Deep levels in the band gap of the carbon nanotube with vacancy-related defects

Gunn Kim[a)]
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695 and School of Physics, Seoul National University, Seoul 151-747, Korea

Byoung Wook Jeong and Jisoon Ihm[b)]
School of Physics, Seoul National University, Seoul 151-747, Korea

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We study the modification in the electronic structure of the carbon nanotube induced by vacancy-related defects using the first-principles calculation. Three defect configurations which are likely to occur in semiconducting carbon nanotubes are considered. A vacancy-adatom complex is found to bring about a pair of localized states deep inside the energy gap. A pentagon-octagon-pentagon topological defect produced by the divacancy is structurally stable and gives rise to an unoccupied localized state in the gap. We also discuss the character of partially occupied localized state produced by a substitutional impurity plus a monovacancy. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2202112]

As excellent conductors[1,2] with long mean free path and remarkably high mobility, carbon nanotubes (CNTs) have diverse potential applications in nanoelectronics. Though the properties of the atomically perfect CNT have been understood relatively well, experimental and theoretical reports on the defects such as vacancy and impurity substitution are limited. Recently, Gómez-Navarro *et al.* showed that even a low concentration of vacancies in single-walled carbon nanotubes (SWNTs) can produce a large decrease in their electrical conductance.[3] Through a sequence of high resolution transmission electron microscopy images recorded *in situ* on one of the SWNTs; on the other hand, Hashimoto *et al.* showed that the adatoms appear mostly in the vicinity of the vacancies.[4] In the scanning tunneling microscopy (STM) experiment on a semiconducting CNT, localized gap states were observed in semiconducting SWNTs.[5,6] In particular, a pair of gap states was found far from the band gap edge forming deep levels in the STM measurement.

In this letter, we report the electronic structure of CNTs with various vacancy-related defects. The first-principles pseudopotential calculations are carried out based on the density functional theory[7] within the local density approximation[8] with spin polarization for the exchange-correlation functional. The ionic potential is described with the norm-conserving Troullier-Martins pseudopotential.[9] Wave functions are expanded in a double-ζ basis set with an energy cutoff of 80 Ry implemented in the SIESTA code.[10,11] As a model system, we choose the (17,0) zigzag CNT of ~13.4 Å in diameter and ~0.5 eV in the band gap. The supercell size in the lateral direction is 25 Å to avoid the interaction between neighboring CNTs and that in the axial direction is 22 Å. The atomic position is relaxed until the forces on the atoms are reduced to within 0.02 eV/Å.

First, we have tested many different geometries with vacancies to reproduce experimentally observed two unoccupied deep levels in a semiconducting nanotube.[5,6] A simple model of a vacancy-adatom complex is presented in Fig. 1(a). If a single atom is removed from the nanotube, two of three carbon atoms around the vacancy rebond (bond length of 1.57 Å) by the Jahn-Teller distortion. The third atom has the dangling bond even after the relaxation.[12–14] The monovacancy alone does not reproduce the experimental spectra of a pair of deep levels.[5,6] The adatom may be mobile because it has a lower diffusion barrier (~0.47 eV) (Ref. 15) than that for vacancy migration (~1.7 eV).[16] Here the bond length between the adsorbed C atom and the atom on the tube is 1.34 Å. It is a typical C–C double bond and indicates that the adatom has two unpaired electrons. The binding energy of the adsorbed C atom in the model system is about 5.6 eV. It is comparable with the bonding energy of the C–C double bond (~6.3 eV). Thus we conclude that our model structure is energetically stable.

When a vacancy-adatom complex like our model structure is introduced, two unoccupied flat levels appear within the semiconducting gap, as plotted in Fig. 1(b). Since they exist far from the band edges of the (17,0) CNT, they can be called deep levels. In many cases, a deep level in the semiconductor acts as a recombination center and decreases

