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Structural and electronic properties of carbon nanotubes under hydrostatic pressures*

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We studied the structural and electronic properties of carbon nanotubes under hydrostatic pressures based on molecular dynamics simulations and first principles band structure calculations. It is found that carbon nanotubes experience a hard-to-soft transition as external pressure increases. The bulk modulus of soft phase is two orders of magnitude smaller than that of hard phase. The band structure calculations show that band gap of (10, 0) nanotube increases with the increase of pressure at low pressures. Above a critical pressure (5.70GPa), band gap of (10, 0) nanotube drops rapidly and becomes zero at 6.62GPa. Moreover, the calculated charge density shows that a large pressure can induce an sp^2-to-sp^3 bonding transition, which is confirmed by recent experiments on deformed carbon nanotubes.

Keywords: carbon nanotubes, hydrostatic pressure, molecular dynamics
PACC: 7125X, 7115Q, 7115M

1. Introduction

Carbon nanotubes have attracted much attention due to their unique structural, mechanical and electronic properties.[1−10] Similar to the graphite, single-walled carbon nanotubes (SWCNs) exhibit high mechanical flexibility along the axial direction and bending flexibility.[11−14] Molecular dynamics simulations indicate that SWCNs can survive under extreme loading without bond breaking.[15] Moreover, an SWCN can be metallic or semiconducting or semimetallic, depending on its diameter and chirality.[16−18] The mechanical and electronic properties of SWCNs have led them to serve as scanning probes, electron field emission sources, and nanoelectronic devices.[19]

It has been shown that electronic properties of SWCNs display a high sensitivity to structural deformation, which provides a useful mechanism for SWCN as an ideal candidate for nanoelectromechanical applications.[20−24] Theoretical studies have shown that external pressures can change the geometrical structures and electronic band structures of SWCNs.[25−29] Furthermore, the pressure-induced transitions of structural and electronic properties, such as semiconductor–metal transitions, have been observed experimentally. For example, recent experiments have indicated that external pressures can result in abrupt transitions of resistance and magnetoresistance of SWCNs.[30,31] In order to fully explore the relation between structural and electronic characteristics, a thorough understanding of structural and electronic properties of SWCNs is necessary. In this paper, we perform the state-of-the-art first-principles and classical molecular dynamics (MD) simulations to elucidate this issue.

2. Model and method

We first perform the constant-pressure MD[28,32] to obtain the optimized structures of (10, 10) and (10, 0) SWCNs under hydrostatic pressures. In MD simulations, the SWCNs are constructed within a tetragonal supercell with lattice constants of a, b, c. The

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values of lattice parameter c are taken to be $5c_z$ and $5c_a$ for zigzag and armchair carbon nanotubes, where c_z and c_a are one-dimensional lattice parameters of zigzag and armchair nanotubes respectively. The intertube separation is 2.4nm so that the tube–tube interaction is negligibly small. The interaction between carbon atoms is described by the Tersoff–Branner many-body potential.[33] After the optimized structures have been obtained, we calculate band structures and electronic density of states within the VASP package in the generalized gradient approximation (GGA)[34,35] We use a cutoff energy of 300eV for the plane-wave basis set in VASP calculations.

3. Results and discussion

Figure 1 shows the curves for volume V of (10, 10) and (10, 0) SWCNs versus pressure P. At low pressures, the cross-section of (10, 10) SWCN remains a circular shape with a bit reduction in volume compared with that under ambient condition. As the pressure increases, the cross section of the (10, 10) tube

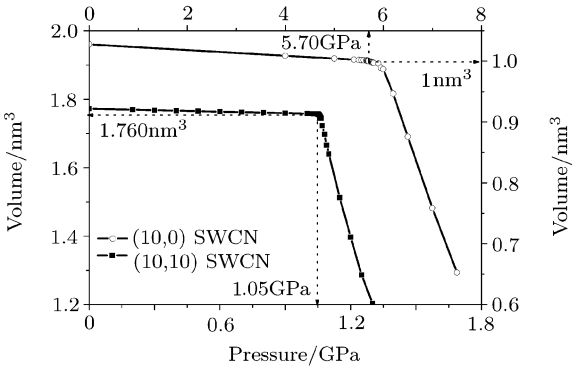


Fig.1. The curves for volume versus pressure for (10, 0) (open circles) and (10, 10) (solid squares) carbon nanotubes at 300K.

