Investigation of quantum conductance in semiconductor single-wall carbon nanotubes: Effect of strain and impurity

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(Received 29 June 2011; accepted 14 August 2011; published online 23 September 2011)

In this paper the effect of strain and impurity on the quantum conductance of semiconducting carbon nanotubes (CNTs) have been studied by *ab-initio* calculations. The effect of strain and impurity on the CNT conducting behavior and physical characteristics, like density of states (DOS), band structure, and atomic local density of state (LDOS), is considered and discussed separately and simultaneously. Our results show that the quantum conductance of semiconductor CNTs is increased by compression strain, elongation strain, and replacing nitrogen and boron doping in its structure. The amount of increasing in the conductance depends on the type of strain and impurity. Conductance of CNT can be increased even more in the presence of both strain and impurity, consequently semiconducting CNT can show metallic properties. This can open the study on the possibility of changing the semiconducting/metallic properties of CNTs along its length and the use of semiconductor CNTs in interconnects. © *2011 American Institute of Physics*. [doi:10.1063/1.3641981]

I. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) by Ijima[1] in 1991, special attention about this material has appeared. The main reasons for attention to this material are ease of large-scale production, special nanometer scale properties, and fair thermal, mechanical, and electronic properties.[2,3] CNTs are in great interest in electronic devices, gas sensors, biosensors, biomedical application, etc.[4–7] Metallic and semiconducting properties of CNTs depend on their diameter and chirality.

Until now different changes of nanotube composition and structure, which affects its conducting properties, have been investigated. Buonocore *et al*. take into account nitrogen and boron doping for two isomers in which substitutive atoms are on opposite sides of the tube and investigate the variation of band structure and density of state in two isomers.[8] The effect of uniaxial strain on the bandgap of zigzag carbon nanotube and the relation between bandgap and strain on the different zigzag nanotubes were also investigated by Zhang and Sreekala. The bandgap of these nanotubes is modified by both compressive and tensile strains and all zigzag single-wall carbon nanotubes show a semiconductor-metal transition with strain.[9,10]

Application of CNTs in electronics includes use of semiconductor CNTs in the transistors and also use of metallic CNTs in the interconnections. Therefore conductance is an important issue for using nanotubes in electronics. Previous investigations show that the electronic properties of metallic carbon nanotubes are influenced by changing their structure and geometrical shape. Bending and twisting of nanotube structure has also been studied,[11,12] and it is shown that the transmission of nanotube decreases as a consequence of these deformations. Strain effect on a metallic CNT's conduction has been investigated by He,[13] and it is shown that in both cases of compression and elongation, the conduction of metallic nanotube decreased. In addition Stone-Wales, monovacancy, and divacancy defects can affect electronic properties of metallic nanotubes and decrease their conduction. Investigations by Choi[14] and Andriotis[15] show that defects such as Stone-Wales defects, vacancies, or doping modify the conduction and electronic properties of metallic carbon nanotubes drastically. In another research[16] transport properties of armchair carbon nanotubes with a double vacancy under strain is studied. It is found that different strains cause different local structures near the defect, which change the transmission function around the Fermi energy and by increasing the strain, the conductance is also increased. Effects of structural deformation and tube chirality on electronic conductance of carbon nanotubes is investigated by Maiti,[17] and it is shown that electronic conductance can be induced by AFM-tip deformation of metallic zigzag tubes and by twist deformation of armchair tubes. Electronic properties of semimetallic (12,0) carbon nanotubes in the presence of a variety of monovacancy, divacancy, and hexavacancy defects are investigated.[18] It shows that tetravacancy and hexavacancy nanotubes have higher conductance than divacancy nanotubes that this is due to the presence of midgap states resulting from the defect.

As we know, there is no study on the effect of the structural deformation or doping on the conducting properties of semiconductor CNTs. It is possible that semiconductor CNTs are used as both a semiconductor device and a metallic interconnect in integrated circuits (ICs). For using a semiconductor nanotube as an interconnect, it is important that the electronic behavior of the nanotube is reversed from semiconductor to

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metallic. In this paper we investigate methods to increase conduction in semiconductor CNTs and to convert its behavior to metallic. In our calculation for semiconducting nanotube, both of the strain and defect effects are considered separately and simultaneously (see Fig. 1). The considered structure in this paper is (8, 0) nanotubes that have semiconducting properties (see Figs. 1 and 2). Our studies of (8,0) CNTs focus on the interplay between structure and conductance.

