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27

Single Wall Carbon Nanotubes in the Presence of Vacancies and Related Energygaps

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1. Introduction

Carbon nanotube family is one of the most important elements in nanotechnology. High ratio of surface to volume of nano materials cause to appear nanotechnology. This matter is one of the most important properties of produced materials at nano scales. At this scale, materials begin replace their bulky behavior with surface one. Some of physical relations that are used for ordinary materials, also abandoned. In fact, at this scale, laws of quantum physics play a key role and it will be possible to control special properties of material such as melting point, magnetic behavier, charge capacitance and even colour of material with no change in their chemical properties. This text is concentrated on some most important carbon nanotubes.

Carbon atoms can form chemical bonds by hybridizing the atomic orbitals of their valence bonds and assume many structural forms such as graphite, diamond, carbon fibers, fullerenes, and carbon nanotubes. Carbon nanotubes (CNTs) discovered by Sumio Iijima in 1991 [Iijima,1991], are one of the most exciting quasi-1-D solids that exhibit fascinating electrical, optical, and mechanical properties such as high current density, large mechanical stiffness, and field emission characteristics [Choi et al., 1999; Saito & Dresselhaus ,1998]. These properties of CNTs enable a wide range of applications in the various fields such as electron emission [Bonard et al., 1999; Dresselhaus et al., 2001; poole et al. 2003], energy storage [Meyyappan , 2005, Chambers et al., 1998], composites [Dresselhaus et al., 2001; Meyyappan et al., 2005], solar cells [Lee, 2005; Pradhan et al., 2006; Wei et al., 2007], nanoprobes and sensors [Dai et al., 1996], and biomedicine [Sinha et al., 2005].

A single-wall carbon nanotube (SWCNT) is a graphene sheet rolled into a cylindrical shape with a diameter of about 0.7 - 2.0 nm [Saito et al.,1998], but A multiwall carbon nanotube (MWCNT) comprises a number of graphene sheets rolled concentrically with an inner diameter of about 5 nm [Harris, 2005]. Since the aspect ratio of the carbon nanotube cylinders (length/diameter) is as large as 104-105 [Saito et al., 1998], these nanotubes can be considered as one-dimensional nanostructures.

CNTs according to their structures are classified to three types of armchair, zig zag, and chiral [Saito et al., 1998]. The terms ‘zigzag’ and ‘armchair’ refer to the arrangement of hexagons around the circumference. Armchair and zigzag nanotubes are defined by a carbon nanotube whose mirror image has an identical structure to the original one. On the contrary, Chiral nanotubes in which the hexagons are arranged helically around the tube axis, exhibit a spiral symmetry whose mirror image cannot be superposed on to the original one [Saito et al., 1998 & Harris, 2009].

SWCNTs can be either metallic or semiconducting, depending on their diameter and chirality. All (n, n) armchair nanotubes yield 4n energy subbands with 2n conduction and 2n valence bands. All armchair nanotubes have a degenerated band between the highest valence band and the lowest conduction band, where the bands cross the Fermi level. Thus, all armchair nanotubes are expected to be metallic. For a general (n, 0) zigzag nanotube, if n is a multiple of 3, the nanotube becomes metallic as the energy gap at k=0 becomes zero; however, if n is not a multiple of 3, the nanotube becomes semiconducting because an energy gap which is proportional to the nanotube diameter opens at k=0 [Saito et al., 1998].
One of the important things which plays essential role on electronic properties, is the energy gap which can inform us about metallic and semi-metallic properties of nanotubes. Variety of probes predict that armchair single-wall carbon nanotubes are always metallic [Dresselhaus et al., 1996] and all the other tubes (zigzag and chiral), depend on whether they satisfy n-m=3I or not (where I is an integer), are metallic or semi-metallic [Wildöer et al., 1998]. In the pervious dedicates, some calculations and experiments have been focused on how we can change the electronic properties of SWCNTs for achieving new nanoelectronic [Andriotis & Menon,2007; Lee et al. ,2007; Tans et al. , 1998] and spintronic [Meyyappan, 2005, Chambers , 1998; Lee ,2005, Pradhan and Batabyal, 2006] devices. Some of them have used the external fields such as electric, magnetic, and radiation fields. In these works, the Probes have demonstrated that the presence of a magnetic field perpendicular to the nanotube axis induces a metal-in, 2005, ulator transition for the metallic (9, 0), (12, 0) . . . nanotubes in the absence of disorder and semiconducting nanotubes can become metallic with increasing magnetic strength [Wei et al., 2007]. Some other works showed that for zigzag tubules (n, 0), the gap varies linearly with stress and independently of diameter, so a uniaxial-stress applied parallel to the axis of carbon nanotubes can significantly modify the band gap and induce a semiconductor-metal transition [Dai et al., 1996].
Some other investigations used structural defects such as substitutional disorders, vacancies, and adatoms on SWCNTs [Dresselhaus et al., 1996; Harris , 2005; Sinha et al., 2005]. Among the various kinds of structural defects in SWCNTs, effects of vacancies have been studied more recently [Wildöer, 1998]. Experimental observations showed that carbon atoms in carbon nanotubes can be released under electron or ion irradiation [Ajayan et al., 1998; Zhu et al., 1999] effectively, leaving vacancies in SWCNTs behind. Lately, Yan Li et al. have showed that by symmetry breaking in armchair carbon nanotubes, metal-semiconductor transition can be occurred. They estimate the band gap opening as a function of both the external potential strength and the nanotube radius and suggest an effective mechanism of metal-semiconductor transition by combination of different forms of perturbations [Li et al., 2004].
In addition, the recent probes have illustrated that vacancies can change the electronic properties of SWCNTs, converting some metallic nanotubes to semiconductors and semiconducting ones into metals, also for most of SWCNTs, the electronic properties strongly depend on the configuration of vacancies [Yuchen et al., 2004]. The influence of vacancy defect density on electrical properties of armchair SWCNTs was investigated and the results showed that there is no simple correlation between mono-vacancy defect density and band gap [Tien et al., 2008].
Quite recently, by considering the vacancies as substitutional disorders we investigate effects of vacancy percentage on the energy gap of different zigzag SWCNTs, by using Green's function technique and self-consistent coherent potential approximation (CPA) method [Faizabadi, 2009].

2. Electronic density of states

The electronic density of states (DOS) is the number of available electrons for a given energy interval. DOS of a crystalline solid, which dramatically depends on the dimension of the system, is fundamental in describing the electronic transport, electrical, optical, thermal, and mechanical properties of the solid [Lu, Pan, 2004, Zhu et al., 1933]. The density of states enters in the experimental study, the application of the electronic properties, and computation of some useful quantities of a system such as electrical resistance and conductance.The helicity or local symmetry of CNTs, along with the diameter which determines the size of the repeating structural unit introduces significant changes in the electronic density of states, and hence provides a unique electronic character for the nanotubes [Hansson et al., 2000]. The DOS of semiconducting carbon nanotubes near the Fermi level located at E=0 is zero, but the DOS of metallic nanotubes near the E=0 is non-zero. In addition, the DOS of zigzag and armchair carbon nanotubes shows van Hove singularities whose numbers are consistent with the number of hexagons around the circumference of the (n, m) nanotube.

3. Synthesis methods of carbon nanotubes

Generally, three techniques are being used to produce carbon nanotubes including the electric arc discharge, the laser ablation, and the chemical vapor deposition (CVD). In each of techniques it is possible we have some vacancies in produced carbon nanotube structures. In the next sections, the method of evaluating the effects of vacancies in the DOS of these structures are discussed, here a brief explanation on Synthesis methods of carbon nanotubes is presented.

