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First-principles study of band-gap change in deformed nanotubes

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The effects of cross-sectional deformation and bending on the electronic structures of single-wall carbon nanotubes (SWNTs) are examined. Upon increasing the deformation, semiconducting SWNTs undergo semiconductor-metal transition, and the conduction band and valence band show asymmetric response to the deformation. The metallic tubes' electronic structures are relatively insensitive to similar mechanical deformation. Using the properties of deformed nanotubes, we propose a conceptual design of SWNT-based single-electron quantum-well devices. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2067697]

Carbon nanotubes are molecular wires with a number of exceptional electronic and mechanical properties[1] which made them one of the promising candidates for novel nanoelectronic applications. Substantial efforts have been devoted to controlling electronic properties of SWNTs by ways of mechanical deformation. It has been experimentally demonstrated that carbon nanotubes are extremely flexible[2] and kinks (from defects in the hexagonal network[3]) or bends (from external mechanical duress[4,5]) in nanotubes may lend to novel quantum phenomena. Recent experiments have shown that an atomic force microscope tip can be used to bend a SWNT at two different locations to transform it into a room-temperature single-electron transistor,[6] demonstrating the strong connection between mechanical deformation and local electronic structure change. There are recent computational studies on the effects of deformation on the electronic structures of particular chirality nanotubes,[5,7] but a systematic exploration on such effects in the context of realistic nanotube device is still lacking.

We report here a systematic study of the band-gap variation as a function of uniform cross-sectional deformation for a variety of tubes, employing first-principles density functional theory (DFT) calculations. It is found that band gaps of semiconducting tubes gradually close under increasing cross-sectional deformation. More importantly, the response of conduction-band edges and valence-band edges to the mechanical deformation shows asymmetric behavior. Band-gap changes in metallic tubes are less pronounced compared to the semiconducting cases. Based on the DFT calculation results, we propose the design of a nanoscale quantum-well device using bent nanotubes. Using sp^3-orbital tight binding (TB), we have shown that the bent regions of semiconducting nanotubes induce cross-sectional deformations, which lead to band offsets in the conduction band and quantum confinements for *electrons*. Strong localization in the wave function is observed in bent semiconducting tubes.

We first discuss first-principles calculation results for the effects of uniform cross-sectional deformations on band gaps in infinitely long tubes. DFT electronic structure calculations with local density approximation (LDA) were performed on a variety of uniformly flattened tubes. Even though DFT/LDA has the well-known problem of band-gap underestimation, it is still capable of capturing qualitatively important aspects of nanotube electronic structure, such as curvature-induced band-gap closure[8] and work function change.[9] The calculation was done using Vienna Ab-initio Simulation Package (VASP).[10] 30 k points and an orthorhombic unit cell with dimensions $(30\times30\times4.26)$ Å^3 were used. Kohn-Sham single-electron wavefunctions were expanded by 285768 planewaves with an energy cutoff of 286.6 eV. The cross-sectional deformation was quantified by the dimensionless parameter $\eta=(d_0-d)/d_0$, where d_0 is the diameter of the undeformed tube, and d is the minor diameter of the deformed tube [Fig. 1(a)]. The geometries of deformed tubes were relaxed in VASP by constraining the tubes to lie between two planes separated by a distance d.

