CHAPTER 6

CHIRALITY AND SIZE EFFECT IN SINGLE WALLED CARBON NANOTUBES

6.1 PREAMBLE

Lot of research work is in progress to investigate the properties of CNTs for possible technological applications. As discussed in detail in the previous chapter, impurity doping largely affects the properties of CNTs, giving rise to novel phenomena. Carbon nanotubes are structure dependent materials and it will be interesting to study the effect of doping in small sized tubes for varying dopant concentration.

Carbon nanotubes with diameters as small as 0.5nm and 0.4nm were subsequently observed in the center of MWNTs. Recently, Tang et al fabricated 0.4nm CNTs in the 1nm channels of AlPO$_4$ (AFI) zeolite single crystals. They have studied the modulation of electronic states of (5,0), (3,3) and (4,2) with Li dopants (Tang et al 2003). Small dia tubes, for example, (3,3), (4,2) and (5,0) can survive up to 790K (Ye et al 2007). Sano et al (2002) have observed that a CNT of sub 0.4nm diameter is stable and its structural energy is very close to that of C$_{36}$ ($D_{6h}$) fullerene. It has also been observed that CNTs of diameter very small in the range of 0.3nm can be grown inside multiwalled carbon nanotubes (Zhao et al 2004). The diameter of the 0.3nm CNT is much smaller than the inter layer spacing of the MWNT, which is about 0.34nm. There are three possible CNT structures for the 0.3nm
CNT, the zigzag CNT (4,0), the armchair CNT (2,2) and the chiral CNT (3,1) with relaxed diameters of 0.332nm, 0.272nm and 0.283nm respectively. All these tubes are predicted to be stable. Successful synthesis of such thin CNTs further makes this study worth for nanodevice designing.

The charge transport properties of nitrogen-doped SWNTs were investigated by Krstic et al (2007) and they predicted that n-type conduction could be achieved by nitrogen doping. Generally achiral type CNTs are widely studied as these tubes have the highest symmetry and is easy to interpret the result. Actually chiral tubes exhibit unique characteristics due to the strong effect of chirality on the chemical and physical properties (Kibis 2002). Moreover, most of the as-grown CNTs are of chiral type and to make use of them for device applications, one has to consider chiral semiconducting tubes. The study of such smaller diameter tubes will be useful for nanoelectronic Industries. In the present study, we have considered both achiral and chiral tubes with smaller diameters for investigating the doping effect.

We have split up this chapter into two parts. One is on small diameter semiconducting chiral carbon nanotubes of diameter ranging from 0.5 to 1.3nm and another one is on very small CNTs of diameter less than 0.5nm. Nanotubes having different diameter have their own curvature and the effective mass value vary correspondingly. Hence we have estimated the m* value for each type of tube and calculated the donor binding energies for different levels of impurity concentration.

In the first part of this work, we have investigated the effect of curvature on the donor binding energies of both chiral and achiral CNTs with n − m = 1, 2 such as (5,4), (6,5), (5,3) and (6,4) with diameter ranging from 0.5 to 1.3nm. Band curvature has been included through the corresponding
effective mass derived from a suitable energy dispersion relation, and binding energies are calculated as a function of impurity concentration.

In the second part, in order to study the effect of doping on electrical property in very small diameter CNTs, we have considered (5,0) achiral and (4,2), (4,3) chiral tubes of diameter ~0.4nm. In very small diameter tubes the carbon-carbon bond is severely bent and stretched that leads to the hybridization of the $\sigma^*$ and $\pi^*$ bands. This strong curvature effect leads to deviations from the band folding theory and their behaviour is vastly different from the large diameter tubes. And so, we have included the tube curvature in energy dispersion relation and evaluated the corresponding effective mass values that reflect the band curvature of the tubes. Theory and formulation are given in section 6.2 and the results are discussed in section 6.3.