II. METHODOLOGY

A. *Ab-initio* calculations

Ab-initio calculations were done in the formalism of density functional theory[19,20] using Quantum Espresso package.[21] The supercell was (8, 0) CNT, that consisted of 96 carbon atoms with 2.43Å diameter in tetragonal structure with parameters $a = 15$Å and $b = 15$Å. The spacing of CNTs in the tetragonal structure is large enough to neglect its interaction. Calculations have been done based on Perdew-Burke-Ernzerhof[22] pseudopotentials with generalized gradient approximation exchange correlation. The number of k-points that was used for sampling the Brillion zone is 1, 1, 20 in kx, ky, kz directions, respectively. The cutoff energy for electronic wave function and electronic density was 400 eV and 4000 eV, respectively. The conjugate gradient algorithm was used for diagonalization of Hamiltonian. The coordinates of all atoms are relaxed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method until the force acting on each atom is less than 0.01 $\frac{eV}{Ang}$. Energy convergence for all calculations is considered 10^{-8}.

B. Conductance calculation method

Conduction of electrons is calculated along the axis of nanotube and Landauer-Butticker formula[23,24] was used to find one-dimensional quantum conductance of carbon nanotube. Effective Hamiltonian is diagonalized by *ab-initio* calculations. The considered system includes two semi-infinite electrodes and a scattering zone. It is supposed that two electrode Hamiltonian is the same to the bulk electrodes. Self-energies matrices, Σ^L and Σ^R that show electrodes effect on the scattering zone, are computed using retarded Green function by the following equation:[25]

$$G^r = \frac{1}{\varepsilon - H - \Sigma^L - \Sigma^L}, \tag{1}$$

where **H** denotes Hamiltonian of the device region. The transmission is calculated by Caroli model:[26]

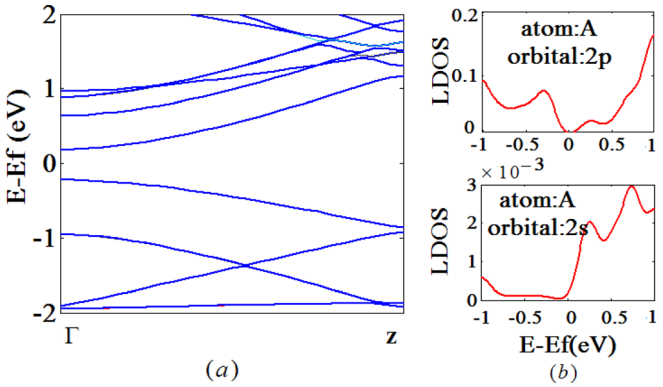

FIG. 2. (Color online) (8,0) pure CNT: (a) Band structure and (b) LDOS for A atom.

$$T(E) = Tr[\Gamma^L G \Gamma^R G^\dagger]. \tag{2}$$

That is a function of energy and $\Gamma^{L,R}$ are broadening matrices that are calculated by

$$\Gamma^{L,R} = i[\Sigma^{L,R} - (\Sigma^{L,R})^\dagger]. \tag{3}$$

The conductance is computed by Landauer expression[25]

$$G = \frac{2e^2}{h} \int T(E) \frac{\partial f(E)}{\partial E} dE, \tag{4}$$

where $f(E) = 1/(1 + e^{E/K_B T})$ is Fermi-Dirac distribution function, K_b is Boltzmann constant, and T is temperature. By computing $\partial f/\partial E$ for different energies, it is seen that its quantity is meaningful only in an interval between -0.2 eV and 0.2 eV around Fermi energy; therefore for computing conductance we only need transmission quantity between 0.2 and -0.2 around Fermi energy.

III. RESULTS AND DISCUSSION

To study the effects of strain and impurity on the conductance, these structures have been studied, respectively: Replacing two carbon atoms with two nitrogen ones in a super-cell structure of carbon nanotube, replacing of two carbon atoms with two boron ones in carbon nanotube structure, compressing strain effect of -10% along the nanotube axis (negative sign is representative for compressing and positive one is representative for elongation), elongation strain effect of 10%, replacing two carbon atom with nitrogen or boron atoms, and simultaneous applying of strains of 10% or -10%.

