Electronic Structure of a Collapsed Armchair Single-Walled Carbon Nanotube*

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The electronic structure modifications by radial deformation are investigated for an armchair (21,21) single-walled carbon nanotube (SWNT), on which scanning tunneling spectroscopy (STS) measurements have recently been made [C. E. Giusca et al., Phys. Rev. B 76, 035429 (2007)]. Plausible radial deformations under hydrostatic pressure are predicted using a semiempirical method based on the continuum elastic shell model [M. Hasegawa and K. Nishidate, Phys. Rev. B 74, 115401 (2006)]. It is found by density-functional electronic-structure calculations that the collapsed (21,21) tube is a semiconductor with small band gap of ≈ 62 meV. This result is consistent with the previous investigations for much thinner armchair SWNTs but contradicts the STS measurements, which indicate that the collapsed tube is metallic with finite density of states at the Fermi level. A possible origin of this contradiction is briefly discussed. [DOI: 10.1380/ejssnt.2009.541]

Keywords: Density functional calculations; Electronic structures; Carbon nanotubes: Radial deformations

I. INTRODUCTION

Since the discovery [1] of carbon nanotubes (CNTs), the electronic structures of individual single-walled CNTs (SWNTs) have been studied on the basis of how the band structure of the underlying graphitic sheet (graphene) is folded when the sheet is rolled up into a seamless cylinder [2–4]. These results of the zone-folding picture are modified by curvature effect [5] and individual SWNTs can be classified according to their electronic band gap into semiconductors, small-gap semiconductors, and metals depending on size and chirality. In recent years, the structural and chemical modifications of CNTs have attracted increasing attention with a motivation of finding possible technological applications. In particular, individual SWNTs are prone to a significant cross-sectional deformation under external stress as demonstrated by experiments [6, 7] and theoretical calculations [8–12]. Of particular interest is that the band gaps of semiconductor SWNTs vary with increasing radial deformation and eventually close at a critical deformation depending on size and chirality. This electronic-structure modulations has been predicted theoretically [13–21] and evidenced by experiments [22, 23]. On the other hand, the band-gap opening by deformation of metallic SWNTs has also been of another interest from theoretical and application-oriented point of view but less investigated [12, 24, 25]. Lu et al. [24] have shown that a combined effect of mirror symmetry breaking and bond formation between atoms on opposing flattened faces is responsible for the band gap opening of armchair SWNTs. They demonstrated this feature for an armchair (8,8) SWNT using tight-binding (TB) molecular dynamics (MD) method. Mehrez et al. [25] have also demonstrated the band gap opening for a series of armchair (n, n) SWNTs with n = 6–12 using constraint-free density functional TB-MD simulations. Their results imply that the symmetry breaking is irrelevant for the band gap opening of metallic SWNTs. Experimentally, Giusca et al. [26] have recently made challenging scanning tunneling microscopy (STM) measurements on the flattened tube, identified as an armchair (21,21) SWNT with diameter ≈ 2.8 nm, and found that the flattened tube is metallic with finite density of states (DOS) at the Fermi level. This result is in contradiction to the theoretical predictions for much thinner armchair SWNTs [13, 24, 25]. In this work we are concerned with this contradiction in the electronic structures of the radially deformed (21,21) SWNT and show that the collapsed tube is a semiconductor with small band gap ≈ 62 meV, in consistent with earlier predictions for much thinner tubes.

In the next section we present the radial deformations predicted by using a semiempirical method developed in the previous work [12]. In Section III we present the results of ab initio electronic-structure calculations for the deformed (21,21) SWNTs and discuss on these results. The final section is devoted to the conclusions.