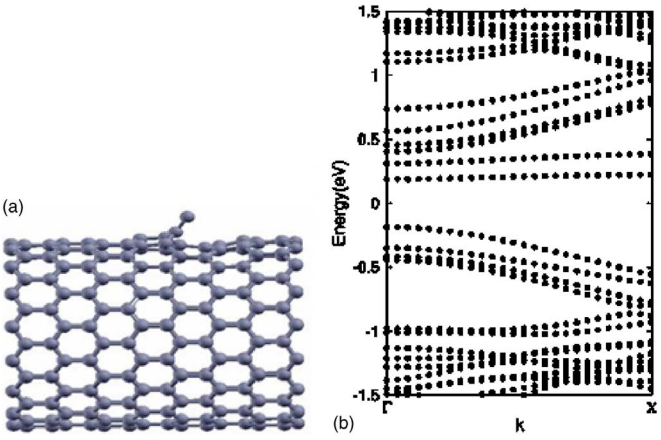

FIG. 1. (a) Side view of the schematic ball-and-stick model and (b) band structure for the vacancy-adatom complex system of the (17,0) CNT. The Fermi level is set to zero. Two unoccupied flatbands occur in the band gap.

a)Electronic mail: gunnkim@chips.ncsu.edu
b)Electronic mail: jihm@snu.ac.kr

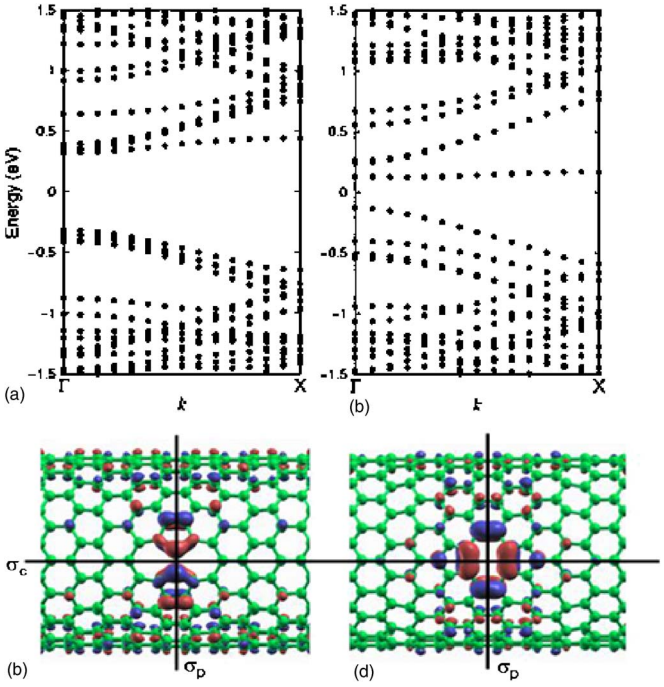

FIG. 2. (Color online) Comparison of the 5-7-7-5 defect with the 5-8-5 defect. Band structures corresponding to the (17,0) tube with the 5-7-7-5 defect and with the 5-8-5 defect are shown in (a) and (b), respectively. Isodensity surface plots of the unoccupied gap state due to the 5-7-7-5 defect and the 5-8-5 defect at Γ point are presented in (c) and (d), respectively. The values for the red and blue isodensity surfaces are $\pm 0.02e/a_0^3$ where the sign is that of the wave function and a_0=0.529 Å, the Bohr radius.

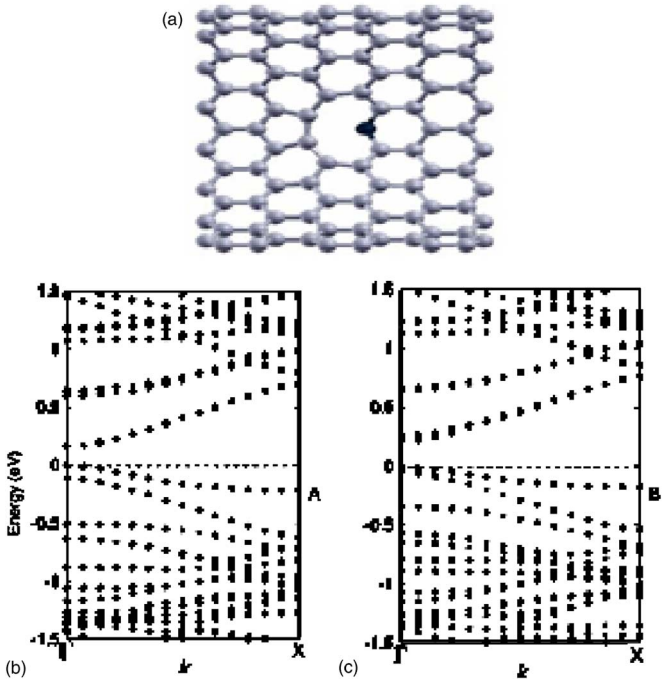

FIG. 3. (a) Schematic ball-and-stick model with a monovacancy and a substitutional impurity in the (17,0) CNT. The darker ball represents the boron or nitrogen atom and the brighter balls carbon atoms. Band structures for the (b) boron atom substitution and (c) nitrogen atom substitution. A and B indicate localized states.

charge carriers. The nonradiative recombination of excess charge carriers via deep levels induced by transition-metal impurities in bulk silicon was investigated experimentally.[17] In the present case, these localized states originate from unpaired electrons (dangling bonds) of the adsorbed C atom mentioned above. However, the charge density is spread out to the vicinity of the nine-membered ring (not shown).