3.1 Electric arc discharge

The electric arc discharge method as one of the first methods to produce CNTs, employs a chamber filled with an inert gas, two electrodes of pure graphite rods, and a DC power supply. A current of about 50–100A passed though the electrodes causes carbon atoms are vaporized from the graphite anode in the form of crystallites and are deposited on the cathode electrode in the form of small carbon clusters. Next, these carbon clusters rearrange themselves into a tubular shape forming the MWCNTs, which drift toward the cathode and deposit on its surface. MWNTs are obtained when a pure graphite target is used and SWNTs when the target is a mixture of graphite and metallic catalysts such as Ni-Co or Ni-Y mixtures. However a cylindrical and homogenous deposit forms on the cathode with a quite high rate, the presence of “unwanted” graphite crystallites that do not form into nanotubes is the limiting factor for high yield CNTs [Peter, Harris, 2009, Dervish et al., 2009].

3.2 Laser ablation

The laser ablation or the evaporation method was introduced by Smalley and his coworkers in 1995. In this technique, a powerful laser is used to ablate a carbon target in an inert atmosphere at low pressure. The laser beam incident results in evaporating carbon from the graphite. The carrier gas sweeps the carbon atoms from the high-temperature zone to a cold copper collector on which they condense into nanotubes. In order to generate SWCNTs using the laser ablation technique, it is necessary to impregnate the graphite target with transition metal catalysts. It is experimentally found that the SWCNT growth time in this

technique is only a few milliseconds long. Generally, along with SWCNTs and MWCNTs, fullerenes, amorphous carbon, and other carbon by-products are produced while using the laser ablation technique. MWCNTs produced by this method have a number of layers varying from 4 to 24 and an inner diameter ranging between 1.5 and 3.5nm. Unfortunately, the laser ablation methode is very expensive because it involves high-purity graphite rods and high power lasers [Dervish, 2009; Loiseau et al., 2006].

3.3 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is a relatively slow method that produces long CNTs quantities. In this method, CNTs are synthesized by taking hydrocarbons (the commonly used sources are methane, ethylene, and acetylene) and using an energy source, such as electron beam or resistive heating, to impart energy to them. At first, the energy source heats The hydrocarbon at high temperatures, typically between 700 and 1000 ˚C, in the presence of catalytic systems (usually a first-row transition metal such as Ni, Fe, or, Co) and breaks it into hydrogen and carbon. Then, carbon atoms dissolve and diffuse into the metal surface and rearrange themselves into a network containing hexagons of carbon atoms and finally precipitate out in the form of CNTs. Higher yields of MWCNTs and SWCNTs are produced when the catalytic system is composed of two different metals. CNTs produced with the CVD method can be scaled up for large scale and high-quality at a relatively low cost. In addition, the growth of CNTs can be controlled by adjusting the reaction parameters such as the catalyst system, temperature, type of hydrocarbon, and the flow rate of the gases. Another advantage of the CVD method is that it enables the deposition of CNTs on pre-designed lithographic structures, producing ordered arrays of CNTs [Dervish, 2009].

4. Coherent potential approximation (CPA)

In 1963, Davis, Langer and Klauder introduced the coherent potential approximation to solve the single-site scattering problem [Yoyozawa,1968]. Then, several authors [Onodera & Yoyozawa, 1968; Soven 1960] used it to calculate DOS in a disordered substitutional alloy in which random elements have short-range potential. In this approximation, random disordered system would be replaced by an effective ordered system which is chosen so that the average of the scattering amplitudes for the actual atoms placed in the effective medium vanishes. Besides, according to this theory, the behavior of a single site or cell specifies the manner of the whole system.

To calculate the averaged Green's function, the single electron Green's function can be expressed as follows,

$$G(\omega) = \frac{1}{\omega - H}, \tag{1}$$

here H is the Hamiltonian of the system. In order to use the multiple scattering theory, H is better to divide into the unperturbed or reference Hamiltonian K and the perturbation term v as,

$$H = v + K. \tag{2}$$

Also, the reference Green's function P is written as,

$$P(\omega) = \frac{1}{\omega - K}, \tag{3}$$

Using P, the t scattering matrix associated with the atom n in the effective medium becomes,

$$t_n = v_n \left[1 - pv_n\right]^{-1}. \tag{4}$$

Next, the average of the total scattering matrix T related to the G given by

$$G = P + PTP, \tag{5}$$

Can be expressed as

$$< T >= \sum_n < T_n > = \sum_n < t_n (1 + P \sum_{m \neq n} T_m) >. \tag{6}$$

On the other hand, the effective Hamiltonian can be defined as,

$$H_{eff} = K + < T > (1 + p < T >)^{-1}, \tag{7}$$

or

$$H_{eff} = K + \sum_n < t_n > (1 + P < t_{n>})^{-1}. \tag{8}$$

Within the single site approximation, the condition of $< t_n >=0$ for any n leads to $< T >= 0$ and as a result $< G >= P$. It means that additional scattering due to a real atom in the CPA environment is averagely zero. Thus, average scattering caused by an impurity is equal to the scattering caused by the environment. In this condition, the effective Hamiltonian is equal to K. Since the K is not exactly specified, it can be computed by the self consistent method.

5. Infinite zigzag single wall carbon nanotubes in the presence of vacancies

The single-wall carbon nanotube in tight bonding model is described by [Economou, 2006, Heyd, 1997],

$$\hat{H} = \sum_{i\alpha} \left| i_\alpha \right\rangle \varepsilon_i^\alpha \left\langle i_\alpha \right| + \sum_{ij\alpha\beta} \left| i_\alpha \right\rangle \gamma_{i,j}^{\alpha\beta} \left\langle j_\beta \right| , \tag{9}$$

where a and β refer to the A or B sublattices, ε_i^a refer to on-site energies, and $\gamma_{i,j}^{a\beta}$ is the hopping integral between sites i and j in A or B sublattices. Since we consider the nearest neighbor interaction, the hopping integrals $\gamma_{i,j}^{AA}$ and $\gamma_{i,j}^{BB}$ take zero values while the off-diagonal hopping integrals, $\gamma_{i,j}^{AB}$ and $\gamma_{i,j}^{BA}$, take a constant value γ_0. The on-site energies associated with the two different sites A and B of a graphene sheet have the same values. We neglect the effect of wall curvature in Hamiltonian. The complete set of $\left\{ \left| i_\alpha \right\rangle \right\}$ is the atomic wave functions localized on site i. in A or B sublattices. The Bloch wave functions of the tube are given by [Heyd, 1997],

$$\left\langle \boldsymbol{X} \middle| \boldsymbol{K} \right\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\boldsymbol{K}.\boldsymbol{R}_j} \left\langle \boldsymbol{X} \middle| j \right\rangle \tag{10}$$

Here, we just consider the electronic properties of π- bonds since every carbon atom has four valance electrons, one 2*s* electron and three 2*p* electrons and the overlap between the p_z wave function with the *s* or the p_x and p_y electrons is strictly zero, we can treat the p_z electrons, form π-bonds of graphene, independently of the other valance electrons. There are also some high symmetric points in Brillouin zone which are located near the Fermi level, so many of the electronic properties of SWCNTs are related to this bonds [Wallace, 1972]. The associated Green's function operator can be described as [Economou, 2006],

$$\hat{G} = \left[\hat{I}z - \hat{H}\right]^{-1} \tag{11}$$

So the local density of states can be written as

$$DOS(E) = \mp\frac{1}{\pi}\mathrm{Im}\left[Tr\left\{\hat{G}(E \pm is)\right\}\right] = \mp\frac{1}{\pi}\mathrm{Im}\left[\sum_m \hat{G}^{(m)}(E \pm is)\right] \tag{12}$$

where *m*, the number of allowed band, is obtained by the half number of at0oms in the first Brillouin zone and *s* is an infinitesimal number for convergence. We present a schematic plot of our system which is a typical zigzag SWCNT in the presence of vacancies as substitutional disorders in Fig. 1.

