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Effect of Pressure on Defected and Defect Free Carbon Nanotubes for Nano-Electromechanical Sensor Applications

N.R.Devi and V.Gayathri

[1]Department of Physics, Thiagarajar College of Engineering, Madurai, India-625 015

Abstract: We have discussed the effect of pressure on carbon nanotubes and the corresponding change in the mechanical and electronic properties. The structural deformation of (10,0), (9,0) and (8,0) zigzag tubes are analyzed. Under external pressure, the circular cross section of the tube first transforms into ellipse and then into peanut shape. From the change in energy gap value, it is observed that the divacancy defected tubes significantly gets affected by the external pressure compared to defect free. From the results, it is found that (8,0) tube are very sensitive to external pressure. This sensitivity further increases when defects are present in the tube. Pressure effect studies on zigzag forms of carbon nanotubes indicate the suitability of fabrication of sensor devices for nano-electromechanical system.
Keywords: Carbon nanotube, Uniaxial pressure, Structural deformation, Band gap, Conductivity.

1. Introduction

The electronic and mechanical properties of carbon nanotubes are outstanding. CNTs have extremely high axial young's modulus of about 1 TPa and tensile strength approaching 60 GPa [1]. These exceptional mechanical properties alone with the special nature of CNT like porous nature, large surface area, low weight, high stiffness and thermal stability makes CNT ideal candidate for reinforcement of various materials e.g polymers, and also have interesting electromechanical sensor applications. Carbon nanostructure based sensors find great applications in biomedical, automotive, environmental and manufacturing and security industries. As an ideal one-dimensional structure, their properties are highly anisotropic. For example, CNTs are extraordinarily hard in the axial direction but along the redial direction it is soft. As CNTs are practically incompressible along the axial direction, much interest has been focused towards their structural and mechanical behavior along the radial direction of tubes. The radial deformation (change in cross-sectional shape) of CNTs in turn influences the electrical and mechanical properties. Generally, the three different types of CNTs are armchair (metallic), zigzag (semiconducting) and chiral tubes on the basis of chirality, which determines the electronic property of carbon nanotubes [2]. In presence of the external perturbations like stress, doping, electric field and so on, carbon nanotubes undergoes structural deformation and hence there is a change in their electronic properties.

In this work, we are interested in studying the mechanical and electrical behavior of SWNT under application of stress. Under pressure, the Nanotubes deformed and hence there is an associated change in the band gap. Structure modification may sometime leads to semiconducting to metallic transition [3, 4]. It is interesting to note that the armchair tube is naturally metallic but open a band gap under torsional strain [5]. The metal to insulator transition happens in armchair CNTs with the application of torsional strain. Whereas in zigzag tube (3q, 0) metallic tube open band gap under tensile strain, not torsional strain. For example (9,3), the chiral metallic tube open band gap in either case. Experiments have confirmed the electromechanical properties of CNTs that show electric response to mechanical deformation [6,7]. The modulation of electrical conductivity in the presence of external pressure is important for designing the transducers or sensors in the optical and microwave ranges. Kleiner et al. [8] have carried out the work on the effect of pressure on CNTs under stress and they also derived an analytical expression for band gap of deformed tubes including intrinsic curvature for primary metallic tubes. The applied uniaxial stress leads to the deformations of tubes along the circumferential, translational directions and nanotube twist. Charlier et al. [9] and Li et al. [10] have investigated the uniaxial stress effect on SWCNTs and reported that the stress can be modified the band gap and it leads to semiconductor to metal transition. They also carried out the pressure dependence change in electronic properties of difference between the three types of (3q-1,0), (3q,0) and (3q+1,0) zigzag nanotubes.

