Electronic structure of single wall carbon nanotubes under transverse external electric field, radial deformations and defects

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ABSTRACT

We present density functional theory and tight binding calculations of a radially deformed (8,0) single walled carbon nanotube under transverse external electric fields. Density functional theory calculations are also presented for radially deformed and defective (8,0) nanotube. Three types of single defects are considered – Stone-Wales, single Nitrogen impurity, and a mono-vacancy. The electronic structure and energy gap changes are explained in terms of orbital admixture in the total density of states and energy band structure as a function of deformation and fields strengths, types of defects, and/or curvature. Our results can be used to understand and interpret experimental data of realistic nanotubes under extreme conditions, as well as to engineer new or build on existing nanoelectronic devices.

Keywords: carbon nanotubes, electronic structure, electric field, defects, deformations

1 INTRODUCTION

Carbon nanotubes (CNT) are cylindrical quasi-one dimensional graphitic structures characterized with a chiral index \((n,m)\) with diverse properties and many potential applications [1]. There has been significant interest in modulating different CNT properties in order to improve our fundamental understanding of these systems as well as to explore possibilities for new devices.

CNT properties can be modified in various ways. One way is to apply a transverse external electric field (TEEF) to the radial direction of the CNT. Strong enough TEEF can couple different energy bands in the nanotube electronic structure resulting in possible semiconductor-metal transitions [2,3]. Understanding the CNT electronic structure as a function of TEEF is an important element in nanotube based field-effect transistors, rectifiers, or p-n junctions [1].

CNT properties can also be modified by incorporating mechanical defects or deformations in their structure. Defects are always present in nanotubes during the stages of synthesis and purification [1], or later on during device production [4]. Defects can also be engineered using electron, ion irradiation [5] or chemical methods. In addition, radial deformation of CNTs has been shown to lead to significant changes in their properties and semiconductor-metals transitions can be achieved. Such deformations can be achieved by applying external hydrostatic pressures [6] or by squashing the nanotube using an AFM tip [7].

Nevertheless, modifying the CNT properties can be challenging experimentally. For example, transforming semiconducting CNTs into metallic ones by radial deformation requires the application of pressures on the order of several ~GPa [8]. Also, relatively strong TEEF ~0.5-0.8 eV/Å are needed to close the gaps for most semiconducting CNTs [3,9]. The large deformation and electric field strengths have led to the search for different ways to modulate the CNT properties. Recently, researchers have shown that weaker TEEF fields can introduce dramatic changes in a defective nanotube resistance and gap as compared to the resistance and gap of a perfect one [10].

Here we investigate additional ways for modulating the CNT characteristics by considering a carbon nanotube under the influence of two external factors. The first case we investigate is related to understanding the combined effect of radial deformation and TEEF on the nanotube electronic structure, and the second one is the combined effect of various mechanical defects and radial deformations. This work presents a fundamental theoretical study of the electronic structure changes as a function of such external factors. Our results reveal that CNT metal-semiconductor transitions can be achieved for various combinations of electric fields and mechanical modifications. Therefore, greater experimental capabilities for new devices are possible when two external factors are applied.

The rest of the paper is organized as follows. In Section 2 the calculation methods are presented. In Section 3 results and discussions are given for deformed CNT under TEEF and for deformed CNT with a defect.

2 CALCULATION METHODS

To obtain and analyze the electronic structure as a function of external electric fields, deformations, and defects, we apply \textsc{ab initio} density functional theory (DFT) and tight binding (TB) methods. To illustrate our results we take a single walled nanotube (SWNT) with a chiral index (8,0). The circular perfect structure is simulated first using the DFT VASP package [11] within the local density approximation for the exchange correlation function. A 1x1x7 Monkhorst-Pack k grid sampling of the Brillouin zone was taken with an energy cutoff of 420 eV. We construct a super-cell consisting of 4 unit cells along the axial direction of the nanotube with length 17.03 Å after relaxation. The
length in the transverse direction is 22.12 Å after the ionic relaxation. The convergence criteria are taken as $10^{-5}$ eV for the energy and 0.005 eV/Å for the force.

The radially deformed (8,0) nanotube was also calculated using VASP with the same super-cell under the same convergence criteria. The tube is squeezed in the $y$-direction and elongated in the $x$-direction. This is characterized by a dimensionless parameter defined as $\eta = (R - R_y)/R$, where $R$ is the radius of the perfect nanotube, and $R_y$ is the semi-minor axis connecting the SWNT regions with lowest curvature – Fig. 1. For all values of $\eta$ the system is relaxed by freezing only the $y$-coordinate of the atoms on the top and bottom rows of the flattened regions while all others are let free.