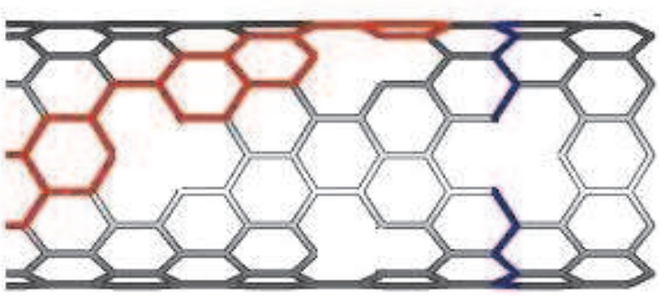

Fig. 1. The schematic plot of zigzag single-wall carbon nanotube with random vacancies

On the other hand, we suppose in the presence of vacancies the structure remain the same as in the absence of them except that some carbon atoms are replaced by holes.
By considering this assumption, in order to investigate effects of vacancy percentage on density of states of SWCNTs, we use coherent potential approximation. As mentioned before, in CPA, the Green's function for a system of scatterers can be written in operator notation as [Györffy, 1972; Korringa & Mills, 1972]:

$$\tilde{G} = G + GTG \tag{13}$$

where $\tilde{G}$ is the Green's function of real nanotube and *G* is the average effective Green's function and *T* is the total scattering matrix of the system. The scattering matrix of the system may be written as [Györffy, 1972]:

$$T = \sum_{i,j=1}^{N} t_i \delta_{i,j} + \sum_{i,j=1}^{N} \sum_{k \neq j} T_{ik} G t_j \,, \tag{14}$$

where T_{ik} is the scattering-path operator which have been introduced by Györffy for the first time and t_i is the t matrix that describes the scattering from the potential on the i-th site which can be written as,

$$t_i = V_i(1 - GV_i)^{-1}, \tag{15}$$

Here, V_i is the extra potential that is caused the scattering i-th site with respect to an effective medium. The effective medium is introduced by the self energy ξ which can be determined by $\langle T \rangle = 0$. Using the CPA, we impose the condition that for any site $\langle t_i \rangle = 0$ which means the extra effective scattering due to the atom at site i vanishes and the following self-consistent equations can be achieved [Datta & Thakur, 1994],

$$G^{(m)\alpha}(E \pm is) = \frac{\Omega}{2\pi N} \times \lim_{s \to 0^+} \int_{(m)band} \frac{E \pm is}{(E \pm is)^2 - \left| \sum_{ij\alpha} e^{i\boldsymbol{K}.(\boldsymbol{R}_i - \boldsymbol{R}_j)} \gamma_{i,j}^{\alpha} \right|^2 - \xi^{(m)}} \tag{16}$$

and

$$\xi^{(m)}(E \pm is) = \frac{-1}{2G^{(m)}(E \pm is)} + \left[\frac{1}{4G^{(m)2}(E \pm is)} + \frac{\varepsilon_c}{G^{(m)}(E \pm is)} - \frac{\eta \varepsilon_c}{G^{(m)}(E \pm is)} \right]^{\frac{1}{2}}, \tag{17}$$

where ε_c is the on-site energy of carbon atoms, η is the vacancy percentage, and $\xi^{(m)}$ is the self-energy.

By using the method described above, we investigate the density of states of zigzag (12, 0) SWCNT. All calculations are performed at zero temperature and we use ε_c= 1 eV and γ_0= 2.75 eV. The density of states of (12, 0) SWCNT as a function of energy in units of γ_0 are depicted in Fig. 2 for η = 0. The energy gap of (12, 0) SWCNT in the absence of vacancy, η = 0, is E_g= 0.02 eV that is in agreement with local density approximation (LDA) calculations [Miyake & Saito,1998]. Saito et al. showed that by just using the π tight-binding method there is no gap in the band structure, but this is not shown in our calculations. The associated experimental probes showed that the energy gap of (12, 0) SWCNT is 0.04±0.004 eV [Ouyang et al., 2001]. The energy gap of three zigzag SWCNTs is compared in Table 1. In regard to Table 1, by increasing SWCNT's index or increasing the diameter of SWCNTs, our results approach to the experimental results of Min Ouyang et al. The difference is as a result of neglecting the effect of wall curvature in Hamiltonian as mentioned before.

(n , 0) SWCNT	E_g (eV)	E_g (eV) from Ref.
(9, 0)	0.022	0.080±0.005
(12, 0)	0.02	0.04±0.004
(15, 0)	0.02	0.029±0.004

Table 1. Comparison between our computational energy gaps with experimental energy gaps from Ref. [Ouyang, 2001].

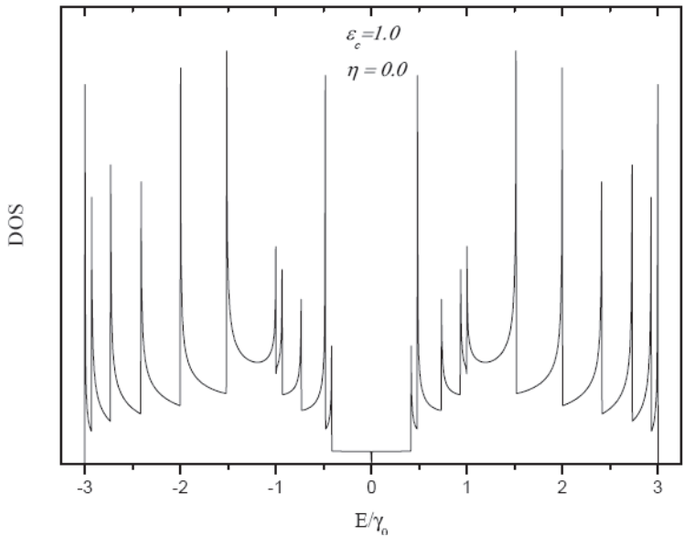

Fig. 2. Density of states for a pure (12, 0) SWCNT

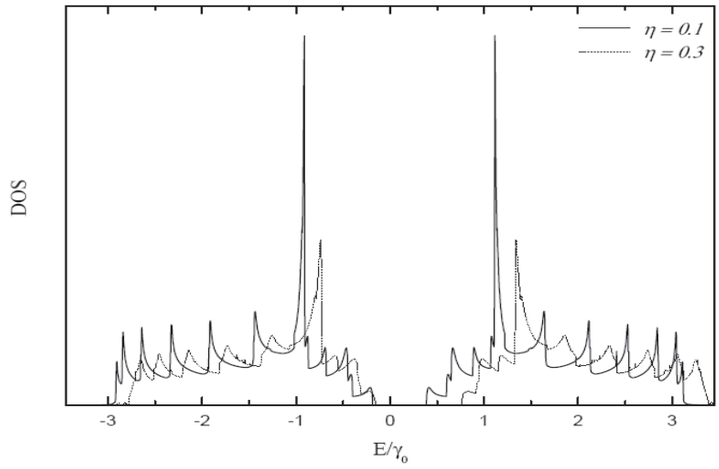

Fig. 3. Density of states for (12, 0) SWCNT in the presence of vacancy for η = 0.1(Solid line), η = 0.3 (Dot line).