6.2 THEORY AND FORMULATION

We have adopted the variational method (Appendix 2) with a suitable wave function to estimate the expectation values of energy as explained in Chapter 5. The impurity concentration parameter is included through RPA dielectric function. The details of effective mass calculation for both small and very small diameter tubes, derivation of the screening function and estimation of donor bound state energies are discussed below.

6.2.1 Effective Mass Calculation

The effective mass of CNTs were calculated by several researchers through density of states (Zhao et al 2004), zone-folding method for electron-phonon scattering (Pennington et al 2003, 2005) and photo galvano effect studies (Ivchenko et al 2002) so far. Here, we calculate the effective mass of
chiral CNTs through the tight binding method to observe the behaviour of
donor binding energy as a function of impurity concentration.

It is known that for \((n,m)\) NTs, the chiral vector, \(C_{h} = n\hat{a}_{1} + m\hat{a}_{2}\),
where \(\hat{a}_{1}\) and \(\hat{a}_{2}\) are the primitive lattice vectors of a graphite sheet, and the
chiral angle \(\theta = \sin^{-1}\left(\frac{\sqrt{3}m}{2\sqrt{n^2 + m^2 + nm}}\right)\) (for chiral CNTs,
\(0^\circ < \theta < 30^\circ\)). The C–C bond length is \(a_{cc} = 1.42\) Å.

The energy dispersion of \((n,m)\) tubes obtained through the tight
binding approximation is given as (Saito R. et al 1998)

\[
E^{c,v}(k_{x},k_{y}) = \pm \gamma_{0} \sqrt{1 + 4 \cos^{2} \left(\frac{3k_{x}a}{2}\right) \cos \left(\frac{k_{x}a}{2}\right) + 4 \cos^{2} \left(\frac{k_{y}a}{2}\right)}
\]  

(6.1)

where, the superscripts \(c\) and \(v\) represent the conduction and valence bands,
respectively. \(\gamma_{0} = 3.033\) eV is the transfer integral without the curvature
effect. The wave vectors \(k_{x}\) and \(k_{y}\) are along the directions of the
circumference (\(\hat{x}\)) and the tube axis (\(\hat{y}\)), respectively. The effective mass of
the tube can be calculated by using the tight binding method near the Fermi
point (Pennington G. et al 2005):

\[
\frac{1}{m^{*}} = \frac{1}{\hbar^{2}} \left. \frac{\partial^{2}E}{\partial k_{y}^{2}} \right|_{k_{y},k_{x} = \Delta k_{y},k_{x},k_{F}}
\]  

(6.2)

where, \(\Delta k_{x} = (2/3d)\) is the displacement of \(k_{x}\) from the Fermi point of
graphene. We have used this \(m^{*}\) expression for small CNTs with diameter
ranging from 0.5 to 1.3 nm.
When we consider very small diameter (< 0.5 nm) tubes, it is more important to include the tube curvature in effective mass calculation, but Pennington et al. discussed the effective mass calculation and applications of small dia tube, but without including chirality and curvature effect (Pennington et al 2003, 2005). In this part of the work, the tube curvature is included in effective mass calculation for very small diameter tubes as follows.

Figure 6.1 Hexagonal structure with primitive lattice vectors and directions of overlap integrals

When the tube curvature is considered, the nearest neighbour transfer integrals differ (Li et al 2006) along the three different directions of carbon-carbon bonding in hexagonal structure as shown in Figure 6.1. For this case, the transfer integrals are worked out to be

\[
\begin{align*}
\gamma_1 &= \gamma_0 \left(1 - a_{cc}^2 \sin^2 \theta / 8R^2 \right) \\
\gamma_2 &= \gamma_0 \left(1 - a_{cc}^2 \left(\sin \theta + \sqrt{3}\cos \theta \right)^2 / 32R^2 \right) \\
\gamma_3 &= \gamma_0 \left(1 - a_{cc}^2 \left(\sin \theta - \sqrt{3}\cos \theta \right)^2 / 32R^2 \right)
\end{align*}
\]  