CNT properties can also be modified by the presence of topological defects in their structure [11, 12]. To explore the role of structural defects under applied pressure the divacancy defect (5-8-5) which is the combination of an octagon and pair of pentagon is inserted in the normal hexagonal structure of nanotubes [13]. The combined radial deformation and effect of defects on single walled semiconducting nanotubes was studied by Shtogun et al. [14]. They found that there is magneto-mechanical coupling behavior in the nanotube properties which can be tailored by the degree of radial deformation and the type of defect. Mechanical properties (Young's modulus, tensile strength and bending stiffness) of carbon nanotubes with vacancies and related defects were investigated by several author [15-17]. We have presented the effect of pressure on three types of zigzag tubes such as (10,0), (9,0) and (8,0). This study was performed using FORCITE module implemented in $Dmol^3$ package. The computational details are presented in the following section.

2. Computational Details

FORCITE module is used to investigate a wide range of systems; the key approximation in this tool is the potential energy surface on which the atomic nuclei move is represented by a classical forcefield. To specify an external model to represent the behavior of the system under tension, we have performed the geometry optimization using conjugate gradient algorithm. This calculation performs until force become smaller than defined convergence tolerances. The pressure is applied along the axial directions of the tubes. This leads to radial deformation in the tubes and the cross section changes from circle to ellipse. The change in band gap due to the applied pressure is calculated with respect to the radial deformation parameter. The corresponding change in electrical conductivity is also calculated. The energy gap (E_g) due to radial deformation is calculated from Equations (5.1) and (5.2) [9] which includes the deformations is as follows,

$$E_g(n = 3q \pm 1) = \gamma_0\left(\pm 2.07\varepsilon + \frac{0.998b}{r}\right) \quad (1)$$

which is for moderate-gap zigzag carbon nanotube (MGZCNT) (satisfies the condition $n = 3q \pm 1$) under uniaxial stress with curvature effect.

$$E_g(n = 3q) = \gamma_0\left(3.19\varepsilon + \frac{0.16b^2}{r^2}\right) \quad (2)$$

which is for narrow-gap zigzag carbon nanotube (NGZCNT) (satisfies the condition $n = 3q$). where, γ_0 is overlap energy and it is equal to 2.5 eV, b = 1.42 Å. r and ε denotes radius of the nanotube and the radial deformation parameter, respectively.

The radial deformation parameter ε is given by,

$$\varepsilon = dR/R \quad (3)$$

where, dR = R ~ R_d is the difference between the radius of original and deformed tube, R is the radius of original nanotubes, the radius of deformed nanotube

$$R_d = \frac{Major\ axis\ radius + Minor\ axis\ radius}{2} \quad (4)$$

The resistivity (ρ) is calculated from the well known Four-Probe expression,

$$\log_e \rho = \left(\frac{E_g}{2k_b T} \right) \quad (5)$$

where, k_b = 8.6 x 10^{-5} eV/K (Boltzman constant), T is the temperature and E_g is the band gap in terms of eV. Then the electrical conductivity (σ = 1/ρ) can be calculated from the resistivity (ρ).