II. RADIAL DEFORMATION UNDER HYDROSTATIC PRESSURE

We considered radial deformations uniformly extended along the tube axis and predicted plausible cross-sectional shapes using a semiempirical method based on the continuum elastic shell model [12]. We briefly summarize this method in the following. In this method, a SWNT is modeled as an elastic shell and its strain energy, defined as the energy increase due to the curvature effect, is calculated by extending the results for undeformed circular SWNTs. It has been found by the density functional theory (DFT) and molecular mechanic calculations that the strain energy per atom of circular SWNTs is well represented as $E_{strain} = \alpha/R_0^2$, where $R_0$ is the tube radius and $\alpha$ is a constant insensitive to $R_0$ and chirality of tube [12, 27]. This result is surprisingly in accordance with the classical result for the continuum elastic shell, implying that...
SWNTs can be viewed as continuum elastic shells and the strain energy of radially deformed tubes can easily be calculated using the above result for circular SWNTs. We used the value of $\alpha = 1.94$ eV/Å$^2$ throughout the present work. Also included in this extension is the effect of the interactions between atoms on the opposing tube faces, which is not taken into account in the elastic shell model but becomes appreciable when the deformation is large enough to reduce the distance between opposing flattened faces to the interlayer separation of graphite. This atomic interaction was obtained by a semiempirical analysis of the interlayer binding of graphite [28,29].

Following the previous work [12], we assumed a model cross-sectional shape whose circumference consists of two ellipsoids smoothly connected by two circles. This model shape is characterized by four parameters and one of them can be eliminated by assuming that the perimeter of a deformed cross section remains unchanged and is equal to $2\pi R_0$. Then, for a given fractional change (decrease) in cross-sectional area $S$,

$$X = 1 - S/S_0 \quad (S_0 = \pi R_0^2), \quad (1)$$

the remaining shape parameters were determined so as to minimize the strain energy with the expectation that such a deformation actually occur under hydrostatic pressure, which is implicit at this stage. Here, we also assumed that no deformation occurs in the axial direction, which implies that $X$ also represents the fractional change in volume of a deformed tube and provides a useful parameter in treating radial deformation under hydrostatic pressure.

Figure 1 shows the optimized deformation energy $\Delta E$, defined as the strain energy per atom relative to the undeformed circular tube, as a function of $X$. Illustrated in this figure are the results for the armchair (16,16), (18,18), and (21,21) SWNTs, whose diameters $D$ are 2.17, 2.44, and 2.85 nm, respectively. These tube sizes correspond to the conformal (ideal) mapping of graphene with the C-C bond length of 0.142 nm and no structural optimization was made. As we see below, the effects of structural optimization on the deformed cross-sectional shape and atomic configuration are minimal for thick SWNTs under consideration. Since we are assuming that the model cross-sectional shape is consistent with an applied hydrostatic pressure, which is implicitly assumed, and $X$ represents the fractional decrease in volume, the pressure necessary to induce a deformation characterized by $X$ is given by

$$P = -2\pi R_0 \rho \left( \frac{\partial \Delta E}{\partial V} \right) = \frac{2\rho}{R_0} \left( \frac{\partial \Delta E}{\partial X} \right), \quad (2)$$

where $\rho$ is the atomic number density of the underlying graphene and $V$ is the volume of a deformed tube per unit length along the tube axis. The minimum pressure $P_0$ required for the radial deformation to occur is given by the above expression at $X = 0$ and nothing but the circular-to-oval transition pressure $P_{0_{-2}}$ in the small deformation regime, the transition pressure $P_0$ is closely proportional to $R_0^{-3}$ and found to be 0.57, 0.40, and 0.25 GPa for the (16,16), (18,18), and (21,21) SWNTs, respectively. We note that the cross section of a tube remains circular and simply shrinks under uniform pressure up to $P_0$ in accordance with the classical buckling theory. Hence, the radius of the cross section at $P_0$ is slightly smaller than the zero-pressure value, but this difference is very small and may be ignored, especially for thick tubes, because the radial bulk modulus of such SWNTs are quite large compared to $P_0$ [31].

We find that the deformation energy $\Delta E$ is almost linear in $X$ in the small deformation regime, indicating that once a tube starts to deform at $P_0$ the deformation proceeds almost spontaneously with a small excessive pressure. The sharp rise of $\Delta E$ at a large $X$ reflects the repulsive interaction between opposing faces, which becomes substantial as their separation $d$ becomes smaller than the interlayer distance of graphite. The results in Fig. 1 indicate that the radial deformations of SWNTs with $D < 2.1$ nm [32], slightly thinner than the (16,16) SWNT, is reversible up to large deformation unless the honeycomb structure of the tube is lost. Such a major atomic rearrangement has been predicted to occur for highly deformed tubes with $d < 0.23$ nm [25]. The large deformations of thicker tubes with $D > 2.1$ nm become irreversible and the collapsed state is stabilized under ambient pressure, which corresponds to the local minimum of $\Delta E$ as a function of $X$ (Fig. 2). The collapsed armchair (21,21) SWNT identified by Giusca et al. [26] in their STM measurements happened to be such a thick tube. Otherwise, the flattened tube under AFM tip would have inflated and returned back to the circular one on removing the tip. The predicted cross-sectional shapes of the collapsed tubes are peanut-like with $d \approx 0.32$ nm, slightly smaller than the interlayer separation of graphite (0.34 nm), irrespective of tube size.

