PHYSICAL REVIEW B **88**, 035423 (2013)

Corrugation-induced metal-semiconductor transition in single-wall carbon nanotubes with a small radius

Hongxia Lu,[1] Jianbao Wu,[2,*] and Weiyi Zhang[1,†]
[1]*National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China*
[2]*College of Fundamental Studies, Shanghai University of Engineering Science, Shanghai 201620, China*

(Received 29 November 2012; revised manuscript received 24 March 2013; published 15 July 2013)

Armchair single-wall carbon nanotubes (SWCNTs) are theoretically predicted to be metallic in the simple zone-folding scheme and protected from the curvature effects. They are, however, found to be small-gap semiconductors, experimentally. Lacking the genuine band-gap opening mechanism for armchair SWCNTs, the Mott insulator concept was proposed previously for the nominally metallic carbon nanotubes. Using the *ab initio* local density approximation method, we show, in this paper, that the carbon nanotubes without corrugation are, in fact, not metastable. The corrugated structures are always lower in energy than those without corrugation. The size of corrugation increases rapidly with the nanotubes' curvature and vanishes for flat graphene. The corrugation breaks the local symmetry between two types of carbon sites, and a *true* band gap starts to develop once graphene sheets are rolled up into nanotubes.

DOI: 10.1103/PhysRevB.88.035423 PACS number(s): 61.48.De, 71.20.Tx, 72.80.Rj

I. INTRODUCTION

The electronic transport in one-dimensional systems has always been a hot topic in physics and material science because of its vast application potential in nanodevices. Such interest has been revived recently due to the discovery of carbon nanotubes by Iijima.[1] A single-wall carbon nanotube (SWCNT) can be viewed as a quasi-one-dimensional cylindrical tube rolled up from a graphene sheet.[2] It can be specified uniquely by a pair of integers (n,m) called chirality index,[3–5] and its electronic property sensitively depends on the chirality and diameter of nanotubes. The construction of SWCNT suggests that the electronic properties can be deduced from that of graphene under the simple zone-folding scheme.[3,4] For an ideal graphene,[2] the valence and conduction bands are classified as σ- and π-orbital characters. Six σ bands lie either deep below or high above the Fermi energy and are responsible for the structural bonding. The two important bands near the Fermi energy are contributed by the π bands of $2p_z$ orbitals which are orthogonal to σ bands. These two bands touch each other at the Brillouin zone (BZ) corners and form a gapless metal.[2–4] The touching wave vectors $\mathbf{K}$ are called the Dirac points because the electrons in the vicinity of $\mathbf{K}$ follow a relativistic linear dispersion relation. Thus, the transport property in graphene is essentially determined by the electrons of p_z orbitals.

When folding a graphene sheet into a carbon nanotube with a given chiral index, only certain sets of $\mathbf{k}$ values in the Brillouin zone satisfy the boundary conditions imposed in a circumferential direction. By checking whether the selected $\mathbf{k}$ sets include the Dirac points or not, Saito *et al.*[3] arrived at a concise prediction that the SWCNT is metallic if the chiral index satisfies the condition $\mathrm{mod}(n-m,3)=0$. However, this simple prediction neglects the curvature effect and works only for large diameter SWCNTs. It does not agree with the recent experiments well,[6–8] in particular for carbon nanotubes with small diameters. To resolve the discrepancy, a curvature induced π-σ hybridization effect was proposed by several research groups.[9–11] The renormalized hopping integrals become anisotropic with respect to the axial and circumferential directions, which effectively shifts the Dirac points. For a nominally metallic zigzag SWCNT, this converts a metal nanotube into a small gap semiconductor nanotube. However, such a hybridization effect does not change the allowed sets of wave vectors in a circumferential direction for armchair SWCNTs. Thus, armchair SWCNTs remain metallic and are protected from such a curvature effect.[11]