3. Results and Discussion

3.1 (10, 0) Tube

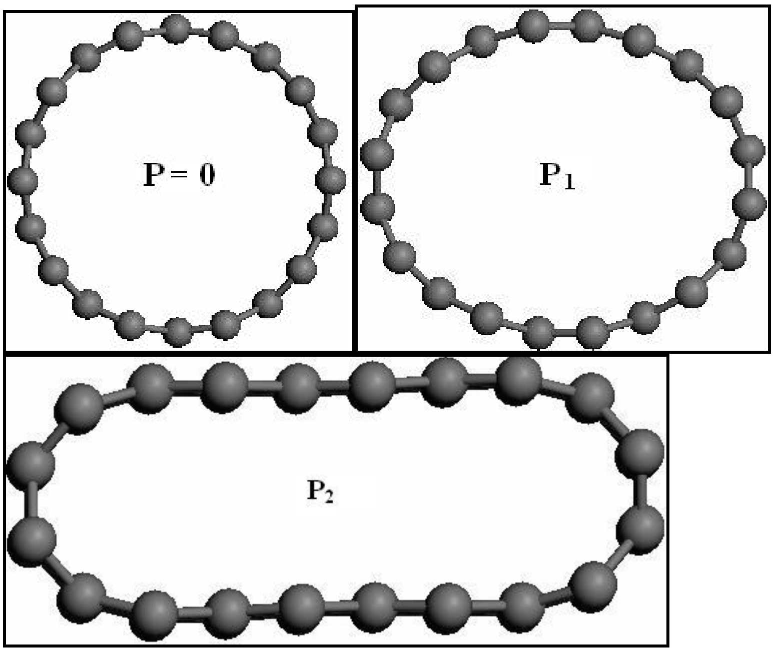

Fig. 1 The cross sectional view of (10,0) defect free tube

In the present investigation, we have considered the moderate band gap semiconducting nanotubes of (10,0) and (8,0) and semi-metallic nanotube of (9,0). The uniaxial pressure is applied along the axial directions of the tubes in the range of 1 to 20 GPa. In the first case, the pressure is applied in semiconductor (10,0) CNT. Small increment of pressure induces the step by step deformation in the tube. Further increment of pressure leads to the symmetry breaking of tube at a particular pressure P_1 at which the circular cross section of the tube deforms into elliptical shape and this pressure is called critical pressure P_1 for the first shape transformation as shown in Fig. 1. When the pressure is increasesd further the elliptical shape of the tube transforms into peanut shape at a particular pressure P_2 and is called critical pressure for the transformation of second shape. The radius of the deformed tube is measured and the deformation parameter ε and E_g values are calculated using the Equations (1) to (4). The ratio of the critical pressure (P_2/P_1 = 14/9) for the first shape transformation over second shape is found to be 1.55. It is consistent with the universal relation (P_2/P_1) = 1.2 [18, 19].

When the pressure is applied, the band gap value for zigzag semiconducting nanotubes is increased linearly and research 1.586 eV at 15 GPa. We have observed that incremental increase of pressure widens the energy gap in zigzag nanotube. The variation of E_g with respect to pressure is shown in Fig. 2. This behaviour of linear variation continues upto the high pressure (say 1000 GPa). The corresponding conductivity value decreases from 2.57 x 10^{-8} mho/Å and reaches the value of 4.5 x 10^{-14} mho/Å at 15 GPa. We have observed 12% and 68% increment in E_g at transition pressure P_1 and P_2 respectively. Our results are in coincidence with the charlier et al. [9] who had reported that the allowed k-line nearest to the K point in the first Brillouin zone moves way from K with stress for (3q+1,0) tubes.