We also performed structural optimization to check
FIG. 2: Cross-sectional atomic structures of the collapsed (21,21) SWNT with (red circles) and without (black circles) geometrical optimization: The latter corresponds to an ideal mapping of graphene onto the circumferential face of the deformed cross section as shown in Fig. 1.

the stability of the collapsed (21,21) tube whose cross-sectional shape and atomic configuration were predicted by using the continuum model and ideal mapping of graphene. The optimization was made by the DFT calculations in the local density approximation (LDA), which underlies the semiempirical method used here [12], starting from the ideal atomic configurations. The details of these DFT calculations are given in the next section. The conjugate gradient method was used in the atomic relaxations within the accuracy that the residual forces acting on all atoms decrease below 0.01 eV/A. Figure 2 shows the optimized cross-sectional structure and its comparison to the ideal one. We find that both shapes are quite similar to each other and the relaxation of each atom is also minimal, suggesting the validity and usefulness of the model calculations. The geometrical optimizations are generally irrelevant for thick SWNTs, typically those with \( D > 2 \) nm [27, 39]. The present result indicates that this is also true for highly deformed such tubes. As we show later, the effect of structural optimization on the electronic structure is also minimal. At this stage, we note that the results in Fig. 1 imply that (21,21) SWNTs with small deformations \( (X < 0.55) \) are not stabilized without external stress. In fact, if we perform structural optimization for such a tube without external stress, it would be relaxed to the circular one. We actually confirmed such a relaxation of the racetrack-like shape (at \( X = 0.26 \)) shown in Fig. 1. The presumed hydrostatic pressure for maintaining such deformations of (21,21) SWNTs in reversible regime can be estimated to be 0.25-0.30 GPa using Eq. (2).

III. ELECTRONIC STRUCTURES OF DEFORMED (21,21) SWNT

In the electronic-structure calculations of deformed SWNTs we assumed atomic configuration obtained by the conformal mapping of carbon atoms on the deformed tube surface, which was predicted using the method described in the previous section. Figure 2 (black points) shows an example of such atomic configurations. This configuration has also been assumed in testing the validity of the simple semiempirical method used to calculate deformation energy [12]. The DFT electronic-structure calculations were performed using the VASP code [33]. In these calculations we employed the LDA with the exchange-correlation energy functional of Ceperley and Alder[34] as parametrized by Perdew and Zunger[35] and the projector-augmented wave (PAW) method [36]. The k-space integration was made using the Monkhorst-Pack method[37] with the \( k \)-points in the irreducible Brillouin zone generated from \( 1 \times 1 \times 9 \) mesh. To simulate an individual SWNT, we used a large super-cell structure in the plane perpendicular to the tube axis, in which the minimum distance between tubes in neighboring cells is larger than 1 nm, about three times the graphite interlayer distance. The cutoff energy of 500 eV was used in the plane-wave expansion.