(6.3)
where, \( \gamma_0 \) is the transfer integral without curvature effect (= 3.033eV), 
\( a_{cc}=1.42 \text{Å} \) is the carbon-carbon bond length and \( R \) is the tube radius. With this, general energy dispersion relation for \((n,m)\) tube can be given as,

\[
E^{cc,x}(J,k_y) = \pm \sqrt{\frac{x_1^2 + 4x_1x_2 \cos \alpha \cos 3\beta + 4x_2^2 \cos^2 \alpha + 4x_1x_3 \sin \alpha \sin 3\beta + 4x_3^2 \sin^2 \alpha}{6.4}}
\]

where,

\[
\alpha = \frac{\sqrt{3}a_{cc}}{2} \left[ \frac{J \cos \theta}{R} - k_y \sin \theta \right],
\]

\[
\beta = \frac{a_{cc}}{2} \left[ \frac{J \sin \theta}{R} + k_y \cos \theta \right],
\]

and

\[
x_1 = \gamma_1 \gamma_0 \left[ 1 - \frac{a_{cc}^2 \sin^2 \theta}{8R^2} \right],
\]

\[
x_2 = \frac{\gamma_3 + \gamma_2}{2} \gamma_0 \left[ 1 - \frac{a_{cc}^2 \left(2\cos^2 \theta + 1\right)}{32R^2} \right],
\]

\[
x_3 = \frac{\gamma_3 - \gamma_2}{2} \gamma_0 \left[ \frac{\sqrt{3}a_{cc}^2 \sin 2\theta}{32R^2} \right].
\]

In Table 6.1, we show the radius, chiral angle of different types of CNTs and the corresponding values of transfer integrals with curvature effect, which is important for very small diameter tubes and the values are discussed in section 6.3.
Table 6.1 Transfer integral values of CNTs with tube curvature

<table>
<thead>
<tr>
<th>Type of tube</th>
<th>Chiral angle ( \theta )</th>
<th>Radius of the tube (nm)</th>
<th>( \gamma_1 ) (eV)</th>
<th>( \gamma_2 ) (eV)</th>
<th>( \gamma_3 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5,0)</td>
<td>0</td>
<td>0.195</td>
<td>3.033</td>
<td>2.883</td>
<td>2.883</td>
</tr>
<tr>
<td>(4,2)</td>
<td>19°6'</td>
<td>0.207</td>
<td>3.014</td>
<td>2.861</td>
<td>2.956</td>
</tr>
<tr>
<td>(4,3)</td>
<td>25°17'</td>
<td>0.238</td>
<td>3.008</td>
<td>2.899</td>
<td>2.989</td>
</tr>
<tr>
<td>(5,3)</td>
<td>21°47'</td>
<td>0.274</td>
<td>3.019</td>
<td>2.933</td>
<td>2.994</td>
</tr>
<tr>
<td>(10,8)</td>
<td>26°19'</td>
<td>0.611</td>
<td>3.029</td>
<td>3.013</td>
<td>3.027</td>
</tr>
<tr>
<td>(10,9)</td>
<td>28°15'</td>
<td>0.644</td>
<td>3.029</td>
<td>3.015</td>
<td>3.028</td>
</tr>
</tbody>
</table>

In the energy dispersion relation, the superscripts \( c \) and \( v \) represent the conduction and the valence bands, respectively. \( \hat{k}_y \) is the wave vector along the nanotube axis and \( \hat{k}_x \) is the azimuthal wave vector, which is given by \( J/R \). Where, \( J \) the subband index = 1, 2, …, \( N_u/2 \) that chosen to be closest to the fermi level \( E_F = 0 \). \( N_u \) is the number of carbon atoms in a primitive unit cell. The effective mass of both chiral and achiral tubes can be calculated by using tight binding method near the fermi point as

\[
\frac{1}{m^*} = \left. \frac{\partial^2 E}{\partial k_y^2} \right|_{(k_y=0)} \tag{6.5}
\]

For zigzag nanotubes, \( m = 0, \theta = 0^\circ, R = \sqrt{3}a_{cc} n / 2 \pi \) and \( J = (2n \pm 1)/3 \) for \( n = 3l \pm 1 \). Substituting these values we have obtained the effective mass for (5,0) zigzag nanotube.