transforms from a circle into an ellipse, and then to a dumbbell. The volume of (10, 10) tube decreases slowly below 1.05GPa while drops sharply as the pressure exceeds 1.05GPa. An analogous variation of V can also be found for the (10, 0) SWCN. In this paper, the pressure under which such a structural transition takes place is called the critical pressure. The critical pressures of (10, 10) and (10, 0) SWCNs are 1.05 and 5.70GPa respectively. We therefore conclude that (10, 10) and (10, 0) SWCNs have experienced a hard-to-soft transition as the external pressure increases. The SWCN below the critical pressure belongs to the hard phase while the tube above the critical pressure is soft. The calculated bulk modulus $B = -V\dfrac{\partial P}{\partial V}$ of hard phase of (10, 10) SWCN is 115.56GPa at P=1.0GPa while that of soft phase is 0.55GPa at P=1.25GPa. Similar to (10, 10) SWCN, the hard phase of (10, 0) SWCN with a bulk modulus of 205.3GPa at P=4.0GPa transforms into the soft phase with a bulk modulus of 4.57GPa at P=6.5GPa. The bulk modulus of hard phase of (10, 0) SWCN we obtained is in good agreement with the *ab initio* results by Reich *et al.*[7] Our results imply that the critical pressure of the hard-to-soft transition is diameter-dependent.[26]

We next turn to the calculation of electronic band gap E_g of (10, 0) SWCN and demonstrate how the band gap varies with external pressure. The pressure dependence of band gap of (10, 0) SWCN is shown in Fig.2. At P=0 GPa, the calculated band gap is 0.8 eV, which is consistent with those calculated by the density functional and the tight binding theory.[36−38]

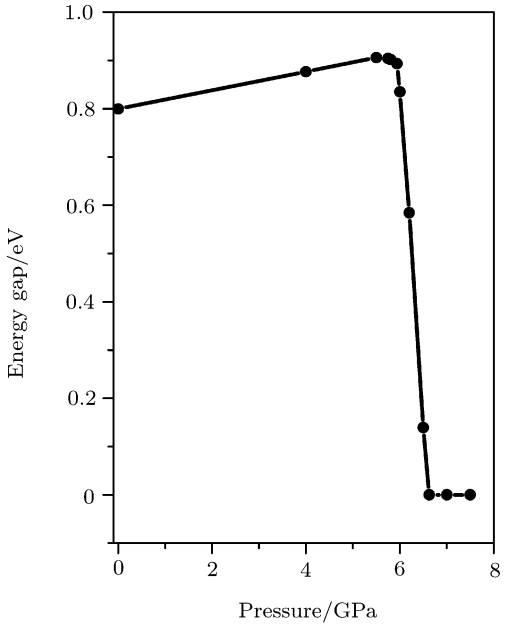


Fig.2. The pressure dependence of band gap of (10, 0) carbon nanotube.

Below the critical pressure, the band gap increases slowly with the increase of pressure and the slope $\dfrac{\Delta E_g}{\Delta P}$ is only 0.019eV/GPa. The increase of band gap can be understood from tight binding theory,[1] which predicts that band gap E_g is proportional to overlap integral t. Under a hydrostatic pressure, the distance of C–C bond is shortened, thereby the orbital hybridization is strengthened. As the pressure is above the critical pressure, the band gap decreases rapidly and eventually the semiconducting tube becomes a metal-

lic tube at 6.62GPa. The semiconductor–metal transition is closely related to the downshift of a single degenerate state under the hydrostatic pressure.[36] Furthermore, slope $\frac{\Delta E_g}{\Delta P}$ between critical pressure and 6.62GPa is –1.43eV/GPa. Thus, we conclude that band gap of (10, 0) SWCN experiences a transition from slowly-rise to rapidly-drop and a semiconductor–metal transition under the hydrostatic pressure. More importantly, the pressure for the transition of band gap from slowly-rise to rapidly-drop is nearly the same as the critical pressure. Such a phenomenon indicates that the abrupt transitions of resistance and magnetoresistance in experiment[30,31] may be associated with the transition of geometrical structures.

Figure 3 shows the charge densities near the Fermi level (E_F–1.0eV< E < E_F+1.0eV) of (10, 10) and (10, 0) SWCNs. For an undeformed (10, 10) SWCN, the charge densities have equal weights inside and outside the tube because they are mostly π or π^* derived. However, the fraction of wave functions localized outside the (10, 0) tube is larger than that inside the tube because of the well-known $\sigma^* - \pi^*$ rehybridization of small diameter SWCNs. As the pressure increases, the SWCN is distorted greatly and can be divided into two