The band gap opening is occurred, as it is depicted in Fig. 3 for η = 0.1, 0.3. According to this figure, the maximum value of the peak of one-dimensional (1D) Van Hove singularities in greater values of vacancy concentrations become less, also at greater values of vacancy concentrations, SWCNTs lose their 1D characteristics and become similar to a kind of 2D disordered graphene sheet. In realistic, by increasing the value of vacancy concentrations, the freedom of valance electrons becomes higher, so we expect the feature of 2D structure. Also there is a small shift in DOS because of influence of vacancy percentage on the on-site energy of carbon atoms. By increasing the value of vacancy concentrations, as it is depicted in Fig. 3, the number of peaks becomes less. In addition, by increasing vacancy percentage on (12, 0) SWCNT the energy gap is increased. This fact can be realized by considering the broken lattice symmetries. By breaking symmetry, the valance electrons do not obey Bloch order, so multiple scattering is occurred, then we have gap opening and metallic SWCNTs is changed to semi-metallic SWCNTs.

The variations of the energy gap versus vacancy percentage is shown in Fig. 4(a), 4(b), and 4(c) for (7, 0), (8, 0), (12, 0) SWCNTs, respectively. The results show that, by increasing vacancy percentage for all three types of zigzag SWCNTs, the energy gap is also increased. This treatment is realized by multiple scattering that is occurred in vacancies. Moreover, the slopes of the graphs for the small values of vacancy percentages are not the same and at low vacancy percentages, the growth of gap opening versus vacancy percentage for (12, 0) SWCNT is higher than the other ones. Also by considering Fig 4(a), 4(b), and 4(c), we realize that for $\eta = 0$, the energy gaps of (7, 0), (8, 0), and (12, 0) SWCNTs, are 1.19, 1.12, and 0.02 eV, respectively. Furthermore, in special vacancy percentage, the energy gap of (7, 0) SWCNT is higher than the other ones. We can realize this result by considering the number of carbon atoms in the unit cell of SWCNTs and the diameter of SWCNTs. The number of carbon atoms in the unit cell of (n, 0) SWCNTs, q, is derived by $q = 2n$, so the number of carbon atoms in the unit cell of (7, 0), (8, 0), (12, 0) SWCNTs are 14, 16, and 24, respectively. Thus the number of carbon atoms and diameter of (7, 0) SWCNT is less than the other ones, so in special vacancy percentage, the affects of breaking symmetries and backscattering are more dominant respect to the others.

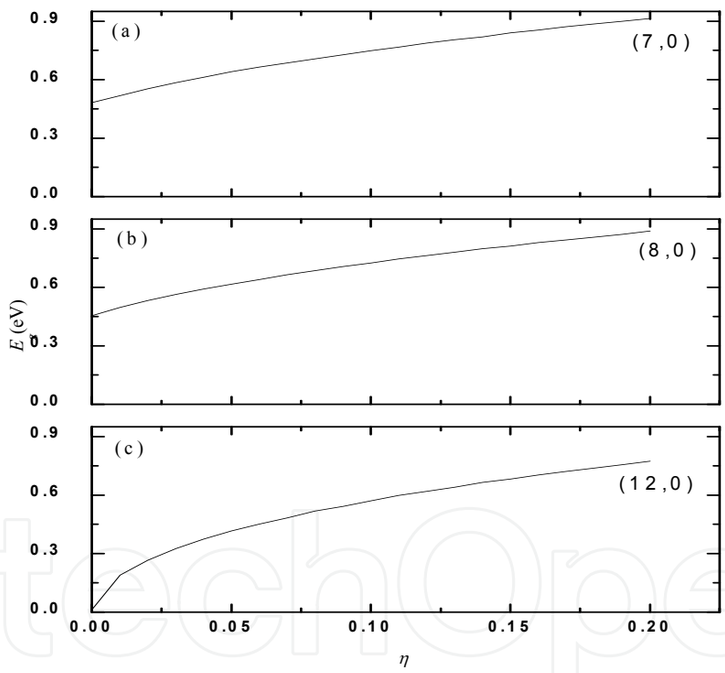

Fig. 4. The energy gap versus vacancy percentage for (a) (7, 0) SWCNT, (b) (8, 0) SWCNT, (c) (12, 0) SWCNT.

The energy gap of different kinds of zigzag SWCNTs as a function of nanotube index n for three different values of vacancy percentage 0, 0.01, and 0.15 is displayed in Fig. 5. This figure shows that for all zigzag SWCNTs the energy gap is also increased by increasing vacancy percentage. Thus metallic to semi-metallic transition is occurred for metallic zigzag SWCNTs that is considered by Yuchen Ma et al. [Yuchen, 2004] by using spin-polarized density functional theory. They investigated the influence of configuration mono-vacancy on electronic properties of zigzag SWCNTs and showed for six kinds of zigzag SWCNTs

with n = 5… 10, the vacancies can change the electronic properties of SWCNTs, converting some metallic nanotubes to semiconductors. Also they found that only (5, 0) SWCNT is always semiconductor by changing configuration of mono-vacancy and here according to Fig. 5, we see that by increasing the value of vacancy percentage, (5, 0) SWCNT remain semiconductor. However, this treatment also occurs for all kinds of semiconductor zigzag SWCNTs such as (7, 0), (10, 0), and so on.

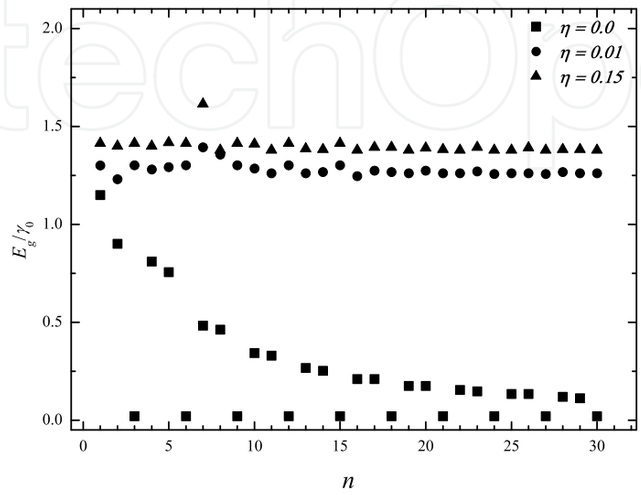

Fig. 5. The energy gap versus the zigzag nanotube index for three values of vacancy percentage η = 0.0, 0.01, 0.15.

In summary by using CPA method, effects of vacancy percentage on the energy gap of zigzag SWCNTs were investigated. It is found that the energy gap of pure (12, 0) SWCNT is 0.02 eV that is in agreement with LDA calculations and the experimental work of M. Ouyang et al., Also by increasing the concentration of vacancies, the energy gap is increased and a metallic to semi-metallic transition is occurred for metallic (n, 0) zigzag SWCNTs. For semiconductor zigzag SWCNTs any transition does not appear. As mentioned before, at large enough vacancy concentrations, the SWCNTs lose their 1D characteristics and the associated density of states become similar to a kind of 2D disordered graphene sheet. In addition, our calculations show that the maximum energy gap is increased by decreasing zigzag nanotube index (n) which is due to decreasing diameter of SWCNT and therefore increasing the effect of vacancies in back scattering. Therefore by creation vacancies in the structure of zigzag SWCNTs the metallic to semi-metallic transition are occurred. In addition, it is possible to achieve the special semiconductor SWCNT with a predetermined energy gap in order to use in semiconductor industry.