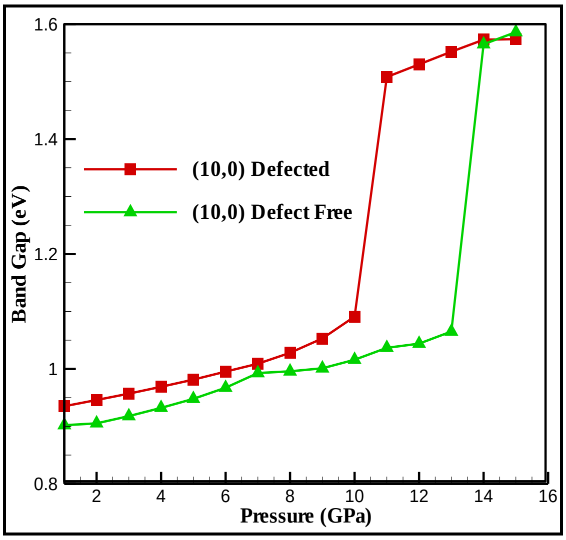

Fig. 2 Change in band gap values with respect to pressure in (10, 0) tube

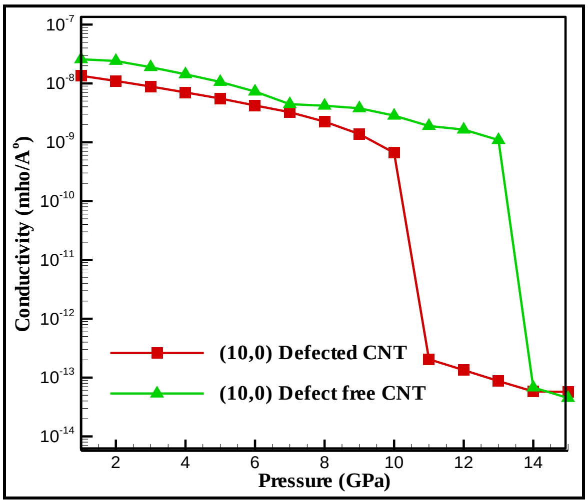

Fig. 3 Variation of Conductivity with respect to pressure in (10,0) CNT

We have also observed the similar trend of linear variation in energy gap in defected (10,0) tube under pressure. Once the pressure is applied the defected tube attains its first transformation due to divacancy defect. At pressure of 11 GPa, it transforms into peanut shape that indicating the reduction in the bond strength of the tube due to divacancy defect and pushes the second shape transformation at earlier pressure than defect free tube [20]. At 15 GPa pressure, the band gap and conductivity value arrives at 1.57 eV and 5.7×10^{-14} mho/Ǻ, respectively. The rate of decrement in conductivity is more in defected tubes than free tube. The change in conductivity ($\Delta\sigma$) due to the introduction of defect at 1GPa pressure is observed as 2.59×10^{-8}mho/Ǻ. We found that 2% increment in E_g at 11 GPa whereas in defected case 6% increment is found. The variation of conductivity with respect to pressure is shown Fig. 3. From the graph it is observed that the sudden decrement of conductivity of 6.79×10^{-14} mho/Ǻ in (10,0) tube at 14Gpa whereas in defected (10,0) tube it happens at 11GPa with the conductivity value of 2.05×10^{-13} mho/Ǻ. The data show the widening of band gap at value of pressure and move over to insulating range when the pressure increases to a higher value.

3.2 (8, 0) tube

In the case of (8,0) tube, as pressure increases, the tube first transforms into ellipse at a value of 13 GPa and second shape transformation occurs at 18 GPa. The ratio over the critical pressure P_2/P_1 is observed to be 1.38. The schematic view of (8,0) tube at the critical pressure P_1 and P_2 is shown in Fig. 4. The change in band gap values with respect to pressure is plotted in Fig. 5. From the graph it is examined that the band gap values are decreased from 1.12 eV to 0.771 eV due to an enhancement of σ^*-π^* hybridization that leads to overlapping of electronic states. The energy gap for this tube is decreased approximately 14% at the operating pressure of 1GPa. The obtained results are in agreement with the reported literature [21, 22]. The corresponding conductivity (σ) is increased from 3.15 x 10^{-10} mho/Å and it reaches 3.24 x 10^{-7} mho/Å. Conductivity variation versus pressure is plotted in Fig. 6. Further increment of pressure leads to breaking of bonds between carbon atoms at 50 GPa. It is noticed that 30% and 43% of decrement of E_g at transition pressure P_1 and P_2.

