Band-gap formation in $(n,0)$ single-walled carbon nanotubes $(n=9,12,15,18)$: A first-principles study

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We study the electronic structure of the carbon nanotube theoretically by the first-principles techniques using the local-density approximation (LDA) with the many-body correction in the GW approximation. We find that the (9,0) tube is gapful irrespective of naive expectation from the graphene band structure. All of the π-σ hybridization effect, lattice relaxation effect, and many-body effect due to electron interaction enhance the band gap, and the value is as large as 0.17 eV when taking into account all effects. For the $(n,0)$ nanotubes with $n=9$, 12, 15, and 18, the LDA gap is found to range from 0.08 to 0.02 eV. These sizable gap values obtained by the most reliable methods to date shed light on the classification of carbon nanotubes by their electronic transport properties.

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Carbon nanotubes[1] have attracted interest partly because their variety of electronic properties can be utilized in electronic devices. One of the remarkable properties is that they are either metallic or semiconducting, depending on the diameter and helical arrangement. A simple π-only tight-binding model predicts that the (n,m) nanotube is "metallic" when the $n-m$ is a multiple of three, otherwise it is semiconducting.[2] This "1/3 rule" can be understood by starting with graphene band structure and imposing the appropriate boundary condition. Looking into the details of the band structure, however, most "metallic" tubes are not gapless, except armchair tubes $(n-m=0)$. When $n-m$ is divisible by three but nonzero, the nanotube is a narrow-gap semiconductor because of hybridization between π and σ orbitals.[3] The effect is caused by curvature of the tube, therefore it is more remarkable at smaller diameter.

The excitation energy associated with adding or removing an electron is a fundamental physical value. Especially, the minimum gap is the most important value for device applications. Some experiments have measured the fundamental gap as a function of tube diameter by combining scanning-tunneling spectroscopy (STS) and scanning-tunneling microscopy (STM).[4,5] However, the samples used in the experiments were a mixture of different chiral indices, thus a direct comparison with theoretical calculation is not possible. Another problem is sizable experimental uncertainty, which prevents us from discussing gap value with the accuracy of <0.1 eV.

Theoretically, the density-functional theory combined with the local density approximation (LDA)[6,7] is a conventional tool for the quantitative description of electronic structures without adjustable parameters. However, LDA has a well-known drawback; it underestimates the band gap of semiconductors and insulators. The GW approximation (GWA)[8] is a computationally much more expensive but feasible method to overcome this problem.[9,10] It has been applied to many materials during last two decades and turned out to give accurate band gap of bulk semiconductors.[11,12]

The GW method was applied to carbon nanotubes and found that the many-body correction significantly opens band gaps compared to the LDA in small-diameter semiconducting tubes.[13,14] In this work, we study the electronic structure of (9,0) nanotubes using the GW method. This tube is of interest because (i) it is classified to be metallic by the 1/3 rule, whereas π-σ hybridization effect should open the gap up, and (ii) the diameter is 0.70 nm, being in the diameter range of carbon nanotubes produced experimentally in macroscopic amounts.[15] We find that the (9,0) tube is indeed gapful. The lattice relaxation effect and many-body correction, as well as π-σ hybridization play important roles in forming a sizable gap.

We calculate the quasiparticle band structure by adding GW many-body correction to the LDA band structure. The Kohn-Sham equation for LDA is solved by the full-potential linear muffin-tin orbital (FP-LMTO) method. The polarizability is then estimated within the random-phase approximation using LDA wave functions and eigenvalues, from which screened Coulomb interaction W is computed. Green's function G is also constructed from LDA wave functions and eigenvalues. The self-energy is evaluated in the GW approximation in which frequency integral for the convolution of G and W is performed numerically. Technical details of the GW method is found elsewhere.[13,16] Nanotubes are placed in a hexagonal supercell with the lattice constant of 27.0 bohr, and 6 k points are sampled in the tube direction. Comparison with the result of 4 k-point sampling showed difference of only 0.01 eV in the quasiparticle fundamental gap.

Two kinds of tight-binding methods are also used for comparison. In the π tight-binding method, only π orbital is taken into account. The transfer integral between nearest-neighbor carbon sites is set to 2.5 eV. On the other hand, both π and σ orbitals are included as a basis set in the π-σ tight-binding method.[3,17] Long-range transfer terms and overlap integrals are also considered in this method.

