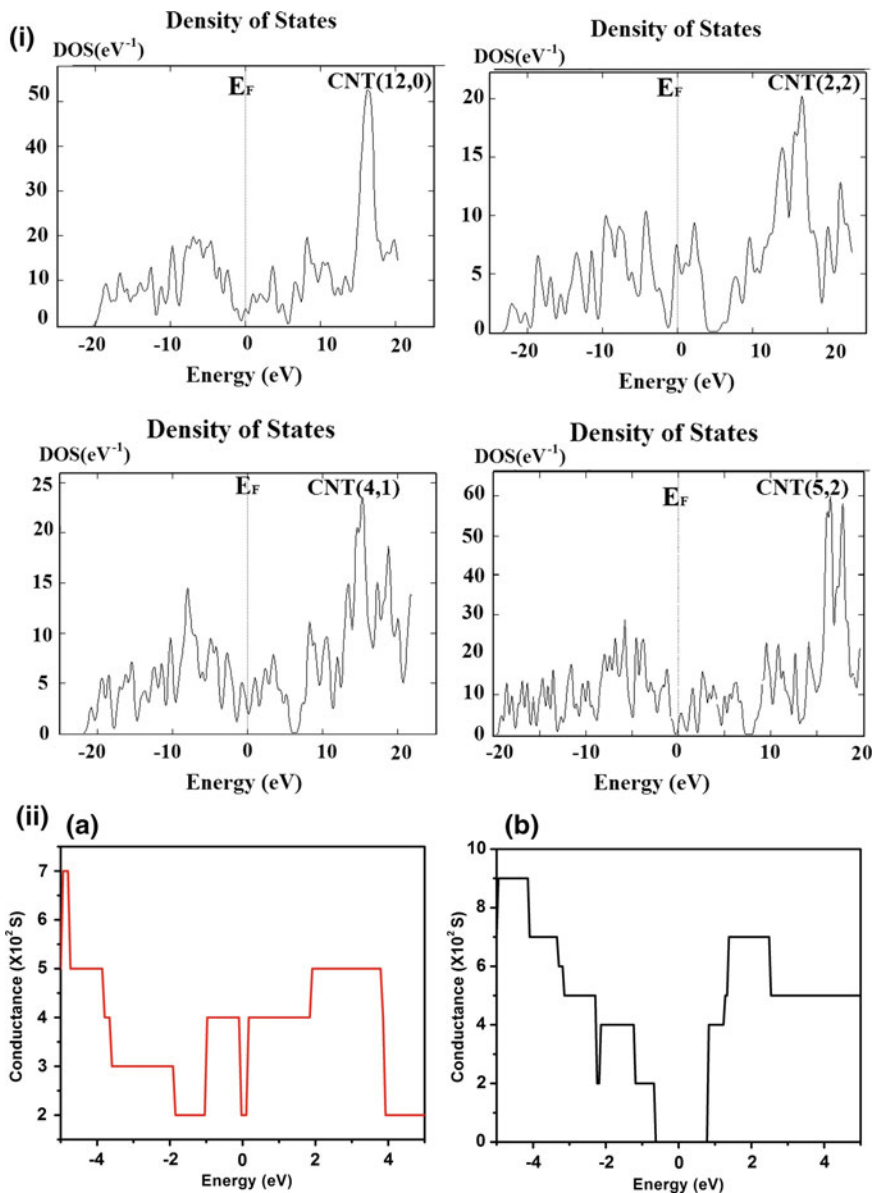


Fig. 11.4 i Figure shows density for states of different chiral nanotubes having $\text{mod}((n - m), 3) = 0$. Chiral nanotubes have finite number of density of states at Fermi level are metallic nanotubes. ii Shows energy-dependent conductance for (a) (4,1) and (b) (4,3) chiral nanotubes. Conductance for chiral nanotube (4,3) is zero which indicate a higher value of energy-gap in this semiconductor nanotube