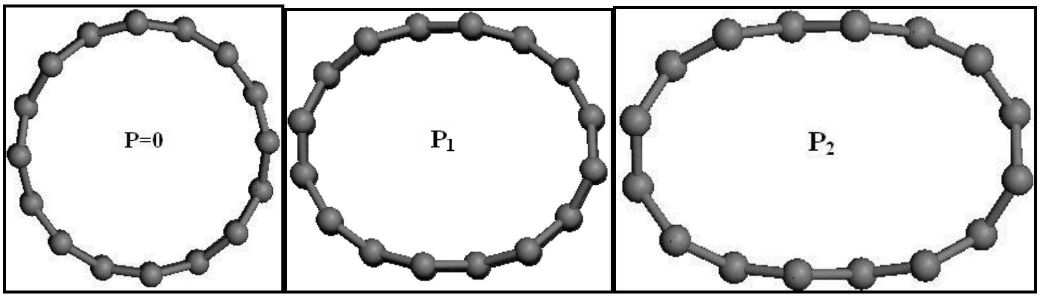

Fig. 4 The schematic view of (8,0) tube at critical pressure P_1 and P_2

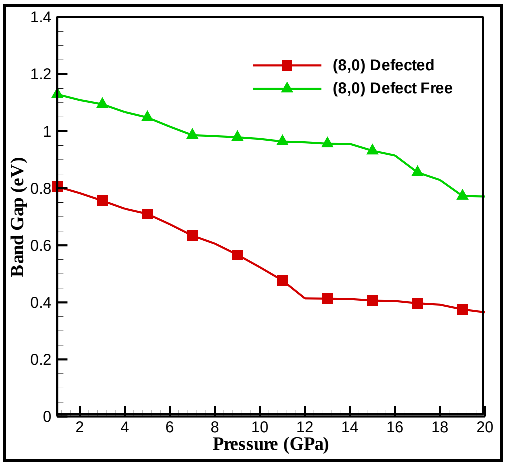

Fig. 5 Change in band gap values with respect to pressure in (8,0) tube

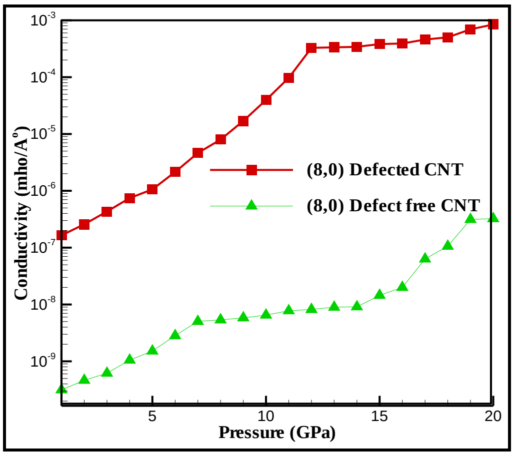

Fig. 6 Variation of conductivity with respect to pressure in (8,0) CNT

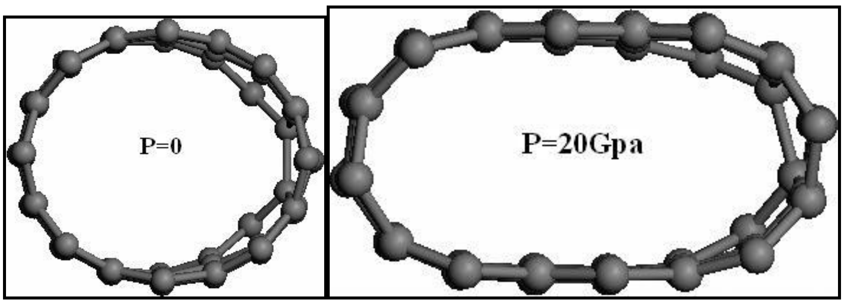

Fig. 7 The cross sectional view of defected (8,0) tube at pressure P=0 and P=20GPa

We have also observed the drastic decrease in band gap value from 0.80 eV to 0.36 eV in defected (8,0) tube . The amount of reduction in band gap is increased to 50% than the defect free case at 1GPa. Further increase in pressure, leads (8,0) tube from semiconductor to metallic nature. The defected (8,0) tube withstand high pressure up to 1000 GPa. Our calculated results are in good agreement with charlier et al. [9] that the allowed k-line moves nearer to the K point with pressure diminishing the gap for (3q-1) tubes. The change in conductivity ($\Delta\sigma$) at 1 GPa with and without defect is calculated as 1.649×10^{-7} and 2.9×10^{-10} mho/Å. The significant change in $\Delta\sigma$ value is examined in defected (8,0) tube. The cross sectional view of (8,0) defected tube at pressure 1 GPa and 20 GPa is given in Fig. 7.