After the relaxed structure of the (8,0) SWNT for various $\eta$ was obtained, various defects were also introduced. We consider three types of defects – Stone-Wales defect, a single vacancy, and a $N$ substitution impurity. Each defect is calculated separately. For a given $\eta$, the Stone-Wales defect is simulated on the highest curvature region in the (8,0) supercell. The same is done for the vacancy and the $N$ impurity. Such procedure corresponds to first deforming the nanotube and then introducing the defect in the structure. The vacancy and impurity defects are simulated with the inclusion of spin polarization effects, while the Stone-Wales defect is done without spin polarization.

In addition, the structure of the perfect and radially deformed (8,0) nanotube is calculated using a four orbital $\sigma-\pi$ non-orthogonal tight binding model [12]. This is motivated by the fact that the application of an electric field breaks the periodicity of the system. Since DFT methods are applicable only to periodic system, the TB method is adapted to determine the TEEF effect on the nanotube electronic structure.

The TB model involves solving the non-orthogonal eigenvalue problem for the matrix $(H_{TB} - ES)$, where $H_{TB}$ is the tight-binding Hamiltonian for the (8,0) tube including the $\sigma-\pi$ orbitals for each atom, $E$ is the energy, and $S$ is the overlap matrix written in the Slater-Koster scheme. The positions of the atoms for the perfect and radially deformed (8,0) tubes are taken to correspond to the results from the DFT calculations. Also, the TB parameters were adjusted in order to have a good agreement with the DFT results for the electronic structure in each case.

The TEEF provides an additional contribution $H^{\text{f}}$ to the tight-binding Hamiltonian matrix $H_{TB}$, [13] with diagonal elements $H^{\text{f}}_{ii} = -eFR_x \cos(\phi_i + \theta)$ and off-diagonal elements $H^{\text{f}}_{ij} = -eS_{ij}FR_y \cos(\phi_j + \theta)$. The notations are as follows: $e$ is electron charge, $F$ is the strength of the external electric field, $\theta$ is initial phase of TEEF with respect to the $x$-axis, $S_{ij}$ are the overlap matrix elements between two nearest neighbor atoms, $R_x$ is the distance from the $i$th atom to the center of the nanotube, $R_y = (R_x + R_y)/2$ is the distance to the center of nanotubes for the center of mass of the two atoms, $\phi_i$ and $\phi_j$ are the angles between the direction of $F$ and $R_x$ and $R_y$, respectively. The inclusion of the $\sigma-\pi$ orbitals and the non-orthogonality condition is necessary to describe correctly the electronic structure changes due to the various energy bands admixture from the electric field and from to the high curvature regions for the radial deformation cases.

3 RESULTS AND DISCUSSIONS

3.1 Radially deformed (8,0) SWNT under transverse external electric field

The electronic structure of the (8,0) SWNT with various degrees of radial deformation $\eta$ is calculated using VASP first. The results are summarized in Fig. 2. The perfect (8,0) tube is semiconducting with a relatively large band gap $E_g=0.55$ eV. Fig. 2a) shows that increasing $\eta$ results in decreasing of the band gap. Eventually the gap closes at $\eta=0.25$. Further increase in the deformation keeps the band gap closed. This behavior is due to the hybridization of the $\sigma-\pi$ orbitals mainly from the regions with higher curvature. We find that if all atomic coordinates of the deformed tube are allowed to relax, the tube returns to its perfect circular form. In fact, this elastic type of deformation is found for all $\eta \leq 0.75$. If $\eta > 0.75$, the tube breaks down.

The DFT structure and band gap evolution are also calculated and reproduced using the non-orthogonal TB model. Next, TB calculations are performed when TEEF is applied to the (8,0) tube with different degrees of deformation. Fig. 2b) shows how the band gap changes as a function of the electric field strength for several deformations $\eta$. The band gap for the perfect tube does not change much for smaller values of $F$, and it eventually shows oscillatory-like behavior as $F$ is increased indicating several metal-semiconductor transitions. As the radial deformation is increased, $E_g$ first increases and then decreases following similar oscillations as in the case for $\eta=0.0$. Even when the gap is closed, the electric field can induce several metal-semiconductor transitions. This is characteristic for a metallic nanotube response to an external electric filed. In fact, we examined several $(n,0)$ SWNTs, and we found that for all tubes (perfect or
deformed) with small or no band gaps, relatively small electric fields can open larger band gaps. For nanotubes with relatively large energy gaps, stronger fields are needed to decrease $E_g$ [3].