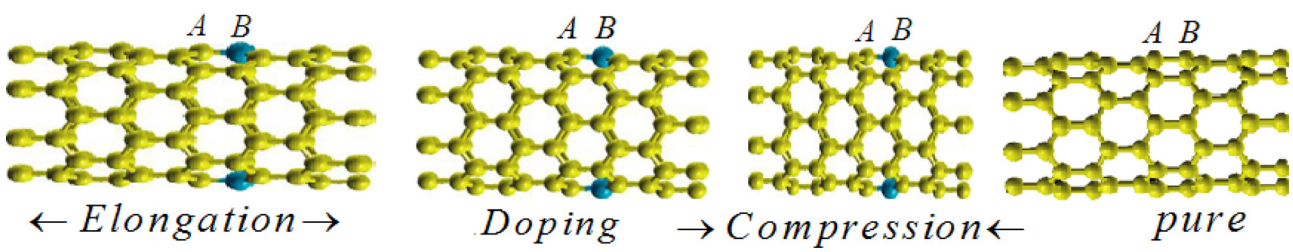

FIG. 1. (Color online) Schematic of (8,0) CNT unit cell under strain and impurity.

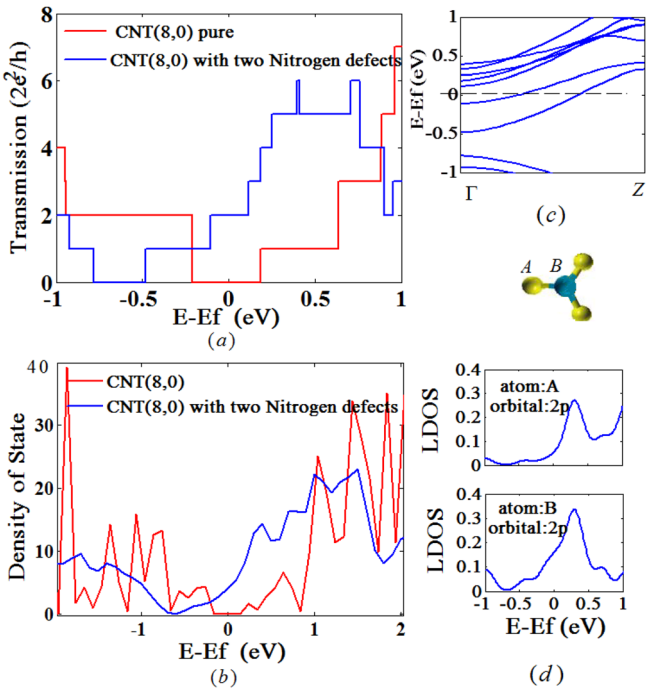

FIG. 3. (Color online) (8,0) CNT with two nitrogen defects: (a) Transmission, (b) DOS, (c) band structure, and (d) LDOS for A and B atoms.

Figures 3–10 illustrate the transmission coefficients as a function of energy and density of states for (8,0) nanotubes with different doping and/or strains. Transmission is normalized with respect to $G_0 = 2e^2/h$. For nitrogen doped CNT, transmission in Fermi energy is reached to $2G_0$ (Fig. 3) and the number of its conduction channels is increased to two; while in pure CNT no conduction channels are observed in Fermi energy and therefore CNTs is a semiconductor. The relative conduction channels that appeared in the nitrogen doped CNT have σ state nature (as can be deduced from LDOS curves, the density state of p orbitals is increased significantly, and the density of pz orbitals is more than px and py orbitals. This shows that the bond is mostly across z axis and parallel to CNT axis). From overlapping of local density of states of s and p orbitals, it is obvious that they are slightly hybridized. The presence of nitrogen atoms creates new levels around Fermi level and shifts the Fermi level upward because nitrogen atoms increase the electrons in the system (as can be deduced from band structure curve). By integrating the LDOS curves of related orbitals of each atom and adding it with nuclear charge plus core electrons contribution, the charge of each atom can be roughly measured. The measured charge of nitrogen atoms is higher than the charge of carbon atoms, because the electronegativity of nitrogen atom is more than carbon. In the case of boron doping, transmission is equal to $2G_0$ at Fermi energy (Fig. 4), it means that two conduction channels is available for this structure. Boron impurities shift the Fermi level downward and a new channel is created in the energy gap (as can be deduced from band structure curve). By introducing boron atoms, the charge of carbon atoms near the boron atom is increased because carbon electronegativity is more than boron. The appeared conduction channels in the boron doped CNT have σ state nature. The density of states of p orbitals also increased in boron doping.