The effort to measure the electronic property of a single SWCNT has made great progress recently. A successful attempt was made by Zhou *et al.*[6] on a SWCNT with unknown chirality and a small band gap was indeed observed. The measurements on SWCNTs with specific chiralities were carried out by Ouyang *et al.*[7] The existence of band gaps was confirmed for nominally metallic zigzag SWCNTs, but the metallic property was initially confirmed for armchair SWCNTs as predicted by the previous model with the curvature effect.[11] In a more recent study on the ultraclean and suspended SWCNTs, which is supposed to be free from twists or axial strains, band gaps of the order of 100 meV were observed for armchair SWCNTs at the Fermi energy.[8] Furthermore, this band gap is named *true* band gap since it does not vanish as the external magnetic field varies.[12] This result rules out the previous model on curvature-induced shifting of Dirac points, and a new band-gap opening mechanism must be present for the following reasons: (1) The circumferential boundary condition may miss the Dirac points for certain SWCNTs, but the Dirac points can always be reinstalled as allowed wave vectors if the periodic boundary condition is supplemented by an Aharonov-Bohm (AB) quantum phase[12] from an external magnetic field. Thus zero band gap should still be observable in magnetic field. (2) The zero band gaps for armchair SWCNTs are supposedly protected from the curvature effect. Lacking the genuine band-gap opening mechanism, Deshpande *et al.*[8] ascribed the semiconducting SWCNTs as the Mott insulators.[13–15] At present, experimental observation of strong correlations remains a challenge since their signature is masked by the charging effect.

While the strongly correlated electronic model is certainly a plausible candidate for the *true* gaps in nominally metallic SWCNTs,[8] other possibilities are also worthwhile to be explored. As the structural deformation is a common phenomenon in low dimensional systems, the structural twist and strain models have been investigated from very early on by several groups.[16–19] The phenomenological calculations showed that band gaps (not *true* band gaps) can be created by the twist distortions in armchair SWCNTs, but the estimated structural transition temperature differs by two orders of magnitude due to the poor material parameters.[18,19] Generally speaking, the twist and strain deformations can be produced during the nanotubes' fabrication. Such extrinsic deformation can be carefully avoided if measurements are made on extremely clean, as-grown, and suspended SWCNTs, as were done by Deshpande *et al.*[8] These results suggested that other intrinsic structural instability, if it exists, should be responsible for the development of *true* gaps. To have *true* band gaps, on-site electronic energies on type-A and type-B carbon atoms of a primitive cell must be different. The widely discussed in-plane Kekule structures,[20,21] which create band gaps, do not create *true* band gaps. Thus, corrugated structures are called for. In fact, the planar graphene structure is not the universally stable structure for group IV elements. The similar Si and Ge can also form a monolayer honeycomb lattice, but with a corrugation where type-A and type-B atoms stay in different planes separated by a corrugation length Δ.[22] Therefore, one may naturally ask whether similar structure, though not favored in planar graphene,[2] becomes a more stable structure when graphene is rolled up into nanotubes. In fact, such corrugated structures have been verified by *ab initio* calculation in boron-nitride nanotubes.[23] Also, such a scenario has been proposed for carbon nanotubes some time ago in a phenomenological model by Viet *et al.*[21] However, to the best of our knowledge, no *ab initio* calculation exists which either proves or disproves the corrugated carbon nanotubes.

In this paper comprehensive *ab initio* calculations have been carried out to analyze the metastability of the corrugated structures of armchair SWCNTs. We show that (1) noncorrugated SWCNT structures are, in fact, not metastable at all. Corrugated SWCNT structures are always lower in energy than the noncorrugated nanotubes. (2) Together with the curvature effect, the corrugated structure breaks the local symmetry between type-A and type-B carbon atoms. As a result, a *true* gap is created which does not vanish even when an external magnetic field is swept.

II. NUMERICAL METHOD

The electronic structure and total energy calculations are performed using the VASP[24,25] package which has an advantage on a large system of a few tens of atoms. The VASP package was an implementation of a highly accurate full-potential projector augmented wave (PAW) method.[26] The generalized gradient approximation (GGA) of Perdew and Wang[27] was adopted for the exchange-correlation potential. As was usually done in the band structure calculation of nanotubes, a basic building block of a nanotube is chosen as a unit cell and periodic boundary conditions are implemented both along the nanotube's axis and lateral directions. For armchair SWCNTs with chiral index (n,n), the basic building block includes $4n$ carbon atoms. They are arranged in a hexagonal lattice with an intertube separation of at least 20 Å to avoid the interaction between neighboring SWCNTs. In the self-consistent field potential and total-energy calculations a set of $(1 \times 1 \times 11)$ **k**-point sampling is used for BZ integration in **k** space. Here the **k**-point mesh is generated by the Monkhorst-Pack scheme,[28] a kinetic energy cutoff for a plane-wave basis set is taken as 500 eV. The convergence criterion of self-consistent calculation is 10^{-6} eV for total energy.