The value of \( J \) can be obtained from the number of atoms \( (N_u) \) present in a unit cell for a particular tube. For (4,2) chiral CNTs \( J \) values are obtained through graphical way as shown in Figure 6.2. The value of \( J \) obtained is 9 and the effective mass is worked out to be \( 0.283m_0 \).
Figure 6.2 Conduction band energy of (4,2) chiral carbon nanotube with respect to subband index ($J$)

For comparison, the effective mass of (5,3), (10,8) and (10,9) chiral CNTs of large diameter 0.55, 1.22 and 1.29nm, respectively, are also evaluated and results are discussed in the next section. Pictorial representation of large and small size tubes are shown in Figure 6.3.

Figure 6.3 Virtual view of a) (10,8) and b) (4,3) chiral carbon nanotubes
6.2.2 Estimation of Screening Function

Since the impurity doping is on the surface of NTs, we have considered the 2D RPA based dielectric function $\varepsilon(\bar{p})$ which is most suitable for NTs. From the screening function in Fourier space $\varepsilon(\vec{q})$, we have deduced the real space dielectric function as discussed in Chapter 5 as

$$\frac{1}{\varepsilon(\bar{p})} = 1 - \frac{\lambda \pi \rho}{2} \left[ H_0(\lambda \rho) - N_0(\lambda \rho) \right]$$  \hspace{1cm} (6.6)

where, $H_0$ and $N_0$ are the Struve and Neumann functions, respectively (Gradshteyn et al. 1994).

The hollowness of CNT is included by taking $\rho = t$, where $t$ is the wall thickness of the NT and is taken as 0.34nm (Odegard et al. 2002):

$$\frac{1}{\varepsilon(t)} = 1 - \frac{\lambda \pi t}{2} \left[ H_0(\lambda t) - N_0(\lambda t) \right]$$  \hspace{1cm} (6.7)

Since we have considered 0.4nm tubes, which are greater than the inter layer separation of the graphene sheets, there is no existence of Van der Waals interaction between the side walls and hence the screening effect on side wall of the tube is neglected.

6.2.3 Estimation of Donor Binding Energy

As explained in Chapter 5, to evaluate the binding energy of donor, we have adopted variational procedure, which is suitable for donor
impurity studies in the semiconductors and the appropriate Hamiltonian (Kostov et al 2002) is given by,

$$H = -\frac{\hbar^2}{2m^*} \left( \frac{\partial^2}{\partial z^2} + \frac{1}{R^2} \frac{\partial^2}{\partial \varphi^2} \right) - \frac{e^2}{\rho \varepsilon(\rho) \varepsilon_0}$$

where, $H$ is the total Hamiltonian in atomic unit. $R$ represents the radius of carbon nanotube, the second term represents the impurity potential including the screening function $\varepsilon(\rho)$, $\varepsilon_0$ is the background dielectric constant (= 2.4 for semiconducting CNT) (Li et al 2005), and

$$\rho = \sqrt{z^2 + 2R^2(1 - \cos \varphi)}.$$  

The trial function, which is suitable for low band curvature tubes, can be taken as,

$$\psi(z, \varphi) = N_3 \exp \left( -\alpha \sqrt{z^2 + 2R^2(1 - \cos \varphi)} \right)$$

where, $N_3$ is normalization constant and $\alpha$, the variational parameter as given in Chapter 5. The expectation value of the Hamiltonian (Schiff 1968) is obtained by evaluating the expectation values of kinetic and potential energies as usual.