We begin with comparing the band structures of the (9,0) tube obtained by three different methods. The geometry is fixed to that of a rolled-up graphite sheet with the C—C bond length of 1.42 Å. The band structure in Fig. 1(a) is obtained by the π tight-binding method. Since no π-σ hybridization is included, the top of the valence band touches

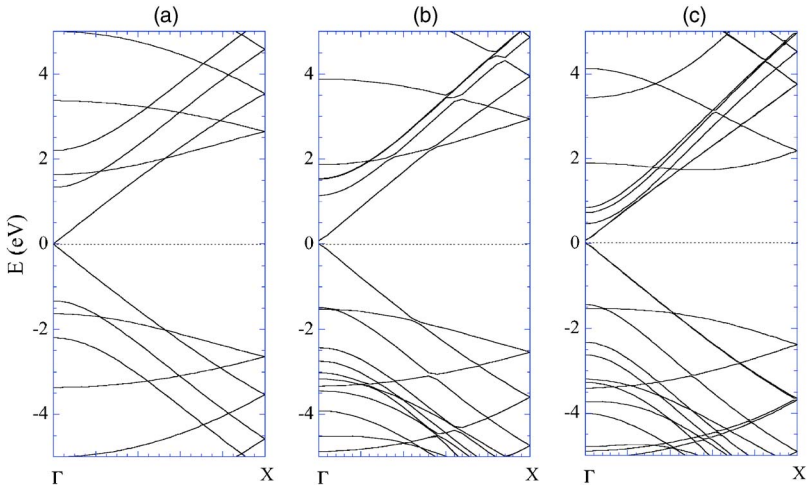

FIG. 1. (Color online) Electronic structure of the (9,0) nanotube obtained by (a) π tight-binding method, (b) π-σ tight method, and (c) LDA. Energy is measured from the top of the valence band, which is shown by a dotted line.

the bottom of the conduction band at Γ point. When we include σ orbitals as a basis set, the band structure becomes gapful [Fig. 1(b)]. This clearly shows importance of curvature effect in this diameter region. We also find that the second and third lowest conduction-band states are pulled down compared to Fig. 1(a). The LDA band structure is shown in Fig. 1(c). The overall feature is similar to the result of π-σ tight-binding method. In particular, both results give the band gap of 0.08 eV. A difference between Figs. 1(b) and 1(c) is that the downshift of the second lowest conduction-band state is larger in the LDA band structure. It has been shown in previous works[13,18] that the downshift is crucial in a small diameter tube because it makes the (5,0) and (6,0) tubes metallic. Another feature in the LDA band structure is an existence of a parabolic-dispersion state at 3.4 eV. This is the nearly free-electron (NFE) state, which is delocalized away from carbon wall.[19] Also, a band at 1.9 eV is flatter in LDA than the tight-binding results, which should change the shape of the van Hove singularity in its electronic density of states.

When geometry is relaxed, the tube gets slightly thinner and elongated. The optimized geometry has diameter of 7.036 Å and lattice constant of 4.216 Å. The bond lengths between neighboring carbon atoms are $d_1=1.398$ Å and $d_2=1.413$ Å. One is longer, and the other is shorter than the optimized graphene bond length of 1.406 Å with the same method.[22] The LDA band structures before and after relaxation are plotted in Fig. 2. The relaxation effect on the electronic structure should generally be minor for this size of nanotubes. Looking at the vicinity of the Fermi level, in detail, however, the band gap is increased from 0.08 to 0.12 eV. We also calculated the LDA gap using the plane-wave basis set with the Troullier-Martins-type pseudopotential[20] in the Kleinman-Bylander separable form[21] and obtained the same value. This gap enhancement is in sharp contrast to the semiconducting (7,0) nanotube in which lattice relaxation significantly reduces the gap.[13] The lowest conduction states are doubly degenerate. The next lowest conduction state is, on the other hand, downshifted by lattice relaxation from 0.47 to 0.40 eV. This is the same tendency with the lowest conduction state of the (7,0) nanotube, although the downshift is much smaller in the (9,0) tube.

