Nature of Single Vacancy in Achiral Carbon Nanotubes

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(Received 7 July 2003; published 12 March 2004)

We have performed systematic calculations for single vacancies and their related point defects in achiral carbon nanotubes using a tight-binding model. Our calculations clarify that the local structures around single vacancies in such tubes do reconstruct with no constraint. We find that the structural configuration and formation energy of the resulting point defect are dependent on the radius and chirality, as well as the electric properties of a tube. The electronic structures of the single vacancies also depend strongly upon the chirality of the carbon nanotubes.

DOI: 10.1103/PhysRevLett.92.105504 PACS numbers: 61.46.+w, 61.72.Ji, 71.15.Nc

Carbon nanotubes have attracted much attention, with interest being driven both by their unique anisotropic structures and by potential applications in the fields of nanometer scale devices. So far, numerous results have been obtained from experimental and theoretical research, revealing novel properties of carbon nanotubes [1–7]. Carbon nanotubes are not defect-free in reality; there are various kinds of defects present in actual carbon nanotubes, such as Stone-Wales defects, single vacancy, and its derivative point defects [8–12]. These defects may influence the physical and chemical properties of carbon nanotubes to some extent. Therefore, a deep understanding of topological defects in single-walled carbon nanotubes (SWNTs) is greatly needed and represents one of the fundamental issues.

Among various kinds of topological defects in carbon nanotubes, the effects of atomic vacancies have been studied more recently [9,10,13–15]. Experimental observations showed that carbon atoms in carbon nanotubes can be released under electron or ion irradiation [13,14] effectively, leaving vacancies in SWNTs behind. The dangling bonds (DBs) around vacancies can serve as bridges for the chemical connection of two tubes [12] or provide active sites for atomic adsorption. The energetic stability of an ideal vacancy in a SWNT was also discussed theoretically. Ajayan *et al.* [13] suggested that an ideal vacancy in a (10, 10) tube is unstable; two of the three DBs prefer to recombine each other, forming a pentagon ring coupling with a DB left, and leaving a so-called 5-1DB defect. On the contrary, the calculations from Ref. [15] indicated that an ideal vacancy is metastable in a (10, 10) nanotube even at $T = 1000$ K. When the defective system is heated to 2000 K, the isolated vacancy in a (10, 10) tube can transform into a 5-1DB defect. Clearly, the transformation mechanism from a single vacancy to a 5-1DB defect in a (10, 10) tube is presently a subject of debate.

On the other hand, the discussions as mentioned above were mainly restricted to the cases of a (10, 10) tube only. It is well known that many properties of SWNTs exhibit size and helicity effects. This suggests that the formation and transformation of a single vacancy in a SWNT is probably dependent on the radius and chirality of the tube as well. However, a systematic study of such fundamental issues is still lacking.

In this Letter, we report a systematical investigation of vacancies in achiral SWNTs by utilizing a tight-binding approach. Our results not only confirm that the single vacancies in the considered tubes are unstable but also show that the resulting structural patterns of point defects strongly depend upon the radius and chirality of the nanotube. We propose that the changes in the hybridization in character from an ideal vacancy to a 5-1DB defect correspond to the structural transformation. Another interesting finding is that the calculated formation energy curve of the point defects in $(n, 0)$ tubes exhibits a pronounced periodic feature.

Our calculations employ the carbon tight-binding (TB) model [16], which has been developed through introducing a correction for environment dependence around each C-C bond. The benchmark studies demonstrated that this carbon TB model can be successfully applied to various carbon crystalline structures. Owing to our concerned carbon systems containing two-coordinated defects, it is necessary to examine the accuracy of this model for such defective systems. We consider a typical example of a single vacancy in a graphite sheet. A supercell containing 720 carbon atoms is chosen to mimic a perfect graphite sheet, and one carbon atom is removed to create a vacancy. After full relaxation for the defective system with treatment of the TB model with inclusion of a Hubbard-like term [17], we obtained the formation energy of a vacancy in the graphite sheet to be 7.20 eV. This energy value is quite close to the previous result of 7.8 eV from local density approximation calculations [18], as well as the resulting structure exhibiting three DBs around the single vacancy. This agreement provides confidence in the accuracy of the methodology employed.