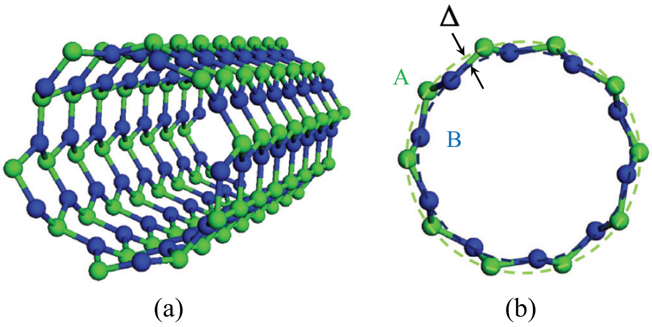
III. RESULTS AND DISCUSSIONS

In this paper we consider the armchair SWCNTs as illustrated in Fig. 1(a). To account for the corrugation of SWCNTs, type-A and type-B carbon atoms are allowed to displace from each other radially and form two cylinders with a corrugation length Δ as sketched in Fig. 1(b). Since SWCNTs as well as their corrugated structures are metastable structures, searching for the metastable structures with even lower energy was a challenging task. We resort to the simple method of sifting through the parameter space spanned by the bond length d and corrugation length Δ. As was shown in the Supplementary Material,[29] we compute the total energies for a set of (d,Δ) so that a local minimum is included. Then, by using the least mean square fitting of elliptic paraboloid, the optimum bond length d_m and corrugation length Δ_m are extracted at the local minimum. The advantage of using the constrained relaxation method over the standard conjugate-gradient relaxation scheme is that the energy landscape around the corrugated structure can be directly visualized, so that the stability and structural distortion type can be easily analyzed.

In Fig. 2 the normalized energy per carbon atom for the six armchair SWCNTs are plotted in (d,Δ) parameter space with respect to the local minimum. The chiral index is from $n = 3$ to $n = 8$ and the radius of SWCNTs ranges from 2.0 to 5.5 Å. The local minima are clearly demonstrated for all the SWCNTs studied and corrugated structures of SWCNTs are proved. Near the local minima, the energy can be nicely fitted with the following elliptic paraboloid:

$$\begin{aligned} E = E_m &+ B_d[v_1(d-d_m)+v_2(\Delta-\Delta_m)]^2 \\ &+ B_\Delta[v_1(\Delta-\Delta_m)-v_2(d-d_m)]^2, \end{aligned} \qquad (1)$$

with the standard deviation less than 10^{-4}. E_m is the minimum energy per carbon atom at d_m and Δ_m. The corrugated structure



(a) (b)

FIG. 1. (Color online) Sketch of (a) a corrugated armchair SWCNT and (b) an exaggerated top view with defined corrugation length Δ. The blue and green spheres are the two types of inequivalent carbon atoms.

TABLE I. The fitting parameters of Eq. (1). σ is the standard deviation and other parameters are described in the text.

(n,n)	d_m (Å)	Δ_m (Å)	E_m (eV)	B_d (eV/Å^2)	B_Δ (eV/Å^2)	v_1	v_2	σ
(3,3)	1.442054	0.029507	−8.750949	32.731062	2.342235	0.981353	0.192213	0.00008
(4,4)	1.434917	0.012034	−8.973734	36.245188	3.854220	0.989635	0.143608	0.00004
(5,5)	1.431160	0.005346	−9.074379	34.210150	4.085503	0.993365	0.115001	0.00004
(6,6)	1.428980	0.002878	−9.127897	33.236982	4.131591	0.994973	0.100141	0.00004
(7,7)	1.427638	0.001747	−9.159929	33.809393	4.123352	0.996357	0.085282	0.00007
(8,8)	1.426803	0.000869	−9.180525	34.227319	4.237852	0.997193	0.074879	0.00001

is lower in energy per carbon atom by 2 meV for (3,3) and 3 μeV for (8,8) nanotube. (v_1,v_2) and $(-v_2,v_1)$ are the eigenvectors defining the two principal axes of elliptic paraboloid and B_d and B_Δ are the corresponding stiffness coefficients. As can be seen from Table I, E_m decreases continuously as the radius increases and shows that SWCNTs are only metastable structures with respect to graphene.[22] The curvature seriously reduces the bonding strength between carbon atoms and the bond length d_m increases monotonically as the radius of the nanotubes is reduced. The stiffness coefficients are strongly anisotropic with an order of magnitude difference and they correspond to soft out-of-tube distortion mode and hard in-tube distortion mode.[22] Generally speaking, the lattice distortion mode mixes bond length and corrugation of SWCNTs. The degree of mixing depends on the curvature of the nanotubes and the in-tube and out-of-tube distortion modes decouple eventually for planar graphene.