The origin of the semiconductor-metal transitions are analyzed by calculating the energy band structure. In Fig. 2c) we show the energy bands for $\eta=0.10$ and several values of the TEEF strength. The electric field couples the states according to the selection rule $\Delta J = \pm 1$. Note that for a perfect tube, each energy level is characterized by the angular momentum quantum number $J$. The radial deformation couples states according to the selection rule $\Delta J = 0, \pm 2$. When both $F$ and $\eta$ are present, the band gap changes are due to $\Delta J = 0, \pm 1, \pm 2$ as well as to the increased $\sigma-\pi$ hybridization from the higher curvature regions. Thus the band gap opening or closure happens as a result of the competing effects between different energy levels admixture originating from the increased curvature and/or the strength of the applied electric field.

### 3.2 Radially deformed (8,0) SWNT with defects

Here we calculate and analyze the electronic structure of radially deformed (8,0) SWNT with various defects imbedded in its structure. Three single defects are considered – a Stone-Wales (SW) defect, a $N$ atom substitution, and a single vacancy. For discussion purposes the cases with $\eta=0.0$ and $\eta=0.20$ are taken as examples. The bare perfect and deformed (8,0) nanotubes are calculated first using the DFT-VASP code as specified in Section 2. After the relaxation was completed, each defect is introduced on one of the highest curvature sides for the deformed tube. The deformed and defective tube atoms are also allowed to relax. This procedure corresponds to first deforming the nanotube and then making the defect.

We consider first the SW defect. It is characterized by rotating one C-C bond in the tube structure by 90°. Since the chemical structure of the nanotube is not changed in this case, the SW defective tube is a closed-shell system as in the case of a perfect nanotube. Thus our calculations do not involve the inclusion of a spin polarization effects. We find that the most energetically stable SW defect is when the bond parallel to the nanotube axis is rotated. In Fig. 3, the total DOS is shown for the perfect, radially deformed $\eta=0.20$, and radially deformed $\eta=0.20$ with a SW defect (8,0) carbon nanotube. The radial deformation decreases the original $E_g=0.55$ eV (Fig. 3a) to $E_g=0.08$ eV (Fig. 3b), while the SW defect increases the gap to $E_g=0.64$ eV (DOS not shown in here). The SW defect also causes increasing in the gap to $E_g=0.13$ eV (Fig. 3c) for the deformed tube with $\eta=0.20$. The electronic structure reveals that the SW effect affects the deeper valence region of the deformed (8,0) tube $\sim$5.4 eV, where a sharp peak is found, and states around the Fermi level are not affected much by it.
Next we consider the defect created by substituting one of the nanotube C atoms on the highest curvature side for the deformed case $\eta=0.20$ with a N atom. This results in obtaining a partially filled electron shell system since the N atom has an extra $e$ as compared to C. Therefore, we include spin polarization in the calculation procedure. The results are shown in Fig. 4a). It is evident that $E_g=0.0$ eV for the radially deformed (8,0) tube with $\eta=0.20$ as compared to $E_g=0.08$ eV for the defect free deformed tube. In addition, small difference in the spin “up” and spin “down” states is found 0.4 eV below the Fermi level indicating that some magnetism can exist in a N-doped carbon nanotube. The peak at -4.15 eV is mainly due to the N impurity in the structure.

Finally, a mono-vacancy is created by removing a C atom on the highest curvature side of the deformed nanotube with $\eta=0.20$. The results are shown in Fig. 4b). One sees that there is no difference in the spin “up” and “down” species due to the spin-polarization effects. The band gap of 0.08 eV for the defect-free (8,0) tube with $\eta=0.20$ is reduced to 0.03 eV for the defective deformed tube. The main contribution from the vacancy is seen mainly in the conduction region $\sim$ -3.5 eV as compared to the DOS of the defect free nanotube (Fig.3a).

![Fig. 4 a) Total density of states for spin “up” and “down” for (8,0) nanotube with $\eta=0.20$ and a N impurity; b) Total density of states for spin “up” and “down” for (8,0) nanotube with mono-vacancy with $\eta=0.20$.](image)

In summary, our comprehensive study shows that by combining different strengths of deformations and electric field, one can achieve several insulator-metal transitions in a single deformed nanotube. In addition, depending on the type of single defect introduced in the deformed tube, various energy gap and electronic structure modulations can be achieved.

REFERENCES