In our calculations, two groups of SWNTs, a series of $(n, 0)$ tubes with $n = 6$–15 and a series of (n, n) tubes with

$n = 3$–12, are considered. For these $(n, 0)$ tubes, the supercells consist of six unit cells, and the supercell length in the tube-axis direction is 25.56 Å. For the considered (n, n) tubes, the supercells contain ten unit cells with supercell length of 24.60 Å. Because of the large sizes of the supercells, the Γ sampling point in the Brillouin zone is adopted in our calculations.

We first address the case of the (n, n) tubes. For convenience, a (10, 10) tube is selected for study. An ideal vacancy is created in a (10, 10) tube [Fig. 1(a)] through removing a carbon atom from the tube wall. There are three DBs around the unrelaxed vacancy. Usually, such a local vicinity of DBs is fairly unstable, and any two of the DBs have the possibility to recombine with each other if the separation between them is suitable; otherwise the three DBs should remain as for the situation in graphite. In order to achieve the optimized structure for the (10, 10) tube containing an ideal vacancy, we perform full relaxation with the steepest-decent algorithm. Our findings are that both C1 and C2 as labeled in Fig. 1(a) can form a weak C-C bond with no constraint. This new C-C bond tilts with respect to the tube axis. Thus, the local atomic network around the point defect features one pentagon and one DB in C3, which is a 5-1DB defect. We notice that structural relaxation with the steepest-decent algorithm may bring a geometry into a local energy minimal configuration. To avoid being trapped into a local minimum, we examine the possibility of the other configuration like the rebonding of C1 and C3. Using the configuration shown in Fig. 1(a), we adjust the spatial separation between C1 and C3 to 1.5 Å. After fixing both atoms, we optimized the remaining atoms in the atomic network and follow with a full relaxation of the entire system. The final geometry shows that the bond of C1-C3 forced by hand at initial stage dissociates; both C1 and C2 form a C-C bond again. That is, the geometry of the point defect 5-1DB regains. Our studies described above demonstrate that a single vacancy in a (10, 10) tube is very unstable; it rapidly transforms into a typical 5-1DB defect, being consistent with the previous theoretical predictions of Ajayan *et al.* [13], but in disagreement with the conclusion that the three DBs around the vacancy in a (10, 10) tube are metastable [15].