We considered an armchair (21,21) SWNT, which is the tube identified by Giusca et al. [26] in their STM measurements on the flattened tube. Figure 3 shows the results for the circular and radially deformed tubes with ideal atomic configurations without structural optimization. The armchair SWNTs with circular cross section are known to be real metals [4] but we find a tiny band gap \( (E_g < 1 \) meV) at \( k_F \approx \left( \frac{2}{3}(\pi/\alpha) \right) \), where \( \alpha \) is the lattice constant of the honeycomb structure. This gap can be interpreted as an artifact due to the finiteness of the supercell used in our plane-wave DFT calculations. Although we used a sufficiently large supercell, the tube-tube interaction is not completely negligible and our calculations may be viewed as those for a lose bundles. In fact, the tube-tube interaction in bundles of armchair SWNTs induces a pseudogap in the density of states [38]. This “metallic” nature remains unchanged and no tendency of the band gap opening is found in the flattened tube (at \( X = 0.26 \)). This deformation of the tube is substantial but the distance between opposing faces is quite large \( (d \approx 1.40 \) nm). This metallic nature also remains even for a highly deformed tube with \( d \sim 0.5 \) nm, which is the tube just before collapsing spontaneously \( (X = 0.55) \). But, the band gap of \( E_g \approx 62 \) meV opens in the collapsed tube with \( d = 0.32 \) nm at \( X = 0.63 \), indicative of semiconducting nature. We note that only one mirror-symmetry plane, which includes tube axis and two edge points, out of 21 such planes in the circular (21,21) tube survives in all the deformations considered in the present analyses. These results imply that a broken symmetry is necessary, but not sufficient for the band gap opening, in accordance with the previous analyses for much thinner armchair SWNTs [25]. The effect of the structural optimization on the electronic structure was found to be minimal as demonstrated in Fig. 4 for the collapsed tube, which might have been expected from the...
results in Fig. 2. In fact, the band gap virtually remains unchanged by the structural optimization, although the Fermi point slightly moves towards lower $k$, which is probably due to a small change in electron transfers along the circumference [13]. We also note that no symmetry constraint was imposed in the structural optimization, but the same symmetry survived in the optimized structure. Summarizing all these results, we may conclude that the deformed cross-sectional shape alone, including its symmetry breaking, cannot induce appreciable band gap, but the distance between flattened faces is responsible for the substantial band-gap opening.

The predicted band gap opening of the collapsed (21,21) SWNTs is in contradiction to the STS measurements by Giusca et al. [26], which shows that the collapsed (21,21) tube is metallic as a whole. In more detail, they observed in their experiments that the flat region shows a metallic nature with finite local DOS at the Fermi level, while the band gap opens in the edge region at either side of the flattened tube, indicative of a semiconducting nature. These observations for the armchair SWNT are in marked contrast to the implications found for the zigzag SWNTs [18, 19, 21], which show the reversed natures of the flat and edge regions. This difference between the armchair and zigzag SWNTs may arise from the different natures of the band-edge state near the Fermi point. Here, we note that in the experiments by Giusca et al. the tube was placed on the gold (Au) substrate and collapsed by AFM tip. The contradiction between our predictions and experiments might arise from the effect of metallic substrate used in the experiments. In fact, the work function of Au is $\sim 5.1$ eV [40, 41] while that of thick SWNTs ($D > 1$nm) is 4.5-4.7 eV [42–44], suggesting that the absolute Fermi energy is higher by $\sim 0.5$ eV in the tube and the charge transfer from the tube to substrate could occur. If this charge transfer actually occurs, its effect may be that the top of the valence band of the tube is unoccupied and metallic nature is expected within the rigid band approximation. The situation also could be similar to a heavy hole doping of the tube. However, this picture is probably much too simple to explain whole story and we have to clarify the electronic-structure change of the combined system of tube and substrate before drawing a definite picture. We also note that the cross-sectional shape of the collapsed tube predicted in our calculations could be different from that in the experiments. However, such a difference is unlikely to cause a major difference in the electronic structure in view of the present and previous [25] results, which indicate that band gap opening is induced by the interaction between opposing flattened faces.

IV. CONCLUSIONS

We have elucidated the band gap opening by radial deformation of an armchair (21,21) SWNT by assuming a realistic cross-sectional shape of the collapsed tube. The semiempirical method used to predict radial deformations of large SWNTs was found to be quite useful. We found that the collapsed (21,21) tube is a semiconductor with a small energy gap of 62 meV, which can be interpreted as arising from the interaction between atoms on the opposing faces as in the case of much thinner armchair SWNTs [25]. Our prediction is in contradiction to the recent STS measurements [26] and a possible explanation for this discrepancy is that the charge transfer from the tube to substrate could occur in the experimental situation. The present analyses imply that the substrate, on which tubes are placed and deformed, plays an important role in determining the electronic properties of the tubes, and the choice of substrate is crucial in experiments and device applications.

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[32] Originally, this critical size of SWNTs has been predicted to be $D = 2.5$ nm (Ref. 12). This value is reduced to $D = 2.1$ nm with the use of the atom-atom interaction potential obtained by the revised semiempirical analysis of the interlayer binding of graphite (Ref. 29).