3.3 (9, 0) Tube

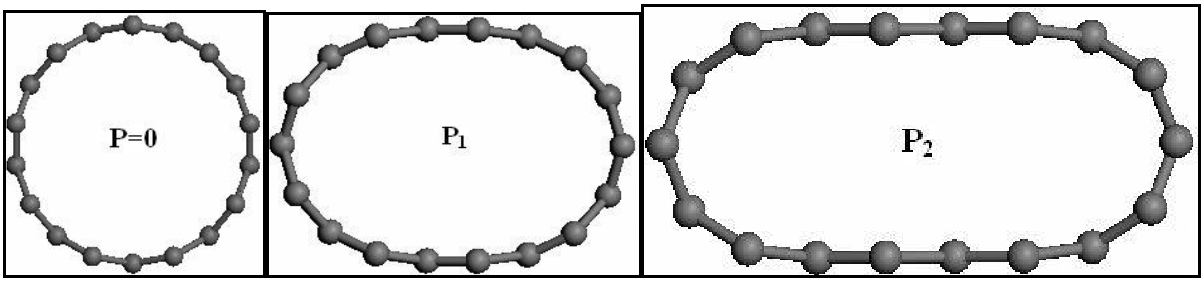

Fig. 8 The cross section view of (9,0) defect free tube

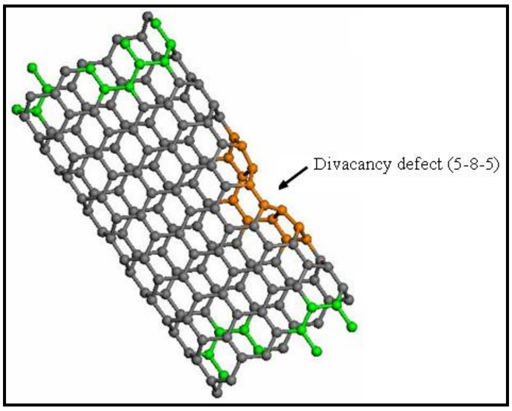

Fig. 9 Cross sectional view of (9,0) defected tube at 30 GPa

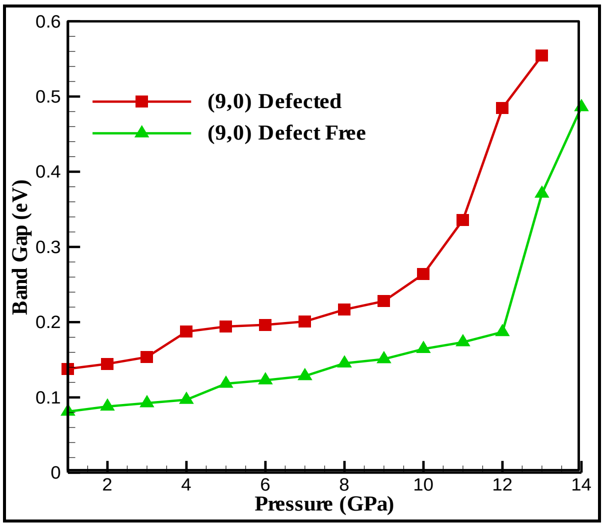

Fig. 10 Change in band gap values with respect to pressure in (9, 0) tube

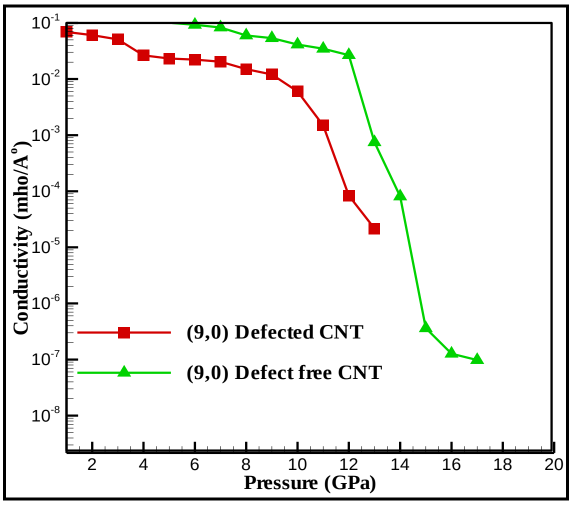

Fig. 11 Variation of conductivity with respect to pressure in (9, 0) CNT

For semi-metallic (9,0) tube, the band gap increases from 0.08 eV to 0.83 eV under external pressure. For large value of pressure at 13 GPa the tube cross section varies from circle to ellipse and peanut shape transformation occurs at 15 GPa. The schematic view of tube at critical pressure is shown in Fig. 8. The ratio over the pressure at first critical transition (P_1) and second critical transition (P_2) is 1.15. The same kind of behavior is also noticed in defected (9,0) tube. The cross sectional view of (9,0) defected tube at 30 GPa is shown in Fig. 9. At the value of around 30 GPa the tube could not withstand the pressure and the bonds between carbon atoms break in both the cases. The 29% and 68% increment in E_g values are found at critical pressure P_1 and P_2. Whereas at low value of pressure the E_g remains the same as observed by Saxena et al. [23]. Table 1 shows the critical pressure at which the shape transformation occurs in CNTs. Change in band gap values with respect to pressure in (9,0) tube is shown in Fig. 10. As the energy gap increases due to the applied pressure, corresponding conductivity decreases. It is estimated as 0.08 mho/Å and 0.147 mho/Å corresponding to (9,0) and defected (9,0) tube. The variation of conductivity with pressure is plotted in Fig. 11. We have monitored an abrupt decrement in conductivity in (9,0) tube at 13 Gpa. The presence of defects in (9,0) tube that gives raise to semi-metallic to semiconductor transition. Change in energy gap (ΔEg in %) before and after applied pressure in defect free and defected CNTs at 1GPa is listed in Table 2. Similarly, Table 3 shows the change in energy gap (ΔEg in %) at pressure P_1 and P_2 in defect free CNTs. Change in conductivity in semiconducting nanotubes is tabulated in Table 4 to 5.