The corrugated structure results from the strong electron-phonon interaction which is a Peierls-like instability widely discussed in the textbook. As can be seen in Fig. 3(a), the corrugation length Δ_m is a monotonically decreasing function of the nanotube's radius. It takes the largest value of 3×10^{-2} Å for the smallest (3,3) nanotube and 8×10^{-4} Å for a relatively large (8,8) nanotube. In agreement with the previous study, the corrugation length approaches zero for planar graphene.[22] Δ_m can be fitted with a simple power law $\Delta_m = 1.1n^{-3.3}$ Å.

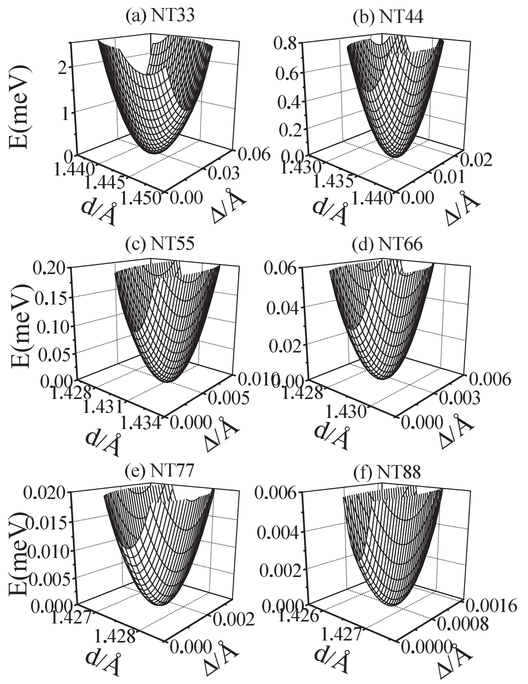


FIG. 2. The normalized energy distribution as a function of bond length d and corrugation length Δ. The local minimum energy is chosen as a reference point. (a)–(f) For (3,3) to (8,8) SWCNTs.

The existence of more metastable corrugated structures of SWCNTs offers a new possibility for the band-gap opening mechanism. While the corrugation does not break the symmetry between type-A and type-B carbon atoms for planar graphene structure, it does so for SWCNTs due to the curvature effect. Thus, a metal-semiconductor transition takes place in the armchair as well as other SWCNTs because the crystal field potential differs among different types of carbon atoms. Although Δ is quite small and difficult to be observed in structures, it does show its influence on transport properties. As shown in Fig. 3(b), a *true* band gap is present for all nominally metallic armchair SWCNTs. The band gap decreases with radius and follows approximately the empirical rule $E_g = 12.6n^{-4}$ eV. Thus the biggest gap of 140 meV occurs for the smallest (3,3) SWCNT. The physical reason why the band gap decays faster than the corrugation length is because the difference in crystal-field splitting among the two types of carbon atoms is approximately given by Δ/R with R denoting the radius. It should be emphasized that the corrugation-induced *true* gap is fundamentally different from the curvature-induced band gap.[9–11] The curvature-induced band gap does not explain the band gap in the armchair

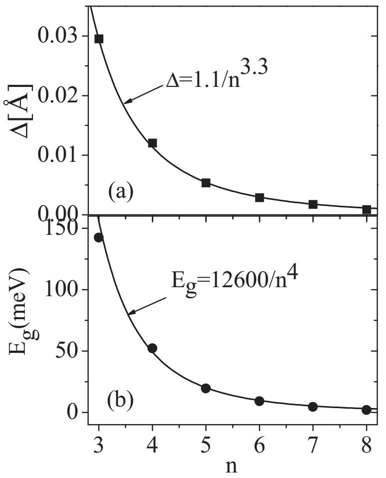


FIG. 3. Dependencies of corrugation length Δ_m and band-gap E_g on the armchair index n. The solid lines are the fitting functions.

SWCNTs, and its size can be made to vanish under the external sweeping magnetic field.[12] While the *true* band gap in our case is present irrespective of the AB effect.