The quantum conductance is closely related to the band structure of (8,0) nanotube; the conducting channels come from the Bloch states that cross the Fermi level in the leads. One major effect of applying impurities in a nanotube structure is shifting the Fermi energy that can be considered as a reason of existence of conduction channels at the Fermi energy. The figures illustrate systematically that the

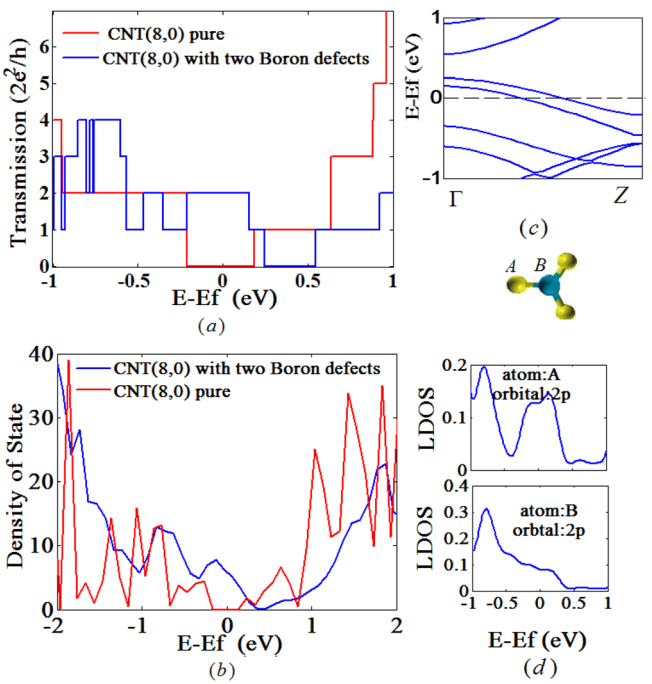

FIG. 4. (Color online) (8,0) CNT with two boron defects: (a) Transmission, (b) DOS, (c) band structure, and (d) LDOS for A and B atoms.

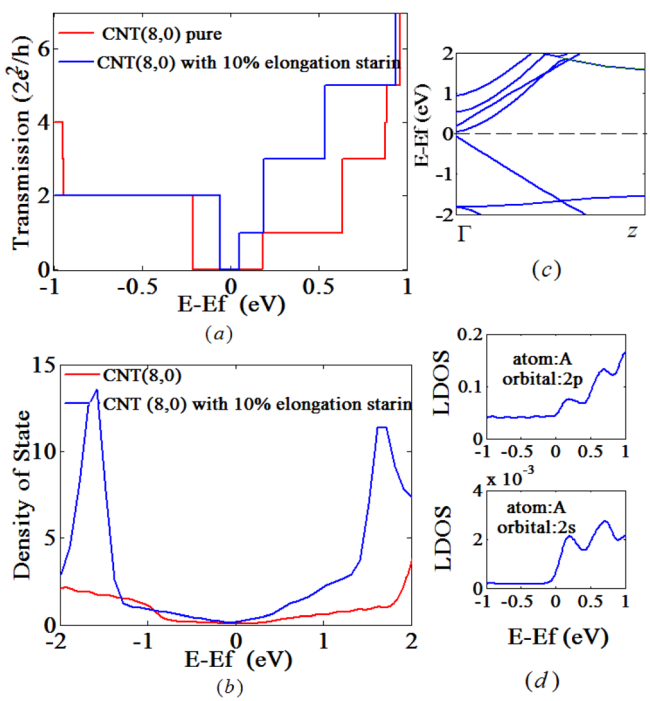

FIG. 5. (Color online) (8,0) CNT with 10% strain: (a) Transmission, (b) DOS, (c) band structure, and (d) LDOS for A atom.