$$\langle H \rangle = \langle KE \rangle + \langle PE \rangle$$

By varying ‘$\alpha$’ we have minimized the Hamiltonian numerically. We have calculated the binding energies for impurity concentration ranging from $10^6$ to $10^{12}$/cm$^2$. The results are discussed in the next section.
6.3 RESULTS AND DISCUSSION

6.3.1 Effective Mass Values in Doped CNTs

In Chapter 5, we have discussed the effective mass of semiconducting zigzag CNTs as a function of tube diameter, and donor binding energies as a function of impurity concentration and compared our results with semiconducting GaAs quantum well. As expected $m^*$ values decrease as tube diameter increases showing the metallic behaviour of large diameter CNTs.

![Graph showing variation of effective mass](image)

**Figure 6.4** Variation of effective mass as a function of different chiral carbon nanotubes

For smaller diameter tubes of chiral type the band gap varies from 0.67 to 2.13eV. The $m^*$ values of n-m=1 set of tubes come out to be 0.598 and 0.168 for (5,4) and (7,6) tubes respectively. Similarly, the $m^*$ values of n-m=2 set of tubes are 0.966 and 0.138 for (5,3) and (8,6) respectively. Compared to zigzag tubes the rate of increase in $m^*$ is higher for these tubes where the chirality has strong effect as observed earlier (Filho et al 2004). The
interaction of $sp^2$ electrons increases, leading to high effective mass than the
tube of high symmetry. Also, the decrease in effective mass for increasing
radius indicates the loss of semiconducting property in larger radius tubes as
expected. The $m^*$ values obtained for a set of zigzag (achiral) and chiral tubes
having approximately the same the same band gap values are given in Table 6.2.

Table 6.2 Effective mass difference between zigzag and chiral tubes
having approximately same energy gap

<table>
<thead>
<tr>
<th>Type of tube</th>
<th>Diameter (nm)</th>
<th>Energy gap (eV)</th>
<th>Effective mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zigzag tube</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7,0)</td>
<td>0.55</td>
<td>1.57</td>
<td>0.110</td>
</tr>
<tr>
<td>(10,0)</td>
<td>0.78</td>
<td>1.10</td>
<td>0.083</td>
</tr>
<tr>
<td>(13,0)</td>
<td>1.02</td>
<td>0.85</td>
<td>0.066</td>
</tr>
<tr>
<td>(16,0)</td>
<td>1.25</td>
<td>0.69</td>
<td>0.055</td>
</tr>
<tr>
<td>Chiral tube</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5,3)</td>
<td>0.55</td>
<td>1.59</td>
<td>0.966</td>
</tr>
<tr>
<td>(8,3)</td>
<td>0.77</td>
<td>1.14</td>
<td>0.249</td>
</tr>
<tr>
<td>(8,7)</td>
<td>1.02</td>
<td>0.84</td>
<td>0.117</td>
</tr>
<tr>
<td>(10,9)</td>
<td>1.28</td>
<td>0.67</td>
<td>0.075</td>
</tr>
</tbody>
</table>

The results in the above table show that the effective mass value is
larger for chiral tube than for achiral tube. This may be attributed to chirality
and chiral tubes are more semiconducting than zigzag tubes.