Now we discuss the many-body correction to LDA. In Fig. 3, the GW quasiparticle band structure is compared with the LDA. The density of states (DOS) is also shown in Fig. 4. Inclusion of the many-body correction increases band gap from 0.12 to 0.17 eV. Although the absolute value of the increase (0.05 eV) is smaller than that of the (7,0) nanotube, it is as large as 40% of the LDA gap and should affect the electronic properties expected for devices utilizing this (9,0) nanotube. The gap value corresponds to ~2000 K; hence, the transport properties may considerably depend on temperature. It should also be noted that the DOS is asymmetric with respect to the Fermi level and has a couple of peaks in the small positive energy region, which should be observed in the STS experiments. The slope of the quasiparticle state energies against wave vector is also increased for both the highest occupied and lowest unoccupied states, upon the in-

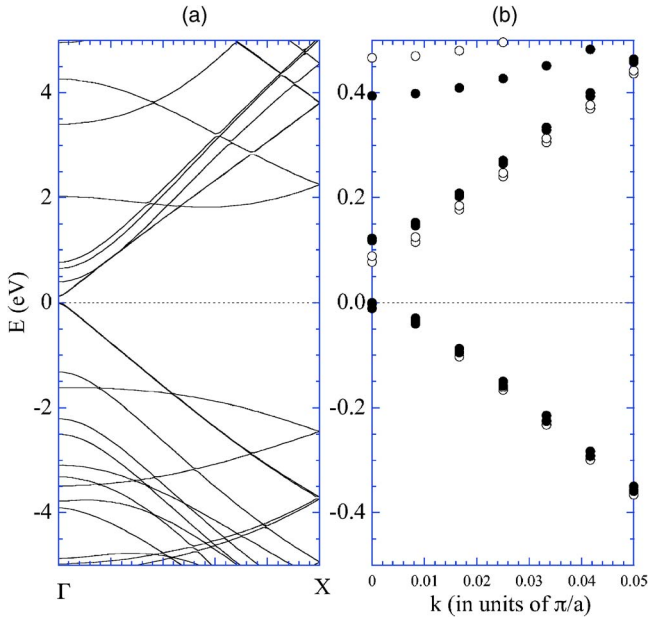

FIG. 2. (Color online) (a) LDA band structure of the (9,0) nanotube for the relaxed geometry. In (b), the band structure for the relaxed geometry (filled circles) is compared to the one for the fixed geometry (open circles) in an enlarged scale.

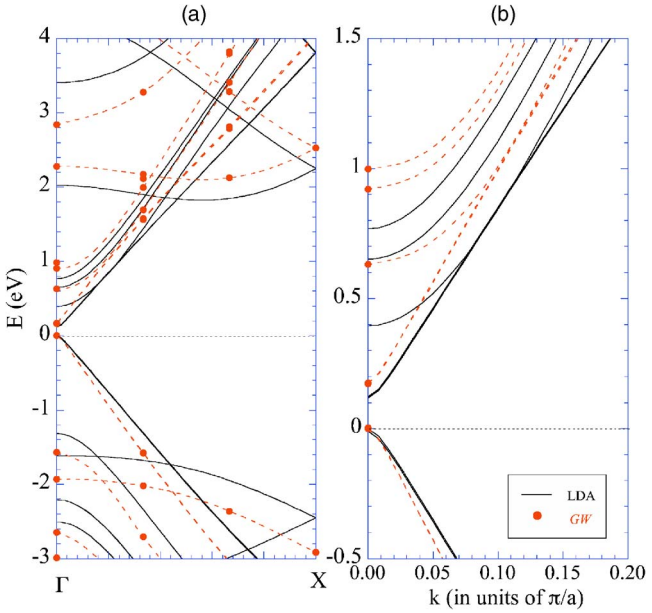

FIG. 3. (Color online) (a) Quasiparticle band structure of the (9,0) nanotube by LDA (solid line) and GW (circles), and (b) those in an enlarged scale. Dashed lines are guides for the eyes.

clusion of the many-body correction. It is in agreement with the case of graphene.[13] The NFE state is, on the other hand, pulled down by 0.57 eV from 3.41 to 2.84 eV by the many-body correction. The downshift of the NFE state is observed also in the (5,0), (6,0), and (7,0) tubes and graphene; thus, it is considered to be a general trend in carbon nanostructures. It was reported before that the NFE state often appears at the Fermi level and alters the electronic and optical properties of the doped tubes.[23–25] The present GW result suggests that the NFE state would play an even more important role in these doped systems than the LDA predicts. Most of other states are pushed away from the Fermi level by 0.3–0.5 eV by the many-body correction in both conduction and valence bands. This shift is sizable. Hence, it could be measured experimentally.