So far, lots of studies have focused on the Stone-Wales (SW) defect of the CNT, i.e., a 90° bond rotation that transforms four hexagonal rings into two pentagons and two heptagons (5-7-7-5). The SW defect creates an unoccupied flatband which is very close to the conduction band minimum (CBM), forming a shallow donor level in the (17,0) nanotube, as shown in Fig. 2(a). The SW defect we study preserves two mirror (reflection) symmetry planes. One plane (σ_p) is perpendicular to the nanotube axis and the other (σ_c) contains the tube axis. The wave function corresponding to the localized state is odd with respect to σ_c and even with respect to σ_p as depicted in Fig. 2(c). Therefore, the 90°-rotated carbon bond of the 5-7-7-5 defect site has an antibonding character. For comparison, we calculate the electronic structure of a (17,0) CNT with a divacancy. Two neighboring atoms are removed, and after the system is fully relaxed, a 5-8-5 defect appears.[12] Two pairs of carbon atoms around the vacancy rebond and produce two pentagons. The bond length of 1.50 Å at present is shorter than that of monovacancy (1.57 Å) described above. A localized deep level is found 0.12 eV below the CBM [Fig. 2(b)], in contrast to the much shallower level (0.024 eV below the CBM) for the 5-7-7-5 defect. The 5-8-5 defect geometry also has the mirror symmetry. The wave function corresponding to the localized state due to the 5-8-5 defect is even with respect to both of σ_c and σ_p [Fig. 2(d)]. Thus, the π-bonding characters are exhibited for rebonded carbon atoms in two pentagons.

Next, we present the electronic structure of a semiconducting CNT with a monovacancy with a boron or nitrogen substitutional impurity. The carbon atom having the dangling bond of the reconstructed CNT with the monovacancy is replaced by a boron or nitrogen atom as presented in Fig. 3(a). In Figs. 3(b) and 3(c), each impurity (boron or nitrogen) atom with dangling bonds results in a more or less flatband (localized state). Because the number of valence electrons is odd (3 or 5), the flatband is half-filled in our supercell calculation. By contrast, it is known that an unoccupied flatband appear for the simple monovacancy (without substitution of C by N or B) with a possible spin polarization depending on the tube diameter.[13,14] Though the structures have odd electrons, they are both nonmagnetic. The localized states associated with boron (A) and nitrogen (B) have some band dispersion as plotted in Fig. 3, which are artifacts ascribed to our small supercell size (~2 nm) in the axial direction. It is interesting that although the localized state (B) is associated with the nitrogen impurity, its level moves closer to the valence band maximum than to the CBM by the influence of the vacancy.[18] Figure 4 reveals that the boron impurity gives rise to the gap state different from the nitrogen in terms of the phase (sign) and direction of the dangling-bond orbital. In the STM experiment, therefore, different topographic images and scanning tunneling spectra may be obtained for gap states of the two structures.

Localized states of semiconducting CNTs with different helicities but almost the same diameter are expected to show similar features to the localized states of the (17,0) tube, because the band structure near the energy gap is similar. It is known that several different semiconducting-semiconducting