For very small diameter zigzag and chiral nanotubes with chiral
angle ranging from 0° to 25° and diameters ~0.4 nm, we have included the
tube curvature through overlap integrals $\gamma_1, \gamma_2$ and $\gamma_3$ in effective mass
calculation. From Table 6.1, we find that $\gamma_1$ along the tube axis direction in
zigzag (5,0) tube is equal to $\gamma_0$ (overlap integral of 2D graphene sheet). The
values $\gamma_2$ and $\gamma_3$ along the other two directions are same but differ from $\gamma_0$
due to stretching along the circumferential direction. In chiral nanotubes,
overlap integral values in all the three directions are different. For larger diameter tubes these values come out to be the same and approaches the value of $\gamma_0$. This trend confirms the importance of tube curvature effect in smaller tubes. The $m^*$ values determined using tight binding approximation including the band curvature with and without the tube curvature are given in Table 6.3. It clearly shows that the values obtained with tube curvature agree well with the literature than the values by neglecting it (Marulanda et al 2008). For larger diameter tubes (10,8) and (10,9), the $m^*$ values for both the cases are almost the same indicating the importance of curvature effect on smaller diameter tubes.

Table 6.3 Effective mass values for various size of the tubes

<table>
<thead>
<tr>
<th>Type of tubes</th>
<th>Diameter (nm)</th>
<th>Effective mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Without curvature effect</td>
</tr>
<tr>
<td>Smaller tubes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5,0)</td>
<td>0.39</td>
<td>0.342</td>
</tr>
<tr>
<td>(4,2)</td>
<td>0.41</td>
<td>0.25</td>
</tr>
<tr>
<td>(4,3)</td>
<td>0.48</td>
<td>0.154</td>
</tr>
<tr>
<td>Larger tubes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10,8)</td>
<td>1.22</td>
<td>0.066</td>
</tr>
<tr>
<td>(10,9)</td>
<td>1.29</td>
<td>0.061</td>
</tr>
</tbody>
</table>

The effective mass values in the brackets are from Ref. (Marulanda et al 2008)

When tube curvature is included, the increase in $m^*$ for a decrease in diameter is more for the set of smaller diameter tubes than for larger diameter tubes. For example, for a diameter difference of 0.07nm (for the case of (4,2) and (4,3)) the corresponding increase is 0.121 while for the same difference in diameter for larger dia tubes ((10,8) and (10,9)) the increase in $m^*$ is only 0.007 indicating the size effect of CNTs.
Out of curiosity, we have calculated the effective mass of (5,3) tube, which has intermediate diameter (0.55nm) between smaller and larger diameter tubes. We have obtained 0.181 that agrees with the existing literature value 0.189 (Marulanda et al 2008). Also, we have observed the m* without curvature as 0.168. This value is in agreement with Pennington and Goldsman model for effective mass (0.16) neglecting curvature effect (Pennington et al 2005).

6.3.2 Donor Binding Energies in Doped CNTs

As a next part of this work, we have evaluated donor binding energies using Equation (6.11) through variational method taking a single parameter trial function. The impurity concentration is included in the screening function and the binding energies are calculated for different values of concentration ranging from $10^6$/cm$^2$ to $10^{12}$/cm$^2$. In achiral tubes, as the tube diameter increases the binding energy decreases moving to the metallic region in agreement with the experimental observation (Wei J et al 2001).

![Graph showing donor binding energies in (5,3), (6,4) and (7,5) chiral tubes as a function of impurity concentration]