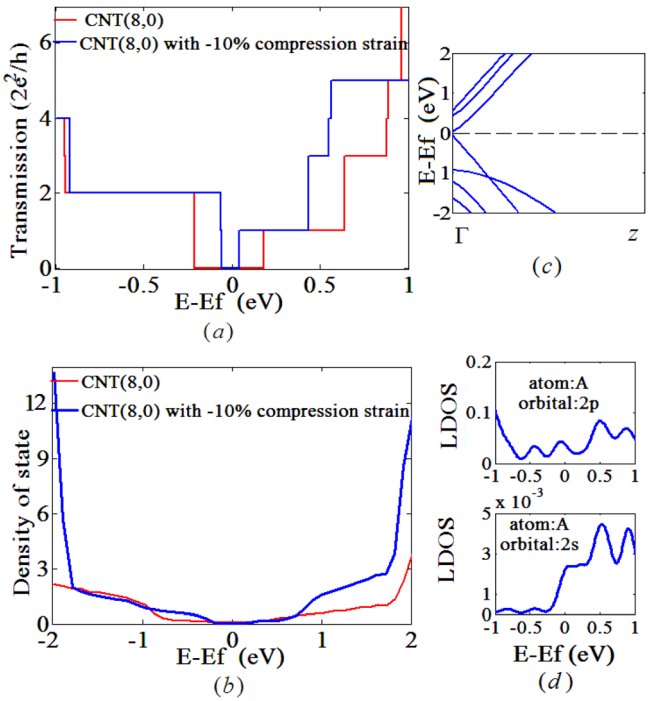

FIG. 6. (Color online) (8,0) CNT with −10% strain: (a) Transmission, (b) DOS, (c) band structure, and (d) LDOS for A atom.

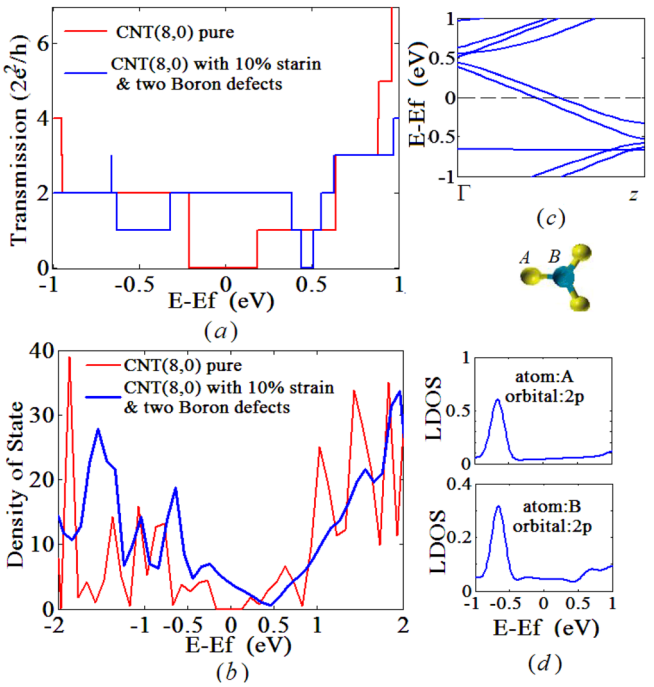

FIG. 8. (Color online) (8,0) CNT with two boron defects and 10% strain: (a) Transmission, (b) DOS, (c) band structure, and (d) LDOS for A and B atoms.

transmission coefficients is directly related to density of states of the nanotube. By computing conductance from Eq. (4) for pure (8,0) CNT, conductance is zero. By replacing two boron or two nitrogen atoms with two carbon atoms, DOS in Fermi energy and around it is increased, the transmission is increased and therefore (8,0) semiconducting nanotube inverts to a metallic nanotube. replacing nitrogen atoms increase the quantum conductance to the $1.998G_0$ and replacing boron atoms increase it to the $1.997G_0$.

In the case of −10% or 10% applied strains, transmission coefficient is still zero at Fermi level, but it is obvious that transmission gap in this case is decreased around the Fermi energy (Fig. 5 and Fig. 6). It is seen that the Fermi level does not change but the form of levels is changed and energy levels