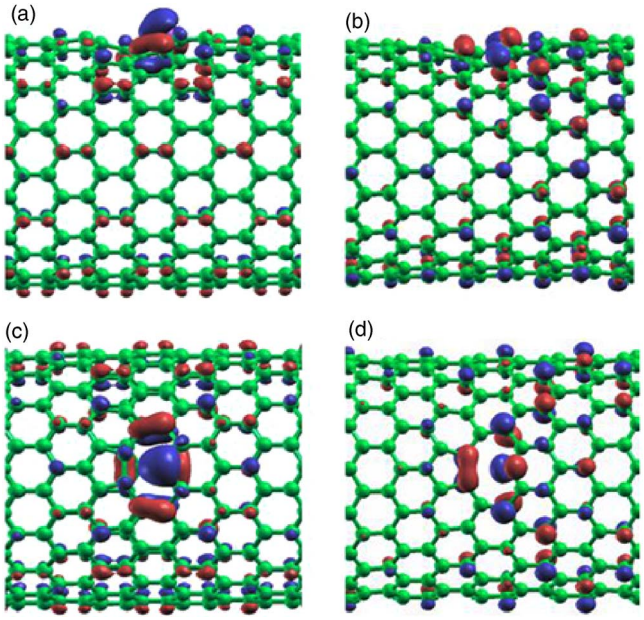

FIG. 4. (Color online) Localized states of the semiconducting (17,0) CNT with a monovacancy plus a substitutional impurity. Side views of the isodensity surface of the gap states due to a monovacancy with a boron and nitrogen substitutional impurity are shown in (a) and (b), respectively, and top views of them in (c) and (d). The values for the red and blue isodensity surfaces are $\pm 0.02e/a_0^3$, where the sign is that of the wave function.

junctions with complex topological defects reveal common features in electronic properties of the localized states.[19] However, the wave functions may not have the mirror symmetry in general. Vacancy-related defects produce localized levels near the Fermi level even in the metallic CNT.[18] The difference from the semiconducting CNT is that, since there exists a finite density of states at all energies in metallic CNTs, the localized states are actually in resonance with the extended states with finite broadening.

In summary, relatively deep localized gap states caused by various vacancy-related defects are found in the semiconducting SWNT in *ab initio* pseudopotential calculations. Because of the periodic boundary condition in the supercell method, our systems correspond to the case where defects are arranged in order. Band structures show weak band dispersions due to weakly interacting gap states in the intrinsic band gap of the semiconducting CNT. In the realistic case of the random distribution of defects, there would be slightly broadened density of states in the gap produced by nearly degenerate localized gap states. The broadening will be enhanced as the defect density increases. These states can behave as recombination centers of electron and hole carriers. As in bulk semiconductors such as silicon and gallium arsenide, these levels can significantly affect the transport and optical properties of the semiconducting CNTs.

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[1] T. Durkop, S. A. Getty, E. Cobas, and M. S. Fuhrer, Nano Lett. **4**, 35 (2004).
[2] A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, Nature (London) **424**, 654 (2003).
[3] C. Gómez-Navarro, P. J. De Pablo, J. Gómez-Herrero, B. Biel, F. J. Garcia-Vidal, A. Rubio, and F. Floresi, Nat. Mater. **4**, 534 (2005).
[4] A. Hashimoto, K. Suenaga, A. Gloter, K. Urita, and S. Iijima, Nature (London) **430**, 870 (2004).
[5] H. Kim, J. Lee, S. Lee, Y. Kuk, J.-Y. Park, and S.-J. Kahng, Phys. Rev. B **71**, 235402 (2005).
[6] S. Lee, G. Kim, H. Kim, B.-Y. Choi, J. Lee, B. W. Jeong, J. Ihm, Y. Kuk, and S.-J. Kahng, Phys. Rev. Lett. **95**, 166402 (2005).
[7] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[8] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[9] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[10] P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996).
[11] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).
[12] S. L. Mielke, D. Troya, S. Zhang, J.-L. Li, S. Xiao, R. Car, R. S. Ruoff, G. C. Schatz, and T. Belytschko, Chem. Phys. Lett. **390**, 413 (2004).
[13] Y. Ma, P. O. Lehtinen, A. S. Foster, and R. M. Nieminen, New J. Phys. **6**, 68 (2004).
[14] J. Rossato, R. J. Baierle, A. Fazzio, and R. Mota, Nano Lett. **5**, 197 (2005).
[15] P. O. Lehtinen, A. S. Foster, A. Ayuela, A. Krasheninnikov, K. Nordlund, and R. M. Nieminen, Phys. Rev. Lett. **91**, 017202 (2003).
[16] A. A. El-Barbary, R. H. Telling, C. P. Ewels, M. I. Heggie, and P. R. Briddon, Phys. Rev. B **68**, 144107 (2003).
[17] A. Hangleiter, Phys. Rev. B **35**, 9149 (1987).
[18] H. J. Choi, J. Ihm, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **84**, 2917 (2000).
[19] Y.-W. Son, S. B. Lee, C.-K. Lee, and J. Ihm, Phys. Rev. B **71**, 205422 (2005).