**Figure 6.5** Donor binding energies in (5,3), (6,4) and (7,5) chiral tubes as a function of impurity concentration
For the set of \( n-m = 2 \) tubes, we have considered chiral tubes having diameters ranging from 0.55 to 1.22\( \text{nm} \) and chiral angle from 21°47’ to 26°19’. The gradual decrease in binding energy for these tubes as a function of impurity concentration is shown in Figures 6.5 and 6.6. From these figures, we could observe the decrement in donor binding energy for increasing impurity concentration in all the tubes. For example, donor binding energy for the \( n-m = 2 \) tube (5,3) with \( 1\text{cm}^{-2} \) is 9.13\( \text{eV} \), which exhibits high semiconducting property. As \( n_i \) increases, its binding energy goes on decreasing and there is a sudden fall from 2.16 to 0.09\( \text{eV} \) when \( n_i \) approaches \( 10^{11}\text{cm}^{-2} \). Finally, the binding energy saturates at 0.02\( \text{eV} \) for the concentration of \( 10^{12}\text{cm}^{-2} \). Such saturation is due to the limitation in the Fermi–Dirac distribution function. Other tubes show the saturation values 0.09, 0.16, 0.20, 0.21 and 0.22\( \text{eV} \) at \( \sim 10^{11}\text{cm}^{-2} \).
Similarly, we could observe the same trend for $n-m=1$ set of tubes also. For example, the donor binding energy of (6,5) with single impurity is 2.56eV. This value is reduced to 0.13eV for the concentration $10^{11}\text{cm}^{-2}$. In both the sets, the range of saturated values agrees with the existing literature value 0.27eV indicated as the impurity level induced by nitrogen in CNTs (Yi et al 1993). The values of binding energy are higher for small diameter tubes, which exhibit semiconducting property. For all values of concentration, donor binding energy increases as the curvature decreases ($m^*$ increases). These trends are the same for all types of tubes that are considered in this work and the result agrees with that obtained by Li and Lin (Li et al 2005) while investigating impurity states in semiconducting CNTs.

Figure 6.7 shows the increase of donor binding energy at a particular concentration $10^{11}\text{cm}^{-2}$ as the radius increases. When we split up the tubes as $n-m = 1, 2$, we could observe that the donor binding energy at $n_s=10^{11}\text{cm}^{-2}$ goes on increasing for small-diameter tubes and saturates for large-diameter tubes. 1% impurity can be achieved by $\sim10^{13}\text{cm}^{-2}$. When the screening effect is neglected (i.e. $\lambda \rightarrow 0$), the binding energy of each tube saturates at $4R^*$, the expected 2D limit of the hydrogenic model. Moreover, for the tube of radius 0.106Å, we could obtain a binding energy of $\sim76.16\text{eV}$, in good agreement with the work of Kostov et al (2002). Part of these results is published in the International journal ‘Physica Scripta’.
For very small diameter zigzag (5,0) and chiral (4,2), (4,3) tubes we have estimated the donor binding energies ($E_b$) as a function of impurity concentration as given in section 6.2.3. The variation of $E_b$ as a function of impurity concentration in zigzag tube is shown in Figure 6.8. Up to the value of $10^8$/cm$^2$ not much change in the binding energy is observed. Afterwards, $E_b$ decreases and the change is drastic as $n_i$ varies from $10^{10}$/cm$^2$ to $10^{11}$/cm$^2$. Beyond this value the binding energy saturates. We can say that the active region of this very small tube lies between $10^{10}$/cm$^2$ to $10^{11}$/cm$^2$ where the $E_b$ approaches the metallic value. To be precise, when $n_i$ approaches 3.2x$10^{10}$/cm$^2$ the donor binding energy reaches the value of 0.408eV (the semiconducting limit of the CNTs is 0.4 - 0.7eV. i.e. the threshold value of $n_i$ for (5,0) tube to be metallic is 3.2x$10^{10}$/cm$^2$). Further increase in $n_i$ results in the lowest value of binding energy $0.117$eV at $6x10^{11}$/cm$^2$, where it saturates.
Figure 6.8 Donor binding energy in (5,0) zigzag CNT as a function of impurity concentration (cm$^{-2}$)

In Figure 6.9 we display the behaviour of donor binding energy in very small diameter chiral (4,2) and (4,3) tube as a function of impurity concentration. Similar to zigzag tube, here also, the estimated binding energy values remain the same up to $10^8$/cm$^2$. And the value for (4,2) and (4,3) tube are 2.8eV and 1.78eV respectively. From $10^8$ to $10^9$/cm$^2$ of impurity concentration, $E_b$ slowly decreases upto $10^{11}$/cm$^2$ and there is a sudden fall to 0.17eV at $5.9 \times 10^{11}$/cm$^2$ for (4,2) and 0.261eV at $3.4 \times 10^{11}$/cm$^2$ for (4,3) tube. The threshold value of $n_i$ that makes the tube metallic is $3 \times 10^{10}$/cm$^2$ for (4,2) and $2.5 \times 10^{10}$/cm$^2$ for (4,3) tube where the $E_b$ goes to 0.402eV and 0.405eV respectively.
Figure 6.9 Donor binding energy in (4,2) and (4,3) chiral carbon nanotubes as a function of impurity concentration