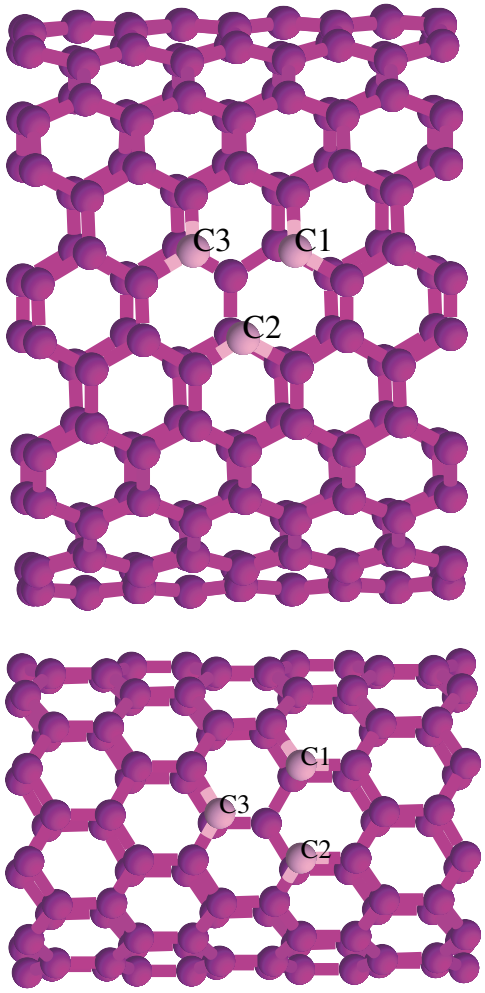

FIG. 1 (color online). Configurations of ideal vacancies in (a) (n, n) tubes and (b) $(n, 0)$ tubes. Carbon atoms in the vicinity of the defect are labeled as C1, C2, and C3, with the light shading.

We extend our above considerations to the other defected (n, n) tubes. After extensive calculations, we find that the basic distortion patterns around the vacancies in these tubes are almost the same as that in the (10, 10) tube as described above. Furthermore, the transformations from ideal vacancies to 5-1DB defects are also spontaneous. One major discrepancy in structural features between the resulting 5-1DB defects in the different armchair tubes is the bond-length variation of the new C-C bonds.

Similarly, we also treat the tubes with zigzag symmetry. It is observed that the transformations from ideal vacancies to their related point defects happen automatically for the armchair tubes under consideration. Surprisingly, for the $(n, 0)$ series the resulting patterns of point defects are size dependent. The local structures of ideal vacancies in the tubes $(n, 0)$ with $n = 6$–8 [Fig. 1(b)] do convert to a defect pattern in which the formed new bonds, C1-C2, are perpendicular to the tube axes, with no constraint. We named this defect as 5-1DB-P. However, in the other cases of $(n, 0)$ tubes, the atoms C1 prefer to bond automatically to the atoms like C3, forming another defect pattern where the orientations of the new bonds tilt about the tube axes, named as 5-1DB-T. We also calculate the configuration 5-1DB-T in $(n, 0)$ when $n < 9$, and 5-1DB-P in $(n, 0)$ when $n > 8$, respectively. As a result, two types of the optimized configurations are both stable for the considered $(n, 0)$ tubes.

Since the stable structures of defective tubes as mentioned above are obtained, it is significant to assess the relative energetic stabilities of these point defects. For this purpose, we evaluate the formation energies of all stable point defects investigated above. Figure 2 plots the formation energy curves of 5-1DB, 5-1DB-P, and

5-1DB-T defects. Obviously, the order of the defect formation energies in the defected tubes of $(n, 0)$ and (n, n) around the same radius follows E(5-1DB-T) > E(5-1DB) > E(5-1DB-P) except for some smaller tubes. So, among the three kinds of defects, the 5-1DB-P defect is the most favored energetically. In addition, all energies shown in the energy curves are lower than the formation energy of a single vacancy in graphite.

In particular, for the cases of defected $(n, 0)$ tubes with $n = 9$–15, our calculations reveal that the initial structures containing single vacancies could not directly convert to the most favored configuration 5-1DB-P but to a metastable state 5-1DB-T. This immediately raises a question: how much energy is associated with defect transformation from 5-1DB-T to 5-1DB-P for these cases? Evidently, searching for the lowest energy barriers for these cases is vexatious. In this study, we select only the case of the $(10, 0)$ tube as an example. By moving both C1 and C2 in the 5-1DB-T pattern toward each other step by step, relaxing rest atoms to equilibrium, we finally reproduce the configuration of 5-1DB-P from 5-1DB-T, undergoing a process of bond breaking of C1-C3 and bond forming of C1-C2. This procedure yields an energy barrier of ~1.9 eV. Without a doubt, this process may not be the best channel for the transformation between the two defected configurations; the energy barrier in a realistic distortion should be no more than 1.9 eV.