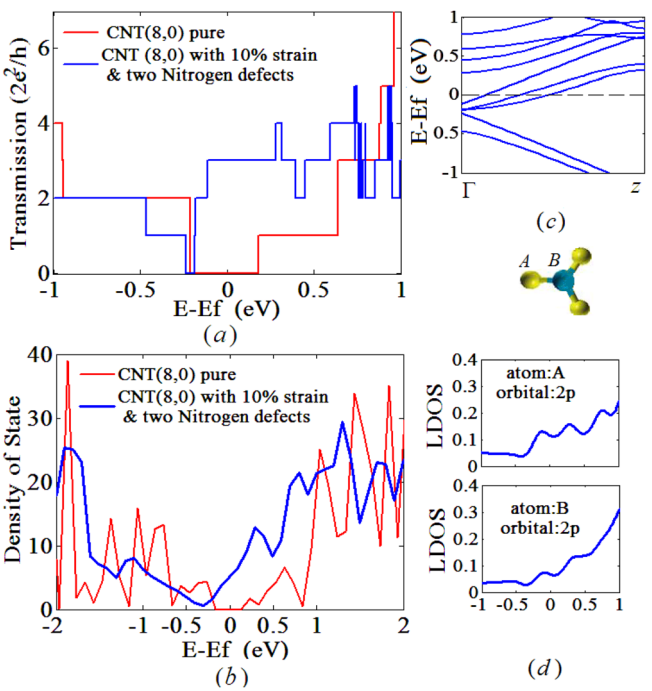

FIG. 7. (Color online) (8,0) CNT with two nitrogen defects and 10% strain: (a) Transmission, (b) DOS, (c) band structure, and (d) LDOS for A and B atoms.

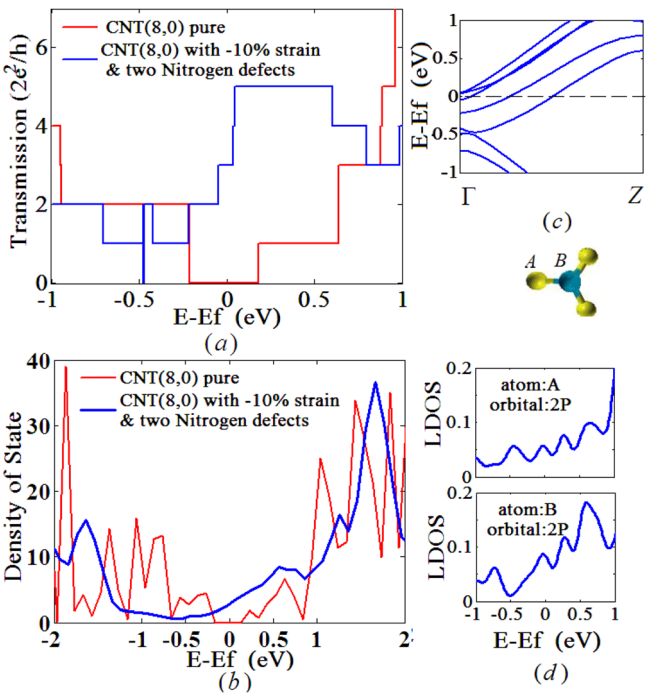

FIG. 9. (Color online) (8,0) CNT with two nitrogen defects and −10% strain: (a) Transmission, (b) DOS, (c) band structure, and (d) LDOS for A and B atoms.

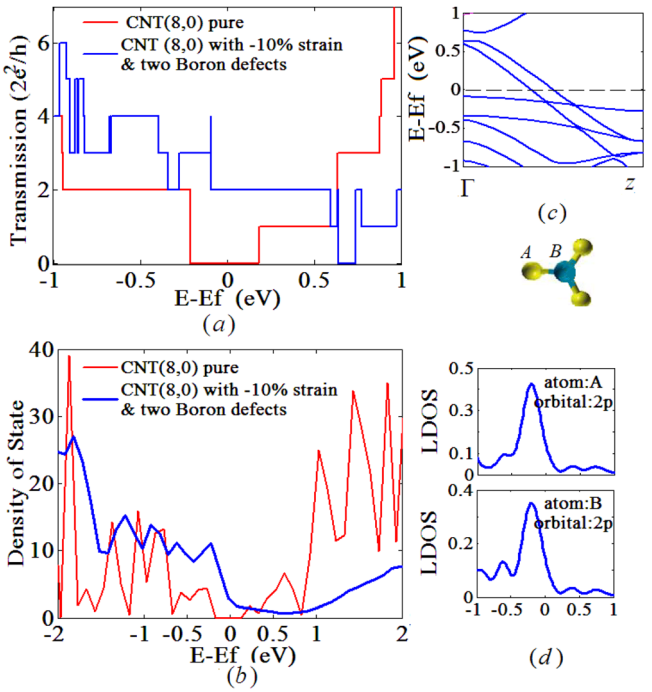

FIG. 10. (Color online) (8,0) CNT with two boron defects and −10% strain: (a) Transmission, (b) DOS, (c) band structure, and (d) LDOS for A and B atoms.

is shifted near to the Fermi energy. The number of conduction channels is two. Using Eq. (4), it obtains that for nanotube with 10% strain conductance is $0.3374G_0$ and for nanotube with −10% strain conductance is $0.337G_0$ that show increasing the quantum conductance by applying the strain. For these two structures density of states near Fermi energy is increased in comparison to pure nanotube (Fig. 5 and Fig. 6). In this case, the conducting channels come from p orbitals and overall DOS of p orbitals in related atoms is increased by applying strain.