6. Semiconductor finite zigzag carbon nanotubes in the presence of vacancies

Carbon nanotubes show promise for applications in future electronic systems, and the performance of carbon nanotube devices, in particular, has been rapidly advancing. Semiconducting nanotubes are suitable for transistors. In order to correctly treat carbon nanotube transistors, strong quantum confinement around the tube circumferential direction, quantum tunneling through Schottky barriers at the metal/nanotube contacts,

and quantum tunneling and reflection at barriers in nanotube channel need to be considered by the non-equilibrium Green's function (NEGF) formalism. We study the density of states of *(n, 0)* carbon nanotubes in which an atom has been removed to produce a vacancy[Faizabadi et al.,2009](Fig 6). Vacancy is one of the most common defects in carbon nanotubes and affects the physical properties of them. The on-site energy of the vacancy element is equaled high value, essentially repelling the carriers from that particular site.

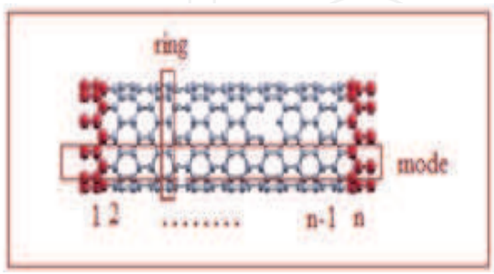

Fig. 6. The schematic of a finite zigzag carbon nanotube in presence a single vacancy. The modes are aligned along the carbon nanotube axis and rings that are around the cylindrical circumference.

Our system consists of a carbon nanotube that coupled to the left L and right R lead described by the following Hamiltonian

$$H = \sum_i \varepsilon_i |i><i| + \sum_{i \neq j} t_{i,j} |i><j| \tag{18}$$

where, E_i is the on-site energy for each carbon atom in the carbon nanotube and is the hopping between the atomic sites which are supposed to be non zero for the nearest neighbors. In this model there are orthogonal basis, corresponding to a spherically symmetric local orbital at each atomic site in the system.
The total Hamiltonian for a system consist of a finite carbon nanotube which is connected into two leads, the left and right ones is

$$H = H_L + H_R + H_C \tag{19}$$

where, $H_{L(R)}$ describes the Hamiltonian for left and right leads. H_C refers to the Hamiltonian for central region. An effective method to describe scattering and transport is the Green's function that is determined by the equation

$$\left[(E \pm i\eta)I - H\right] G_C^{r,a} = I \tag{20}$$

here, r and a refer to retarded and advanced Green's function. For an isolated non interacting system the Green function is obtained after the matrix inversion.
The Green function coupled to the leads is determined by the expression

$$G_C^r(E) = [(E + i\eta)I - H_C - \Sigma_L - \Sigma_R]^{-1} \tag{21}$$

where, $\Sigma_{L,R}$ is called self-energy that describe the interaction between leads and system

$$\Sigma_{L(R)}(E) = \tau_{L(R)C} g_{SL(R)} \tau^{\dagger}_{L(R)C} \tag{22}$$

where, $g_{SL(R)}$ is the surface green function of the decoupled left and right leads that is calculated in the absence of the scattering region and different from the $G_C^r(E)$.
The density of states (DOS) as a function of the incident electron energy for a carbon nanotube is [*Datta,*1995]

$$DOS = -\frac{1}{\pi} \mathrm{Im}\left[\mathrm{Trace}\left(G_C^r(E)\right)\right] \tag{23}$$

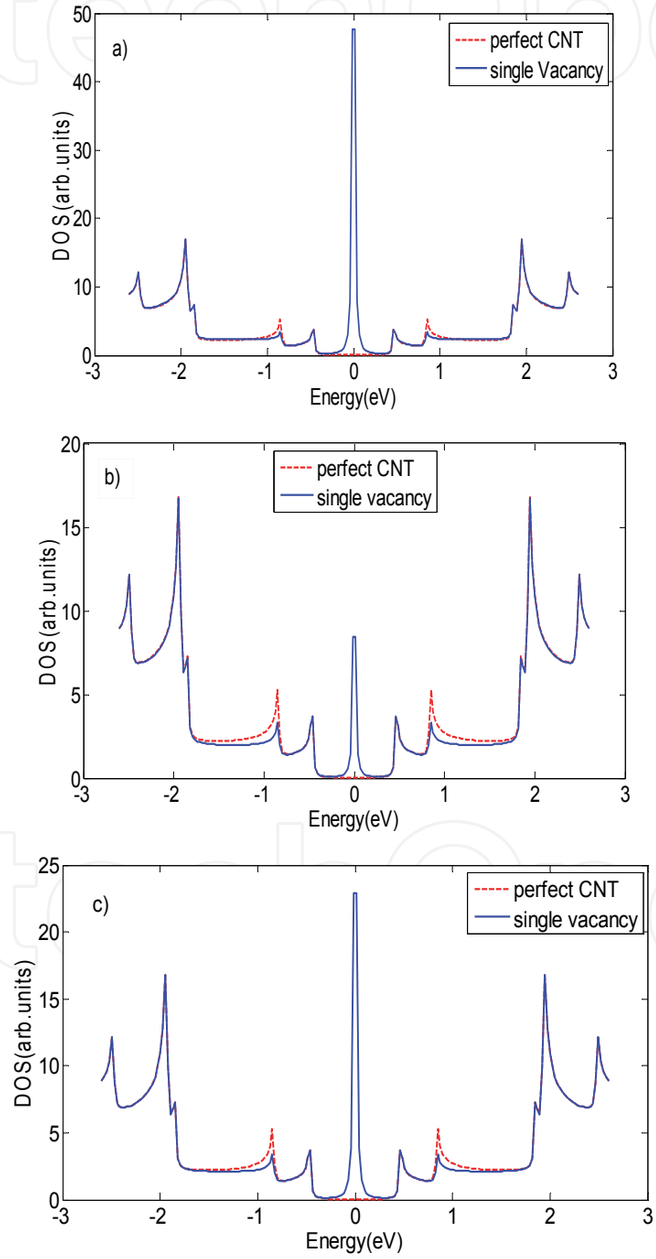

Fig. 7. The density of states of finite zigzag carbon nanotubes (11,0) in presence of the single vacancy in a: 2th ring b: 3th ring c: 4th ring of 4th mode

The hopping parameter for the nearest neighbour is fixed to $V_{pp\pi} = t = -2.66\ [eV]$ and the on-site energies for this system are set to zero.

By using this model the effect of vacancies on the density of states of finite zigzag carbon nanotubes (11, 0), is investigated. This kind of carbon nanotube is semiconductor with an energy gap around the Fermi energy.

In Fig 7 the density of states of finite zigzag carbon nanotubes (11, 0) in presence of the single vacancy is calculated. In these figures we consider the vacancy site in the same mode and different rings. The presence of vacancies breaks the symmetry of the system and creates available states around zero energy, in prohibited band gaps. The density of states around the Fermi level rises due to the broken π bands at the vacancy site. These states filled with electrons around the Fermi level that in perfect carbon nanotubes there aren't any states in Fermi energy.

In other work the density of states of finite zigzag carbon nanotubes in the channel of (11, 0) in presence of two vacancies is investigated that they are in different rings and modes (Fig 8 and Fig9). The two vacancies are placed at different sites in the channel. In these figures the states that they are near the Fermi level filled with electrons. The vacancies decrease the density of states of finite semiconductor zigzag carbon nanotubes totally.