The threshold value of impurity concentration that makes a tube metallic is higher for tube with larger effective mass (high tube and low band curvature) than for tubes with small effective mass (lower tube and high band curvature). This trend is expected as more donors are needed to transit a highly semiconducting to a metallic type. Part of the results is published in the International journal ‘Superlattices and Microstructures’.

6.4 CONCLUSION

For small diameter tubes, it is concluded that the curvature effect is strong in chiral carbon nanotubes than in achiral tubes. Moreover, for all sets, the binding energy remains constant up to a value of $10^8$/cm$^2$ and then starts
decreasing. The decrease in binding energy as $n_i$ increases indicates the raise in electrical conductivity. The rate of increase is quite considerable. Also, the fundamental band gap in semiconductor nanotubes ranges from 0.4eV to 0.7eV. From our results the energy required for an electron to jump into the conduction band is 0.25eV approximately for all the chiral tubes considered due to the formation of impurity band in the forbidden gap. Since this energy is less than 0.4eV (falls in metallic region) we can say that the n-type doping leads to metallic behaviour of chiral carbon nanotubes. It is expected that further confinement due to electric or magnetic field will definitely lead to metallic transition in chiral carbon nanotubes. This shows the strong effect of chirality on the n-type doped single walled carbon nanotubes. This is an important result for designing nanoelectronic devices such as nano diodes, single electron transistors etc.

From our results for very small diameter tubes, the energy required for an electron to jump into the conduction band comes out to be 0.408eV (the metallic region) at threshold concentration of $3.2 \times 10^{10}/cm^2$ for a doped semiconducting (5,0) tube due to the formation of impurity band in the forbidden gap. This threshold concentration decreases for chiral semiconducting (4,2) tube and is found out to be $3.0 \times 10^{10}/cm^2$. For the other chiral tube (4,3) we could observe the metallic transition at the threshold concentration of $2.5 \times 10^{10}/cm^2$, which is smaller than that of other tubes. These observations once again confirm the fact that, as the tube diameter increases the metallicity increases.

It is interesting to note that at the cross over point of impurity concentration $5 \times 10^{10}/cm^2$ this trend becomes reverse, i.e. from this concentration the binding energy follows the trend of $(5,0) < (4,2) < (4,3)$ for increasing concentrations, which does not exist in larger diameter nanotubes. It could be interpreted as the occurrence of enhanced metallicity in the smaller
nanotube due to doping. This is because, in these tubes the bond between carbon-carbon atoms bent and highly stretched. Hence, it looses the behaviour of the normal larger diameter CNTs. Also, the binding energy of the impurity in (5,0) tube reduced by 3.596eV, from 3.713eV with single impurity to 0.117eV with saturation concentration $6 \times 10^{11}$/cm$^2$. When we consider the chiral tubes, there exist 2.608eV reduction in (4,2) and 1.518eV reduction in (4,3) tubes from single impurity to saturation concentration $5.9 \times 10^{11}$/cm$^2$ and $3.4 \times 10^{11}$/cm$^2$ respectively, that indicates the effect of strong chirality in smaller diameter tubes.

The decrease in binding energy for the increase in impurity concentration is given in Figure 6.8 and 6.9. The rate of fall in binding energy increases as tube diameter becomes smaller as noted in the previous section. It is expected that further confinement due to electric or magnetic field will definitely lead to metallic transition at a still lower concentration in very small carbon nanotubes leading to some more interesting phenomena.