In studying of simultaneous effects, in the case that strain is 10% and two nitrogen atoms substituted with two carbon atoms, the transmission in Fermi energy reached a value of $3G_0$ that means the number of conduction channels is three (Fig. 7). This conduction channel comes from σ sates. Density of states of p orbitals in atoms near the impurities is increased compared to the case of pure CNT. Nitrogen shifts the Fermi level upward and strain changes the form of levels and brings the levels near to Fermi energy. Also the number of energy levels increased near to Fermi energy. From LDOS graph, it is found that total charge in related atoms is increased compared to the pure CNT. By computing conductance from Eq. (4), its value is obtained as $G = 2.987G_0$. For 10% strain and substituting two boron atoms instead of carbon atoms, transmission is $2G_0$ in Fermi energy (Fig. 8) and computed conductance value is $G = 2.01G_0$. Boron shifts the Fermi energy downward and strain shifts energy levels near to Fermi energy and the number of channels reaches two. This channel comes from σ states and it is seen from LDOS curves that the local density of states of p orbital is increased dramatically in atoms near to the impurity. Total charge of related atoms is increased in this structure. In the case of −10% applied strain accompanied with nitrogen impurity, transmission in Fermi energy is reached at maximum value of $3G_0$ and conductance value is $G = 3.14G_0$, while with boron impurity and −10% strain transmission in Fermi energy is $2G_0$ and value of conductance is $G = 2.15G_0$ (Fig. 9 and Fig. 10). We showed the quantum conductance of (8,0) CNT for different defects in Fig. 11. The important point is that if strain and nitrogen impurity applied simultaneously, conduction is increased further. As we seen if strain is −10% and nitrogen impurity applied simultaneously, the transmission curve of (8,0) a semiconductor CNT becomes similar to a transmission curve of a metallic CNT.

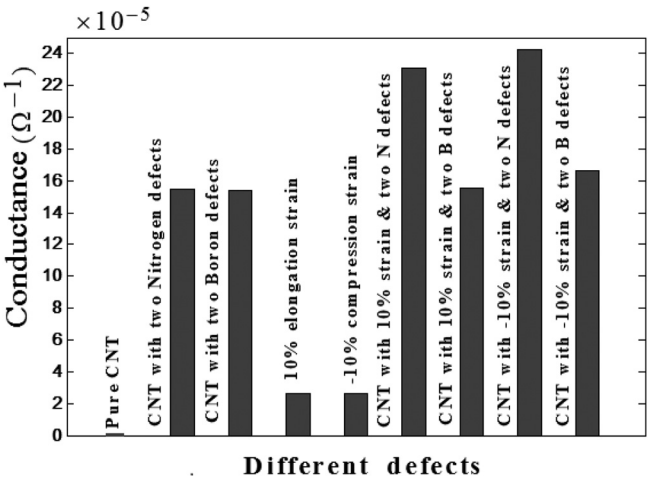

FIG. 11. The quantum conductance of (8,0) CNT with different defects.

IV. CONCLUSIONS

We studied strain and impurity effects on the (8,0) semiconductor CNT and our results show that applying impurities and strains to (8,0) CNT separately or simultaneously causes CNT to have conduction channels in the Fermi energy. It is more tangible when strain is −10% and impurity is of type nitrogen-dopant. The appeared conduction channels around Fermi level have almost σ nature. The reason for appearing: This channel is shifting the Fermi energy in the gap and/or the creation of new bands due to the change imposed on CNT. Our results show that any changes in the structure of a (8,0) semiconductor CNT cause variation of its conduction, changing it to metallic CNT.

ACKNOWLEDGMENTS

The authors thank M. M. Kafashan and A. Mehdi Rezaei for helpful discussion.

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