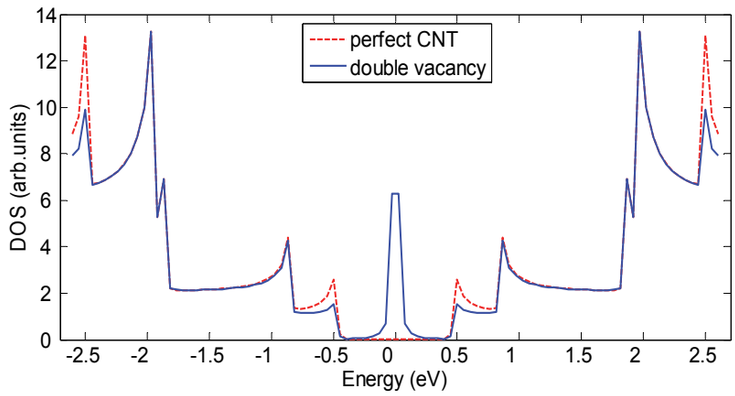

Fig. 8. The density of states of finite zigzag carbon nanotubes (11, 0) in presence of two vacancies in 5th ring of 2th and 8th modes

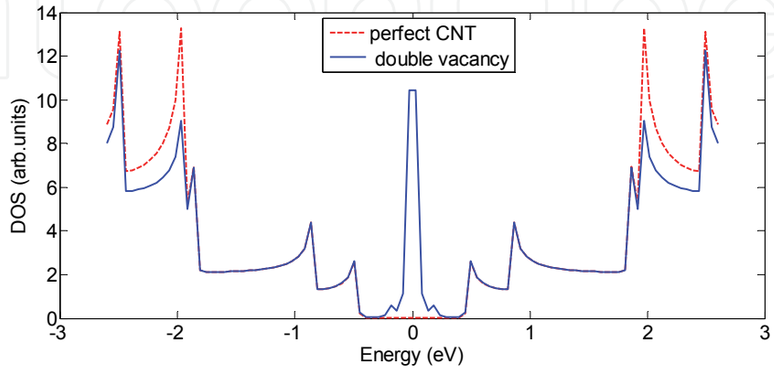

Fig. 9. The density of states of a finite zigzag carbon nanotube (11, 0) in presence of two vacancies in 2th and 7th rings of 6th mode

7. Finite armchair carbon nanotubes in the presence of vacancies

Here by using the method which described in the previous section the density of states of finite armchair carbon nanotubes for different finite length are probed [Orlikowski et al.,2007]. Besides the effect of two vacancies on different length of the finite armchair carbon nanotubes (6, 6), is investigated [Faizabadi & Heidaripour, 2010]

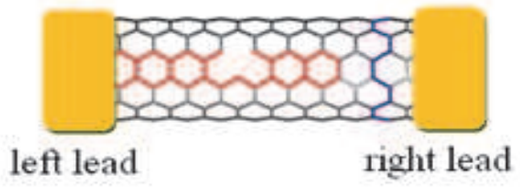

Fig. 10. The finite armchair carbon nanotube with metallic leads in the presence of a vacancy.

Our Probes show that the presence of two vacancies that they are near each other has little affect on the density of states at Fermi energy (Fig 11). When two vacancies are far from each other, by breaking π orbital of atoms, create available states around the Fermi energy and increase the density of states (Fig12).
The vacancies by breaking the system symmetry create available states around zero energy and omit the carbon atomic potential in carbon nanotube. The π bands break at the vicinity of the vacancy site and density of states around the Fermi level rises and electrons filled the states.

8. Carbon nanotube quantum dot in the presence of vacancies

Carbon nanotubes of different chiralities can be joined through a small number of pentagon heptagon defects, forming a nano scale metal/semiconductor or metal/metal carbon nanotube heterojunction (HJ). Carbon nanotube heterojunctions (HJs), which continuously connect nanotubes of different chiral structure using a small number of atomic scale defects, represent the ultimate scaling of electronic interfaces [Chico et al.,1996].
We consider a quantum dot (QD) that is built of zigzag $(2n,0)$ and armchair (n,n) carbon nanotubes connected by n pair of pentagon- heptagon interface defect. The interface itself has n fold rotational symmetry and by connecting the armchair and zigzag nanotubes together a quantum dot is created. We denote this kind of structure by $m(2n,0)/l(n,n)/m(2n,0)$, where $(2n,0)$ on both sides of the quantum dot used as the contacts, one armchair carbon nanotube is central part of the system with specific length. To understand this peculiar behaviour, we plot the structure of a carbon nanotube quantum dot in Fig13.
The junction between two single wall Carbon nanotubes is a pentagon–heptagon (p-h) pair that is the smallest topological defect with minimal local curvature and zero net curvature (Fig 14).

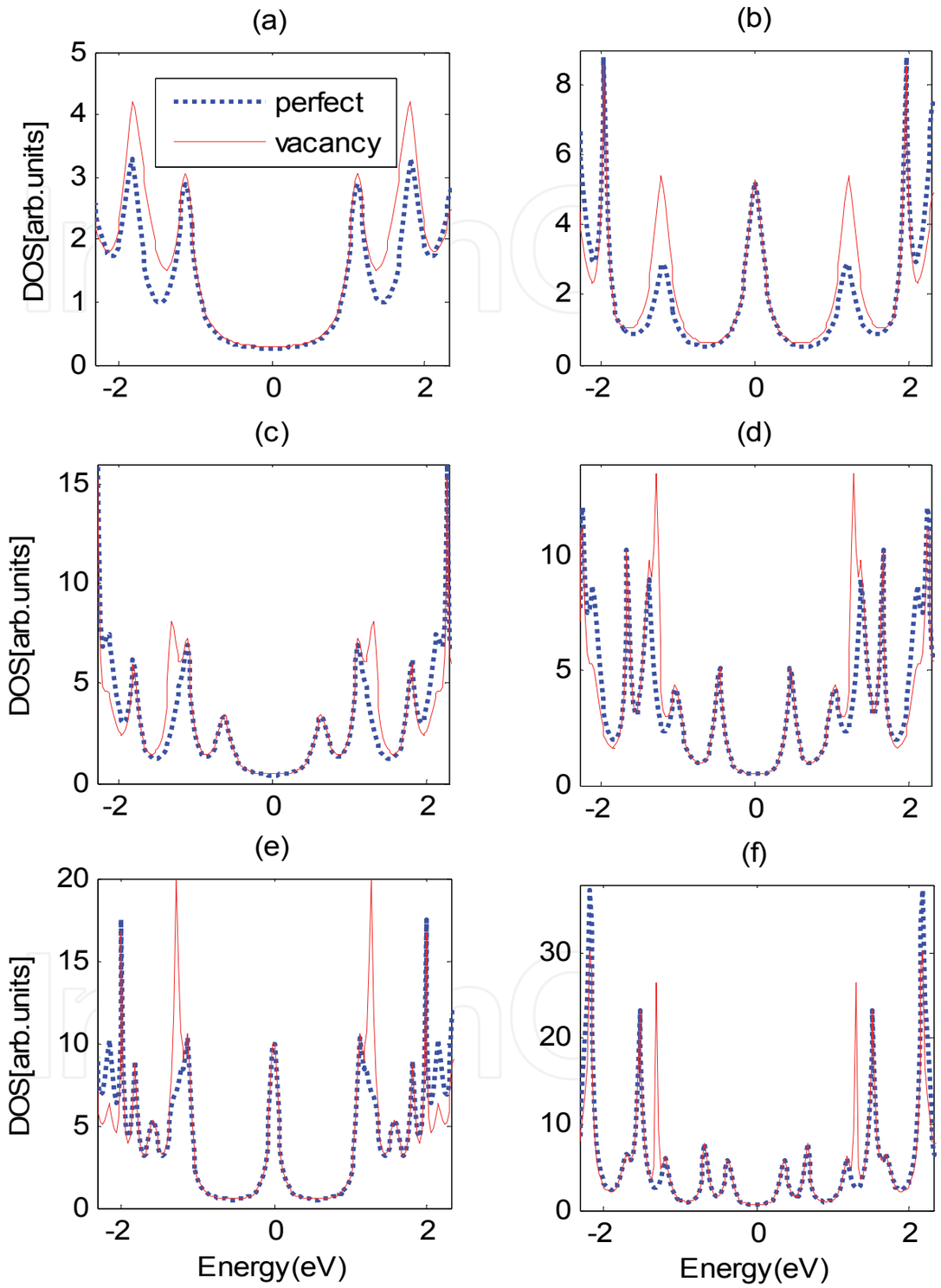

Fig. 11. The density of states of an armchair carbon nanotube (6,6) in the presence of two vacancies which they are near each other for different length of carbon nanotube a: 3rings b: 5 rings c: 7 rings d: 9 rings e: 11 rings f: 13 rings