Table 1 Critical pressure at which the shape transformation occurs in CNTs

Type of tube	P_1 (GPa)	P_2 (GPa)	P_2/P_1
(8,0)	13	18	1.38
(9,0)	13	15	1.15
(10,0)	9	14	1.55

Table 2 Change in energy gap (ΔE_g in %) before and after applied pressure in defect free and defected CNTs at 1GPa

Tube	ΔE_g in %	
	Without defect	With defect
(10,0)	2	6
(9,0)	0.2	5
(8,0)	14	45

Table 3 Change in energy gap (ΔE_g in %) at pressure P_1 and P_2 in defect free CNTs

Tube	ΔE_g at pressure P_1	ΔE_g at pressure P_2
(10,0)	12	68
(9,0)	29	68
(8,0)	30	43

Table 4 Change in conductivity (Δσ in mho/Å) at pressure 1GPa in defect free and defected CNTs at 1GPa

Tubes	Δσ in mho/Å	
	Without defect	With defect
(10,0)	$1.37x10^{-8}$	$2.59x10^{-8}$
(9,0)	0.08	0.147
(8,0)	$2.9x10^{-10}$	$1.64x10^{-7}$

Table 5 Change in conductivity (Δσ in mho/Å) at pressure P_1 and P_2 in defect free CNTs

Tube	Δσ at pressure P_1	Δσ at pressure P_2
(10,0)	$3.5x10^{-8}$	$3.93x10^{-8}$
(9,0)	0.215	0.215
(8,0)	$8.9x10^{-9}$	$1.5x10^{-7}$

4. Conclusions

The mechanical behavior of the nanotube varies in the presence of external pressure which can be explicitly seen from the circular cross section of the tube changing to novel geometries in all nanostructures. This leads to band gap variation in all tubes considered in this work. From the data, we could conclude that a small change in applied pressure alters band gap values drastically showing the sensing capability of the CNTs. Another interesting outcome of this work is that the sensitivity of the tubes enhanced when defects present in the nanostructures. Similar changes occur in the conductivity values also. From the analysis we can say that the effect of pressure on semiconducting tube are significant and in some cases phase transition also occur. Since the defect has a control over structural and electrical behaviors of the CNTs under external pressure, this study is be useful for designing the nano-electromechanical sensor devices.

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