Finally, we discuss the diameter dependence of the fundamental gap. We calculated the LDA gap of $(n,0)$ tubes with $n=5-18$. They cover the diameter range of the most abundant nanotubes produced by the laser vaporization method.[15] Geometry is fixed to that of a rolled-up graphene in these calculations. Thin tubes $(n=5,6)$ are metallic, as discussed above. For $n \geqslant 7$, the tube is a moderate-gap semiconductor when n is not divisible by three, as has been suggested by the 1/3 rule. When n is a multiple of three, it is a narrow-gap semiconductor. The gap is decreased as the diameter is increased. The narrow-gap values obtained range from 0.08 to 0.02 eV and can be fitted to the following equation:

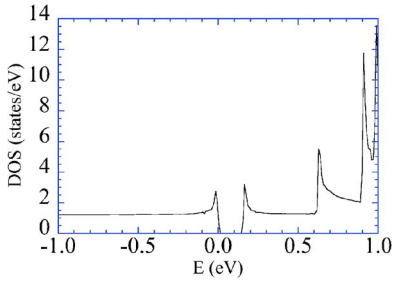

FIG. 4. (Color online) Density of states of the (9,0) nanotube taking account of the GW self-energy correction. The energy is measured from the top of the valence band.

$$E_g^{\mathrm{LDA}} = 0.043 \times d^{-1.73}, \tag{1}$$

where E_g^{LDA} is the band gap in electron volts and d is the tube diameter in nanometers. The diameter dependence has been discussed theoretically before in the effective mass theory[26] and in the tight-binding approximation,[27] and $E_g \propto d^{-2}$ was obtained. These previous works are complementary to ours in the sense that they are valid in the large-diameter region and semiquantitative. As we discussed above, the gap value of the (9,0) tube is enhanced from 0.08 to 0.17 eV when we include the lattice-relaxation effect and many-body correction. Thus, the actual gap values are considered to be larger than what one would expect from Eq. (1). These values are to be compared to the STM-STS experiment.[28] The present results show somewhat larger gap values than the observed values, the cause of which is not yet clear. Further experiments are awaited to clarify the issue.

In summary, we have discussed gap formation in metallic carbon nanotubes. Our results suggest that most of so-called metallic nanotubes are not metallic but semiconducting with sizable fundamental gap except the armchair nanotubes. The gap value is of the order of 1000 K in the diameter range of the most abundant nanotubes produced by experiments. Not only π-σ coupling but also geometry optimization and many-body effects are found to be important for quantitative description of the gap. They should be even more important in designing carbon-nanotube devices in the future.

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[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992).
[3] N. Hamada, S. I. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).
[4] J. W. G. Wildöer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) **391**, 59 (1998).
[5] T. W. Odom, J.-L. Huang, P. Kim, and C. M. Lieber, Nature (London) **391**, 62 (1998).
[6] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[7] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[8] L. Hedin, Phys. Rev. **139**, A796 (1965); L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23.
[9] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); Phys. Rev. B **34**, 5390 (1986).
[10] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986); Phys. Rev. B **37**, 10159 (1988).
[11] S. G. Louie, in *Topics in Computational Materials Science*, edited by C. Y. Fong (World Scientific, Singapore, 1998).
[12] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).
[13] T. Miyake and S. Saito, Phys. Rev. B **68**, 155424 (2003).
[14] C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402 (2004).
[15] H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, and Y. Achiba, Synth. Met. **103**, 2555 (1999).
[16] T. Kotani and M. van Schilfgaarde, Solid State Commun. **121**, 461 (2002).
[17] S. Okada and S. Saito, J. Phys. Soc. Jpn. **64**, 2100 (1995).
[18] X. Blase, L. X. Benedict, E. L. Shirley, and S. G. Louie, Phys. Rev. Lett. **72**, 1878 (1994).
[19] S. Okada, A. Oshiyama, and S. Saito, Phys. Rev. B **62**, 7634 (2000).
[20] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[21] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[22] K. Kanamitsu and S. Saito, J. Phys. Soc. Jpn. **71**, 483 (2002).
[23] S. Okada, S. Saito, and A. Oshiyama, Phys. Rev. Lett. **86**, 3835 (2001).
[24] T. Miyake and S. Saito, Phys. Rev. B **65**, 165419 (2002).
[25] T. Miyake and S. Saito, Solid State Commun. **125**, 201 (2003).
[26] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **78**, 1932 (1997).
[27] L. F. Chibotaru, S. A. Bovin, and A. Ceulemans, Phys. Rev. B **66**, 161401(R) (2002).
[28] M. Ouyang, J.-L. Huang, C. L. Cheung, and C. M. Lieber, Science **292**, 702 (2001).