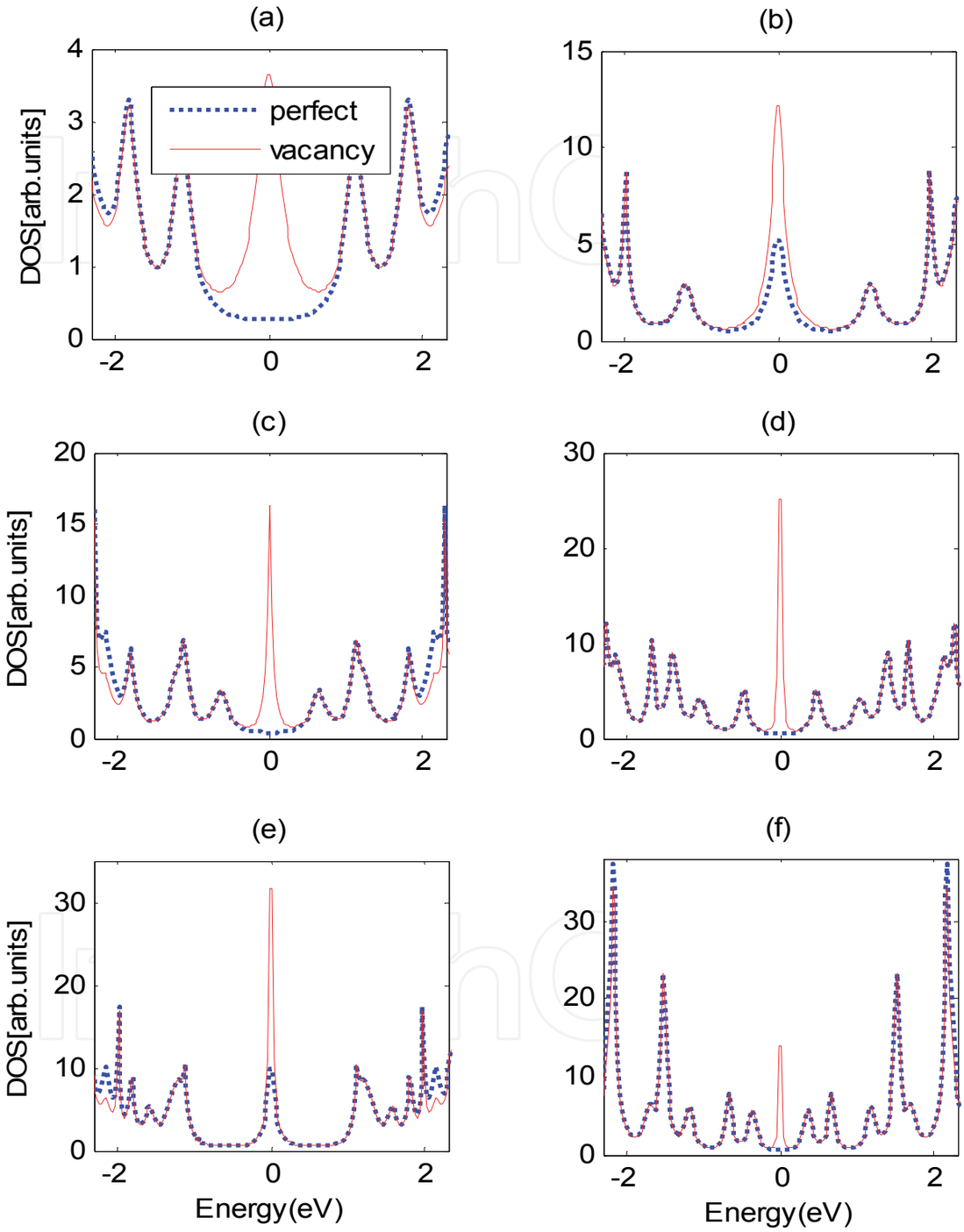

Fig. 12. The density of states of an armchair carbon nanotube (6,6) in the presence of two vacancies which they are far from each other for different length of carbon nanotube a: 3 rings b: 5 rings c: 7 rings d: 9 rings e: 11 rings f: 13 rings

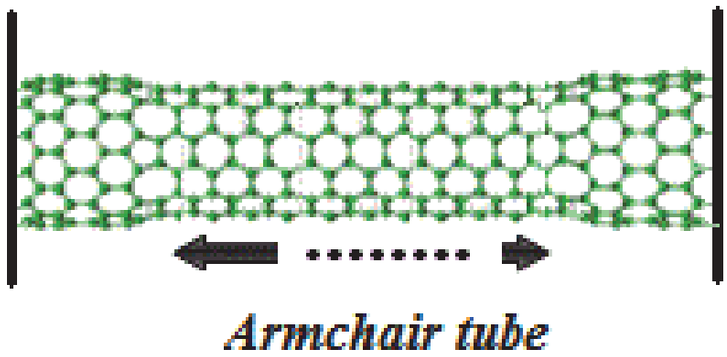

Fig. 13. Schematic view of a carbon nanotube quantum dot.

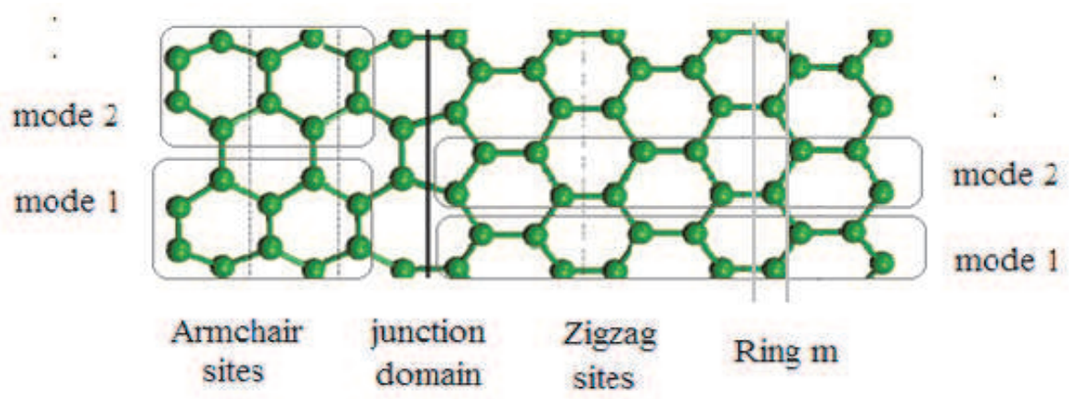

Fig. 14. Schematic representation of Armchair and zigzag modes and rings in real space, a pentagon-heptagon ring as a junction between zigzag and armchair carbon nanotubes quantum dots are shown.