Figure 2 clearly shows that the defect formation energies for (n, n) tubes increases monotomically with increasing tube radii, whereas the formation energy curves of 5-1DB-P and 5-1DB-T for $(n, 0)$ tubes exhibit steplike and sawtoothlike features, respectively. These dispersion curves are size dependent for the tubes. Interestingly, both sawtoothlike and steplike features are periodic, and such periodicity is somehow characterized by the lower formation energies of defected $(n, 0)$ tubes with $n = 3m$ ($m = 2$–5) as compared to their neighbors, $(n - 1, 0)$ and $(n + 1, 0)$ tubes. Similar periodic features were also found in the evolution of energy gaps in perfect $(n, 0)$ tubes [19], as well as in the formation energy curves for 5-77-5 defects in $(n, 0)$ tubes [20]. On the other hand, previous work such as the "band-folding" language [21] and the concise relation between the symmetry and the electronic states for perfect tubes [22] demonstrates that the perfect $(n, 0)$ tubes can be sorted into metals or semiconductors. Such a classification shows periodic evolution of the electrical characterization of $(n, 0)$ tubes, where the periodic feature is also characterized by the metallic $(n, 0)$ tubes. All events mentioned above are distinct in physical properties but the same in the periodic features. Thus, we can conclude that the observed periodic features either in the energy gaps or in the defective cases are essentially associated with the intrinsic geometrical property of the related perfect $(n, 0)$ tubes. We stress that this periodic character is hidden in some cases. For example, the strain energies of perfect $(n, 0)$ tubes [23] vary smoothly with index n. So, as compared to such a smooth trend, our revealed steplike and sawtoothlike formation energy curves of defective $(n, 0)$ tubes are advantageous to display differences in the electric properties between various $(n, 0)$ tubes effectively.

Moreover, we examined the local structure around a defect in each defected tube. We find that the bond lengths of the formed weak bonds around point defects in the cases of defective $(3n, 0)$ tubes are systematically shorter than those in either $(3n - 1, 0)$ or $(3n + 1, 0)$ at any fixed index n (Fig. 3), just reflecting the different electrical characteristics (either metallic or semiconducting). Totally, the observed distribution of the concerned bond lengths correlates very well with the relative stabilities of defective $(n, 0)$ tubes. As a contrast, all (n, n) tubes

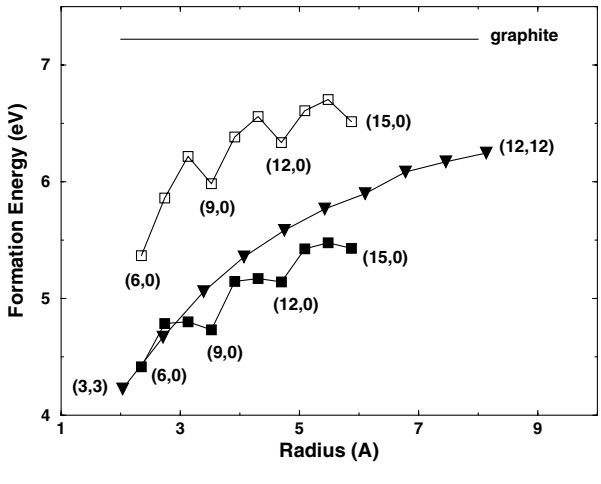

FIG. 2. Defect formation energies as a function of radius of a tube. Down triangles stand for 5-1DB defects in (n, n) tubes, filled squares for 5-1DB-P defects in $(n, 0)$ tubes, and open squares for 5-1DB-T defects in $(n, 0)$ tubes.