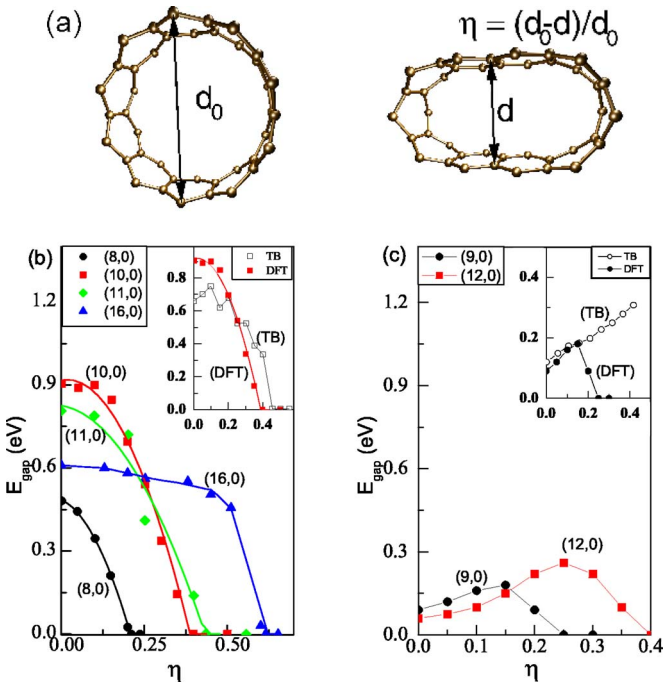

FIG. 1. (a) Displays a unit cell of an undeformed and a flattened (η=0.5) (10,0) carbon nanotube. Parts (b) and (c) display the DFT/LDA predictions of the band gap as a function of cross-sectional flattening for a variety of semiconducting and metallic SWNTs. The insets in (b) and (c) compare the sp^3 TB and DFT results for (10,0) and (9,0) tubes, respectively.

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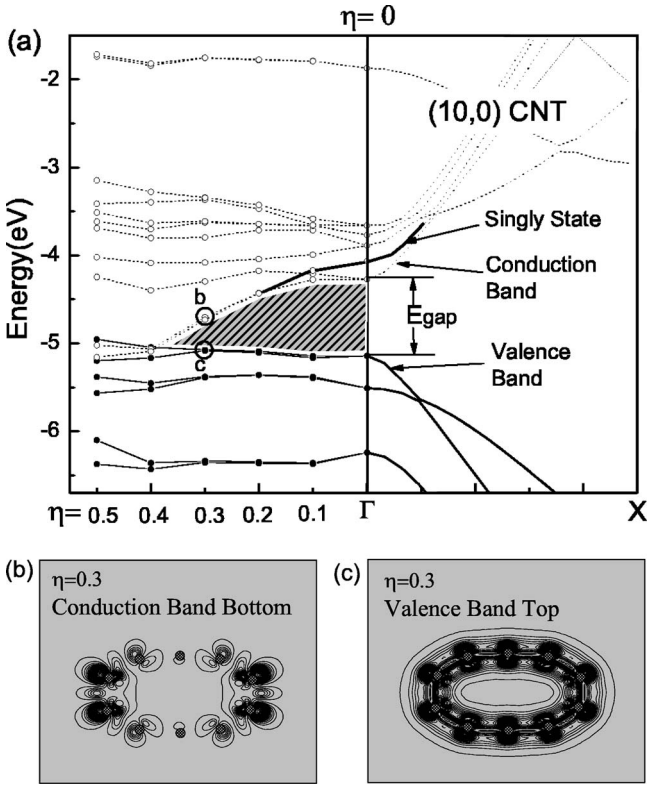

FIG. 2. (a) Bandstructure of an undeformed (10,0) tube (right panel) and the corresponding energy levels at Γ point for tubes under different deformation η (left panel). Vacuum level is set to zero. We trace the singly degenerate state around the center of Brillouin zone as well as its lowering at small η as a guide for the eyes. The band gap closes at approximately $\eta=0.38$. (b) Charge density associated with conduction-band bottom is concentrated on atoms at high curvature regions. (c) Charge density associated with valence-band top is uniformed distributed across the whole nanotube.

Variations of the band gaps as a function of η for various tubes are displayed in Fig. 1. The DFT/LDA results for semiconducting tubes [Fig. 1(b)] clearly demonstrate the existence of a semiconductor-metal transition, consistent with other calculations.[7] Note that in all cases, the band gap is reduced to zero at $d \approx 0.48$ nm indicating that regions of maximal curvature could be the major determinants of the electronic structure of the flattened semiconducting tubes. Examining the (n,0) metallic tubes [Fig. 1(c)], we see that the hybridization-induced secondary band gaps[11] initially increase under moderate degrees of flattening, followed by closing at higher levels of deformation. This band-gap closing for both semiconducting and metallic nanotubes is driven by the lowering of the singly degenerate conduction-band state.[8]