We work in a single π-band tight-binding approximation. The Hamiltonian in the site representation is

$$H = \sum_r \varepsilon_r C_r^{\dagger} C_r + \sum_{r \neq s} t_{rs} C_r^{\dagger} C_s \tag{24}$$

where r, s denote carbon sites, C and $C^{\dagger}$ the electron annihilation and creation operators, ε_r the on-site energies, and t_{rs} the nearest-neighbors hopping integral between the atomic sites . The on-site energies are set equal zero, while t = −2.66 eV as for graphene which yields the Fermi energy at *0 eV*. It is well known that this approximation gives good description of the band structure of pure nanotubes around the Fermi energy [Reich, et al., 2002].

$$H_{QD} = \begin{bmatrix} H_L & \tau_{LC} & 0 \\ \tau_{LC}^{\dagger} & H_C & \tau_{CR}^{\dagger} \\ 0 & \tau_{CR} & H_R \end{bmatrix} \tag{25}$$

where, H_{QD} is the Hamiltonian for the quantum dot where $H_{C,L,R}$ refers to the Hamiltonian for left and right leads and the Hamiltonian for central region between two leads and there are some terms $\tau_{C(R,L)}$ describe the coupling between zigzag and armchair carbon nanotubes. The density of states of the system is

$$DOS = -\frac{1}{\pi} Im\left[Trace\left(G_{QD}^{r}(E) \right) \right] \tag{26}$$

$G_{r,a}$ are the retarded and advanced Green functions inside the system, taking into account the coupling with the electrodes via the self-energies Σ_L and Σ_R

$$G_{QD}^{r}(E) = [(E + i\eta) I - H_{QD} - \Sigma_L - \Sigma_R]^{-1} \tag{27}$$

where, $\Sigma_{L(R)}$ is the self energy due to the left (right) lead and is defined by

$$\Sigma_{L(R)}(E) = \tau_{L(R)}\, g_{s\,L(R)}^{r}\, \tau_{L(R)}^{\dagger} \tag{28}$$

where, $\tau_{L(R)}$ is the coupling matrix between the system and the left (right) lead, and $g_{s\,L(R)} = [\epsilon - H_{L(R)}]^{-1}$, is the Green's function of the semi-infinite leads which we evaluate using an iterative procedure [Datta,1995a, 1995b].

We investigate, the density of states of a single wall Carbon nanotube $m(2n,0)/\,l(n,n), m(2n,0)$ quantum dot with several armchair length with a method combining the Green's Function formalism with tight binding model. By increasing the length of armchair carbon nanotube in metal-metal system $m(12,0)/l(6,6)/m(12,0)$ and metal-semiconductor system $m(8,0)/l(4,4)/m(8,0)$, we observe changing in the density of states and increment of oscillation of the density of states. In the presence of the single vacancy and omission of a carbon atomic potential, we observe small changes in the density of states of the system (Fig15 and Fig16).

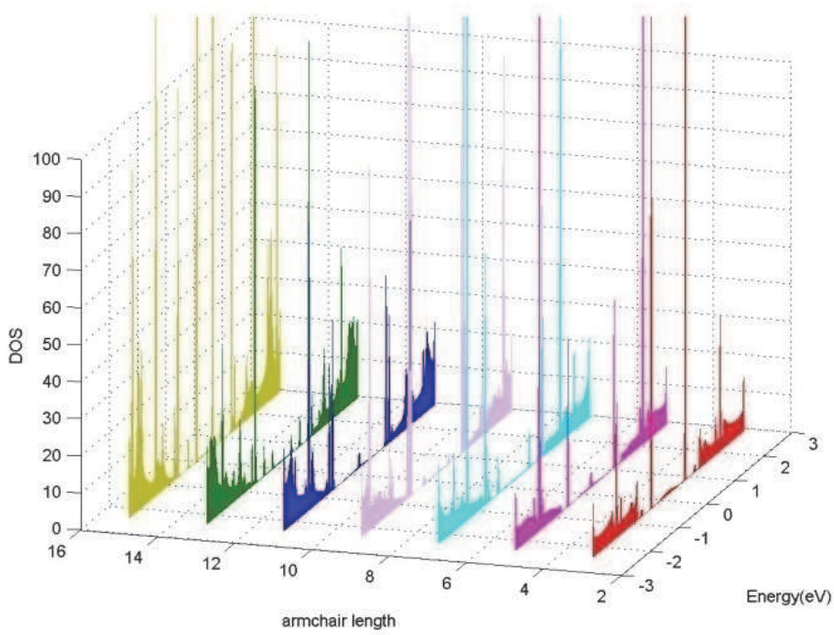

Fig. 15. The density of states of a single wall Carbon nanotube quantum dot with several armchair length

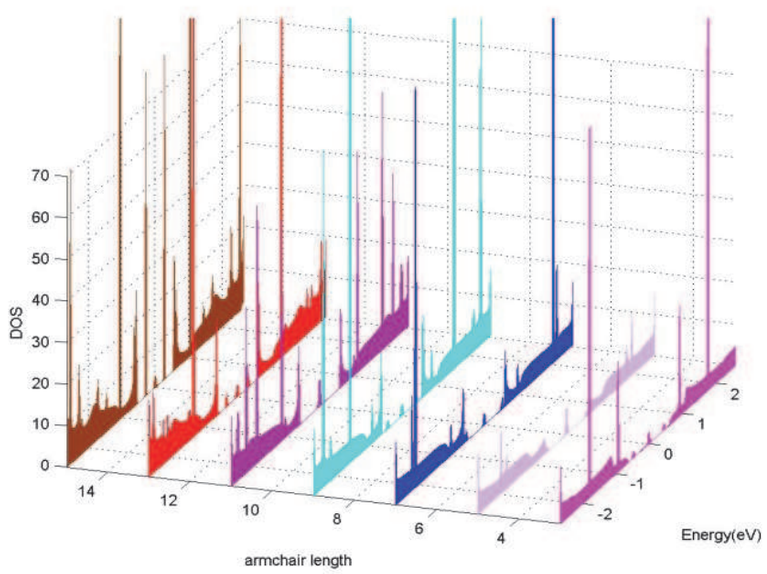

Fig. 16. The density of states of a single wall Carbon nanotube quantum dot with several armchair length.

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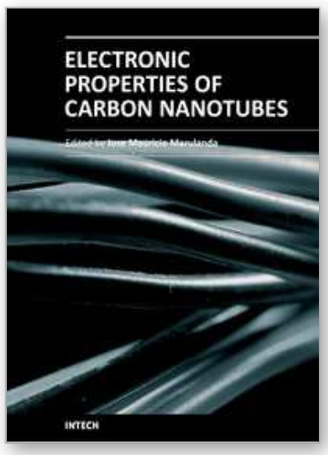

Electronic Properties of Carbon Nanotubes
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Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. These one-dimensional (1D) graphene sheets rolled into a tubular form have been the target of many researchers around the world. This book concentrates on the semiconductor physics of carbon nanotubes, it brings unique insight into the phenomena encountered in the electronic structure when operating with carbon nanotubes. This book also presents to reader useful information on the fabrication and applications of these outstanding materials. The main objective of this book is to give in-depth understanding of the physics and electronic structure of carbon nanotubes. Readers of this book should have a strong background on physical electronics and semiconductor device physics. This book first discusses fabrication techniques followed by an analysis on the physical properties of carbon nanotubes, including density of states and electronic structures. Ultimately, the book pursues a significant amount of work in the industry applications of carbon nanotubes.

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