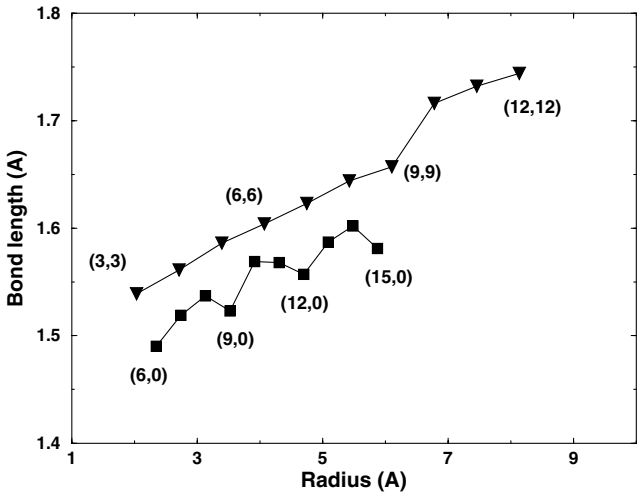

FIG. 3. Evolution of bond lengths of the formed weak bonds in both 5-1DB-P (filled squares) and 5-1DB (down triangles) defects.

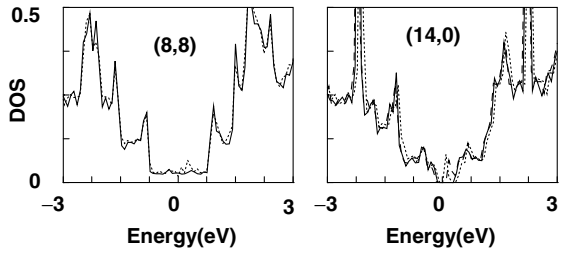

FIG. 4. Comparisons of DOS between perfect and defected tubes for both (8, 8) and (14, 0) tubes. Solid lines stand for the DOS of perfect tubes, dotted lines for 5-1DB in an (8, 8) tube and 5-1DB-P in a (14, 0) tube, and long dashed lines for the 5-1DB-T in a (14, 0) tube. The Fermi levels are at 0.0 eV.

are metallic, so the monotonous trend in the bond lengths of the weak bonds around 5-1DB varying with the tube radii is observable. Our calculations indicate that the distortion caused by the considered point defect in a tube is localized spatially within two atomic shells. Thus, a point defect, which is dilute in our considered tubes, could not effectively alter the σ-like–π-like hybridization for a whole system. These vacancies in the tubes yield typical defect states with sharp peaks at about 0.2 eV above the Fermi level according to our calculated electronic density of states (Fig. 4). These sharp peaks predominately result from the atoms in two shells around the corresponding vacancies, indicating that the electronic states of the single vacancies in the tubes are localized. Furthermore, we find that at these specific defect states, the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals (z axis is along the tube axis) of the dangling bond atom are hybridized heavily for the case of 5-1DB defects, whereas the components of $2p_y$ ($2p_z$) are much larger than those from the other three atomic orbitals of the dangling bond atoms in 5-1DB-T (5-1DB-P) defects. This clearly shows that at the concerned defect states, the mixture of four atomic orbitals of each dangling bond atom relies strongly on the types of the vacancies, implying that the hybridization of the DBs is highly chirality dependent. In fact, when a single vacancy is present in a SWNT, the original local σ-like–π-like hybridization around the vacancy is destroyed, introducing additional constraints. These constraints can be reduced through forming a new σ bond in the local vicinity of the DBs, driving the structural transformation from an ideal vacancy to its derivative defect.

In summary, we extensively studied single vacancies and their related defects in achiral carbon nanotubes. Our results demonstrate that the reconstruction of a network around a single vacancy in our concerned tubes does happen with no constraint. Both the orientations and bond lengths of the recombined bonds around the point defects vary with the sizes and chiralities of tubes. The calculated formation energy curves of point defects in the cases of $(n, 0)$ are periodic, which is mainly characterized by the metallic $(n, 0)$ tubes. All of the trends of the formation energies of the point defects in $(n, 0)$ and (n, n) tubes are associated with the relative strengths of the formed σ bonds around the point defects. Surprisingly, the dangling bond atoms in the stable vacancies cause unoccupied defect states, where the hybridized features of the atomic orbitals for the dangling bond atoms are dependent on the chirality of the tubes.

This work is supported by the Fund of USTC, by the Fund of Chinese Academy of Science, and by NSFC (50121202).

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