Although the corrugated structures are more stable metastable structures of SWCNTs and explain the *true* band gap in nominally metallic armchair SWCNTs, the discrepancy still exists for the calculated and measured band gaps.[8] The calculated band gaps are large only for very small SWCNTs, while the measured data suggested that they are sizable even for SWCNTs with a radius up to a nanometer. The difference can be caused by the ideal model system and realistic sample setting. In the theoretical simulation, no substrate effect is considered while the substrate effect is unavoidable in measurement.[30] For example, the impurity atoms and electric charges on a substrate can create a potential gradient across the SWCNTs. Recently, a hybrid functional method which mix exact exchange with density functional approximations to exchange and correlation has become a standard tool in quantum chemistry. We have also checked the total energy and band gap under the HSE hybrid functionals method.[31] The stability of corrugated structures is enhanced by 4 times while the *true* band gap is doubled. The corrugated structure is lower in energy per carbon atom by 8.1 and 1.1 meV for (3,3) and (4,4) SWCNTs, while the band gap is 280 and 95 meV for (3,3) and (4,4) SWCNTs, respectively. This significantly enhances the stability of corrugated structure under finite temperature. The rough estimate suggests that the corrugated structure for (3,3) SWCNT is stable above room temperature, while (8,8) SWCNT is stable in the Kelvin temperature range. Thus, further studies are required to discern the various candidates for the band-gap opening mechanism in nominally metallic armchair SWCNTs.

IV. CONCLUSION

In summary, the corrugated structures of SWCNTs are shown to have lower energy than noncorrugated SWCNTs using the *ab initio* calculations. A metal-semiconductor transition is found as a result of the symmetry breaking between the two types of carbon atoms and a *true* band gap exists for nominally metallic armchair SWCNTs. Both the corrugation length and band gaps are decaying functions of the nanotubes' radius and approach zero for flat graphene. Our conclusion is valid also for zigzag and chiral SWCNTs, i.e., all SWCNTs with small radius are semiconductors if the corrugation effect is accounted for. The quantitative discrepancy between the theory and measurement may due to the substrate related effect which are worth further investigation.

ACKNOWLEDGMENTS

This work was supported in part by the National Basic Research Program of China (Grant No. 2010CB923404). We wish to thank Professor Haifeng Ding for carefully reading of the manuscript.

---

[*] wujianbao@sues.edu.cn

[†] wyzhang@nju.edu.cn

[1] S. Iijima, Nature (London) **354**, 56 (1991).

[2] P. R. Wallace, Phys. Rev. **71**, 622 (1947).

[3] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992).

[4] N. Hamada, S. I. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

[5] J. W. Mintmire and C. T. White, Phys. Rev. Lett **81**, 2506 (1998).

[6] C. Zhou, J. Kong, and H. Dai, Phys. Rev. Lett. **84**, 5604 (2000).

[7] M. Ouyang, J. L. Huang, C. L. Cheung, and C. M. Lieber, Science **292**, 702 (2001).

[8] V. V. Deshpande, B. Chandra, R. Caldwell, D. S. Novikov, J. Hone, and M. Bockrath, Science **323**, 106 (2009).

[9] X. Blase, L. X. Benedict, E. L. Shirley, and S. G. Louie, Phys. Rev. Lett. **72**, 1878 (1994).

[10] H. Yorikawa and S. Muramatsu, Phys. Rev. B **52**, 2723 (1995).

[11] J. Chen, Z. Yang, and J. Gu, Modern. Phys. Lett. B **18**, 769 (2004).

[12] H. Ajiki and T. Ando, J. Phys. Soc. Jpn. **65**, 505 (1996).

[13] C. Kane, L. Balents, and M. P. A. Fisher, Phys. Rev. Lett. **79**, 5086 (1997).

[14] R. Egger and A. O. Gogolin, Phys. Rev. Lett. **79**, 5082 (1997).

[15] A. A. Odintsov and H. Yoshioka, Phys. Rev. B **59**, R10457 (1999).

[16] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **78**, 1932 (1997).

[17] L. Yang and J. Han, Phys. Rev. Lett. **85**, 154 (2000).

[18] Y. H. Huang, M. Okada, K. Tanaka, and T. Yamabe, Solid State Commun. **97**, 303 (1996)

[19] D. Connétable, G. M. Rignanese, J. C. Charlier, and X. Blase, Phys. Rev. Lett. **94**, 015503 (2005).

[20] K. Harigaya and M. Fujita, Phys. Rev. B **47**, 16563 (1993).

[21] N. A. Viet, H. Ajiki, and T. Ando, J. Phys. Soc. Jpn. **63**, 3036 (1994).

[22] H. Sahin, S. Cahangirov, M. Topsakal, E. Bekaroglu, E. Akturk, R. T. Senger, and S. Ciraci, Phys. Rev. B. **80**, 155453 (2009);

[23] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Eur. Phys. Lett. **28**, 335 (1994).

[24] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[25] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[26] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[27] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[28] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[29] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.88.035423 for the extensive numerical calculations of the total energies for various configurations of bond length d and corrugation length Δ.

[30] M. P. Amer, A. Bushmaker, and S. B. Cronin, Nano. Lett. **12**, 4843 (2012).

[31] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).