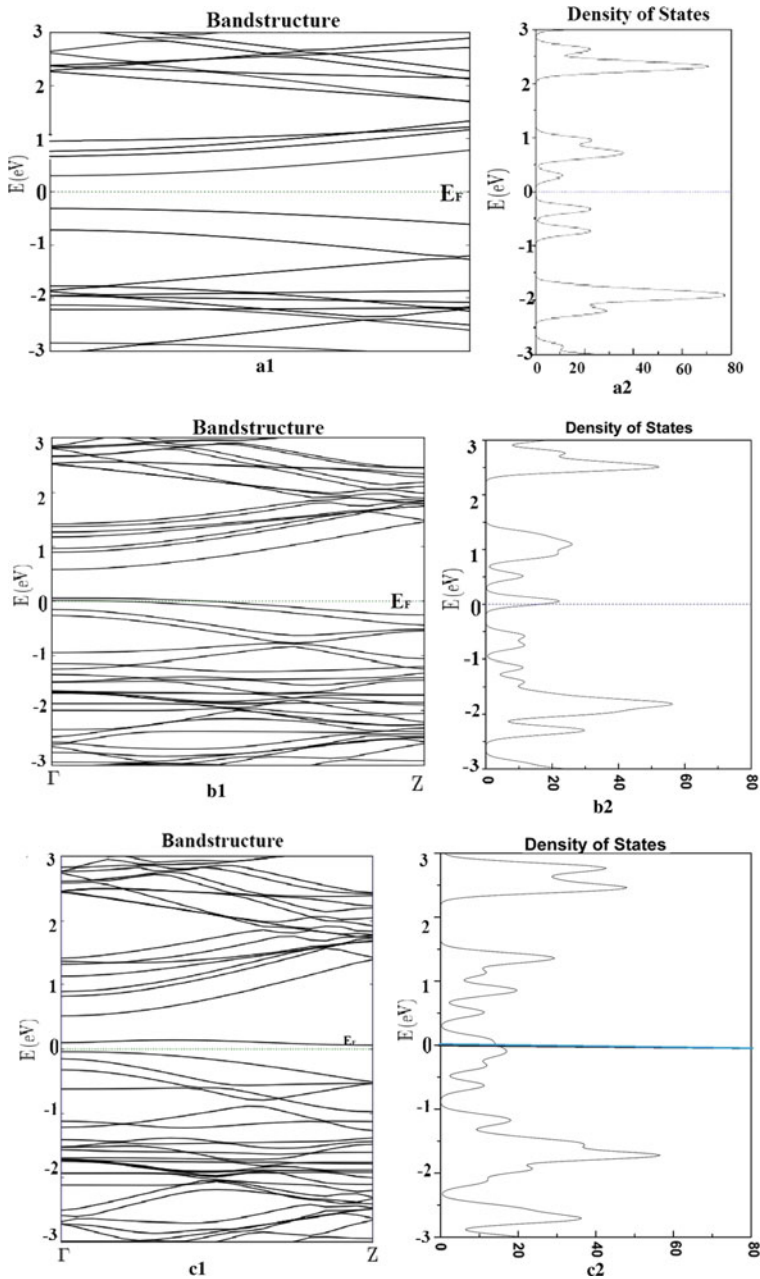
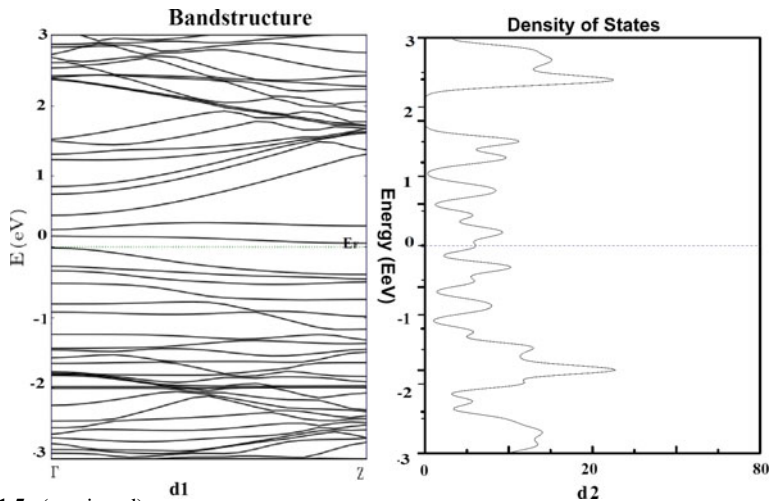


Fig. 11.5 **a1** Electronic band structure of CNT(8,0), **b1**, **c1** and **d1** Electronic band structure of doped CNT(8,0) with 1-atom of boron, 2-atoms of Boron and 4-atoms of Boron respectively. It can be depicted from the band structure of CNT (8,0) that with the increase in doping atoms the bandgap of CNT (8,0) decreases. **a2–d2** shows the corresponding density of states of undoped and doped CNT(8,0). These results can be used in fabrication of high speed electronics as well as logical electronics



◀Fig. 11.5 (continued)

11.4 Conclusion

It was observed that the density of states near the Fermi level E_F increases with the increase in doping concentration. CNTs shows potential as future material for the development of next generation devices. The study about band gap and electronic properties of CNTs will help in the development of high speed devices and transistors.

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