For semiconducting nanotubes, band structure analysis reveals the detailed mechanism driving the observed behavior of the band gap closing. Figure 2(a) displays the bandstructure for an undeformed (10,0) SWNT as well as the evolution of energy levels at Γ point upon increasing cross-sectional deformation. All of the energy levels are drawn with respect to vacuum level which is set to zero in all cases.[9] In the undeformed (10,0) nanotube, both the conduction-band bottom and valence-band top states are doubly degenerate and show π-orbital characteristic. Upon deformation, the doubly degenerate conduction band splits into two bands due to lower symmetry. One of the them and the initially singly degenerate state [Fig. 2(a)] are driven down in energy due to increased $\sigma^* - \pi^*$ hybridization.[8] These two bands are continuously lowered down in energy upon increasing cross-sectional deformation and remain almost degenerate for η up to 0.4, beyond which the two bands split and cross the valence band, respectively, transforming the semiconducting tube into a metallic one. The valence band of the deformed nanotube shows little change in energy under moderate deformations. Figures 2(b) and 2(c) show the charge density associated with the conduction-band bottom and valence-band top at $\eta=0.3$. The charge density associated with conduction-band bottom is localized on atoms in the regions of maximal curvature while the charge density associated with valence-band top is uniformly distributed across the whole tube and retains its π characteristic. This confirms that: (1) Most of the electronic structure change takes place in the conduction band and that (2) regions of maximal curvature are primarily responsible for the observed band gap change in deformed nanotubes.

Metallic tubes also exhibit band-gap variation upon cross-sectional deformations, but the magnitude of induced band-gap change is substantially smaller compared to the semiconducting case at similar degree of flattening. As a benchmark, real-space sp^3-orbital TB calculations using Harrison's universal parameterization[12] were also performed on both kinds of tubes. sp^3 TB correctly captures closing of the band gap in the semiconducting case [Fig. 1(b) inset] and the initial opening of the band gap in metallic case [Fig. 1(c) inset]. The re-closing of the gap under higher deformation in the metallic case, which is due to lowering of the singly degenerate state,[11] is not reproduced within sp^3-orbital TB. This indicates that the sp^3 TB model overestimates the band-gap opening under a higher level of deformation in metallic tubes and may lead to an overestimation of wave function localization. Table I summarizes the results of different approximations applied to the prediction of nanotube band-gap change under cross-sectional deformation.

Our first-principles calculations indicate that: (1) Semiconducting tubes are more susceptible to deformation-induced band-gap change and (2) *electrons* and *holes* would respond differently to cross-sectional deformation. To utilize such deformation-induced band-gap change in the creation of quantum electronic devices, we have studied the semiconducting tube geometry displayed in Fig. 3(a). The tube consists of 44 unit (10,0) cells and was created by inducing two bends of 45° about the same axis. The geometry was relaxed using the Tersoff–Brenner empirical potential.[13] We found

TABLE I. Band gaps of uniformly deformed nanotubes predicted by different models.

$(n,0)$ tubes	DFT/LDA	sp^3-orbital TB	π-orbital TB
Semiconducting	E_g closes upon deformation	E_g closes upon deformation	qualitatively predicts closing of E_g
Metallic	E_g increases upon initial deformation	E_g increases upon initial deformation	$E_g=0$ under all deformations
	E_g closes at higher level of deformation	E_g continue increasing at higher level of deformation	

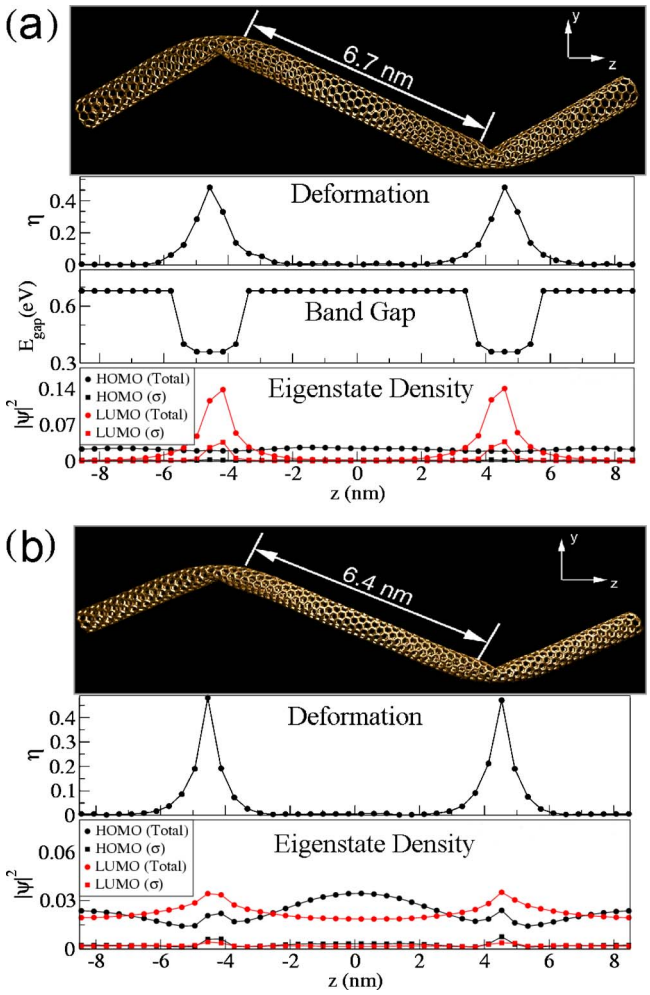

FIG. 3. The geometry of tubes used to create nanotube-based quantum wells. The two bending regions are separated by an undeformed segment 6.7 nm long in the (10,0) tube (a) and 6.4 nm long in the (9,0) tube (b).

the outer sections of the tube were under ~6% tensile strain while the inner portions of the tube were under ~4% compressive strain, which was sufficient to induce buckling in the inner portion of the tube, but was not sufficient to induce Stone–Wales[14] transformations. At room temperature, the bent nanotube is metastable, and returns to the undeformed configuration when the bending force is removed.

We have investigated the electronic structure of the doubly bent nanotube using the sp^3-orbital TB model. Performing a local density of states analysis on the doubly bent (10,0) semiconducting tube, we found the band-gap variation displayed in Fig. 3(a). The band gap shows sharp decreases centered on the two bends, which is consistent with the prediction based on uniform cross-sectional deformation. An examination of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states shows that while the HOMO is relatively insensitive to the bending deformation, the LUMO shows strong localization at kink regions. This is consistent with the asymmetric electronic structure change in semiconducting tubes under uniform deformation from the DFT simulations. In addition to the LUMO state, three other states were also found to be localized to the bent regions, with almost degenerate energy levels. Viewing this doubly bent nanotube as a pair of quantum wells for *electrons*, we find that the four well states are highly degenerate and show exceptionally good confinement within the well regions. Such localization in a wave function is not observed for *holes*.

The response of metallic tubes to the double bending is considerably different. Figure 3(b) displays wave functions of a similar bent (9,0) tube. Neither HOMO or LUMO state show strong localization. The weaker localization of the metallic state can be explained by noting that these states are dominated by the strongly nonlocal π-bond network characteristic of metallic tubes and deformations in bent regions are not sufficient to produce a significant change in the band gap as in the semiconducting case. An examination of a (12,0) nanotube deformed in a similar manner revealed the same pattern in the HOMO and LUMO states.

These results indicate that semiconducting and metallic tubes respond very differently to similar mechanical deformations. Doubly bent semiconducting tubes form a pair of quantum wells for electrons, but similarly bent metallic tubes would show only weak localization. There are previous experiments on deformed metallic tubes, indicating mechanically induced electronic property changes.[4,6] Based on our simulations, however, doubly bent semiconducting tubes show more pronounced quantum effects than metallic tubes.

In conclusion, we have presented a systematic study on the effects of cross-sectional deformation on the nanotube band gap. In semiconducting tubes, the primary effect of cross-sectional deformation is the lowering of the conduction-band bottom. The magnitude of the band-gap change in metallic tubes is smaller under similar degrees of flattening. We have proposed and investigated the possibility of using a doubly bent SWNT as quantum-well device. The simplicity of the design and the exceptional properties of the resulting wells demonstrate the potential of the proposed structure as a means of creating robust nanotube-based electronic devices.

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