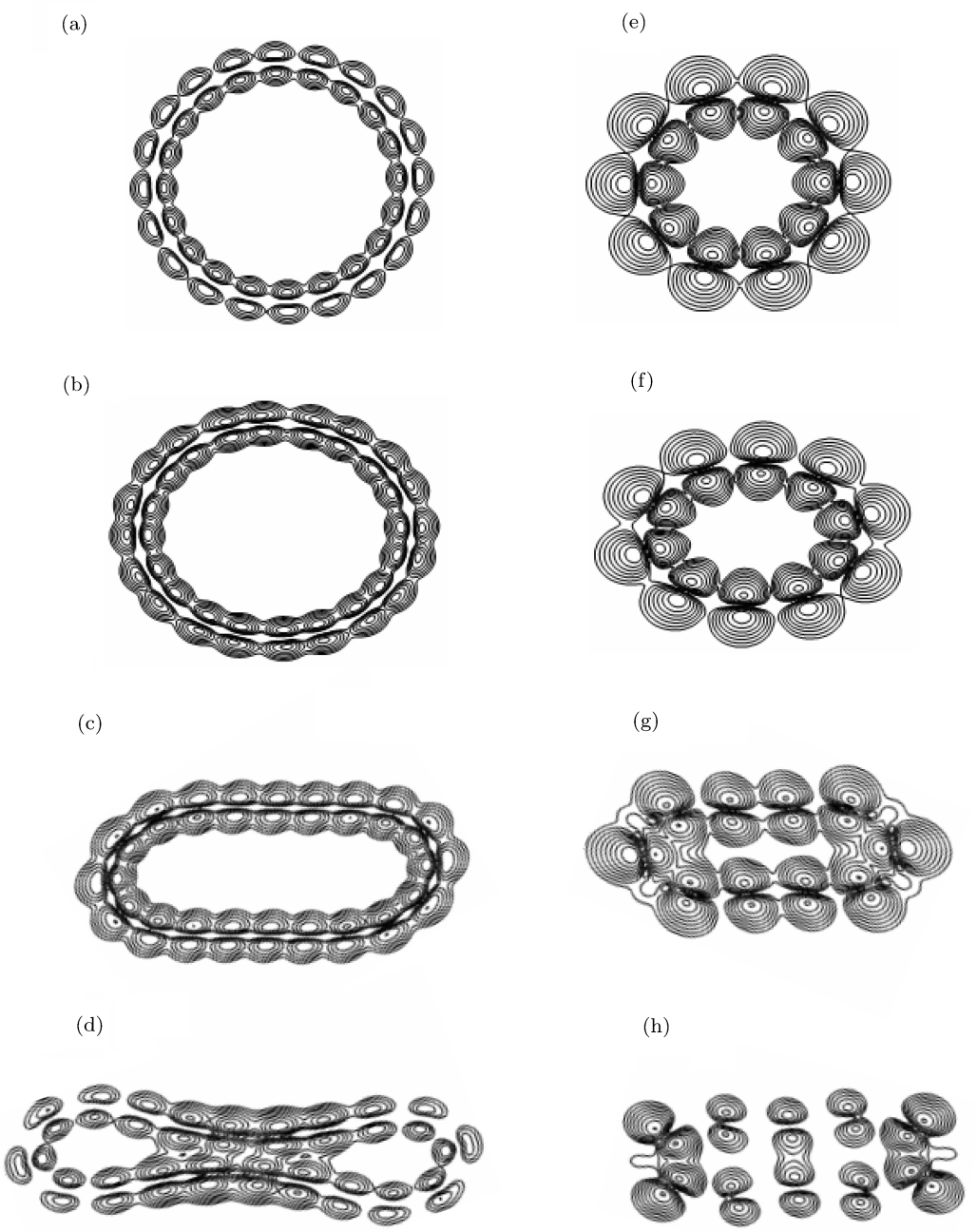


Fig.3. Contours of charge densities around the Fermi level in (10, 10) (left column) and (10, 0) (right column) carbon nanotubes under pressures: 0.0 (a), 1.05 (b), 1.2 (c), 2.0 (d), 0.0 (e), 5.7 (f), 7.0 (g) and 7.5GPa (h).

zones, i.e. the flattened and curved zones. In the flattened zone, the charge density of (10, 10) tube below the critical pressure presents almost equal weights inside and outside the tube. Above the critical pressure (see Figs.3(d) and 3(h)), the p orbitals of atoms in the facing layers are overlapped with each other in the flattened zones. In addition, the sp^3-like bonding configuration can be seen in the curved zone due to large structural deformations. The semiconductor–metal transition mentioned above may be related to the sp^3-like bonding configuration in the curved zone.

To give further insight into the bonding configuration, we show the projected density of states (PDOS) for atoms in the flattened zone (solid lines) and curved zone (dotted lines). The results, shown in Fig.4, give the PDOS of (10, 10) SWCN in the vicinity of Fermi level at pressures: 0.0, 1.05, 1.2 and 2.0GPa, separately. From Fig.4(a), it can be seen that the undeformed (10, 10) SWCN is metallic. The PDOS of flattened zone is the same as that of curved zone in the whole energy range, which is attributed to the perfect symmetry of SWCN. This behaviour holds even when the SWCN is pressed under low hydrostatic pressures. This fact indicates that the sp^2 bonding configuration is not broken greatly by low pressures. As the pressure becomes larger than the critical pressure, several new peaks (denoted by dashed arrows) appear around the Fermi level in the PDOS for atoms in the curved zone. These new peaks arise from the sp^3 bonding configuration of atoms in the curved zone. Above behaviour gives a clear picture of how the external pressure brings about a sp^2-to-sp^3 bonding transition, which has been confirmed by recent experiment on bent carbon nanotube.[39] In addition, there is a sharp peak, indicated by a solid arrow in Fig.4(d), in PDOS for atoms in the flattened zone. This peak may be ascribed to the strong covalent interaction between atoms of two facing layers.

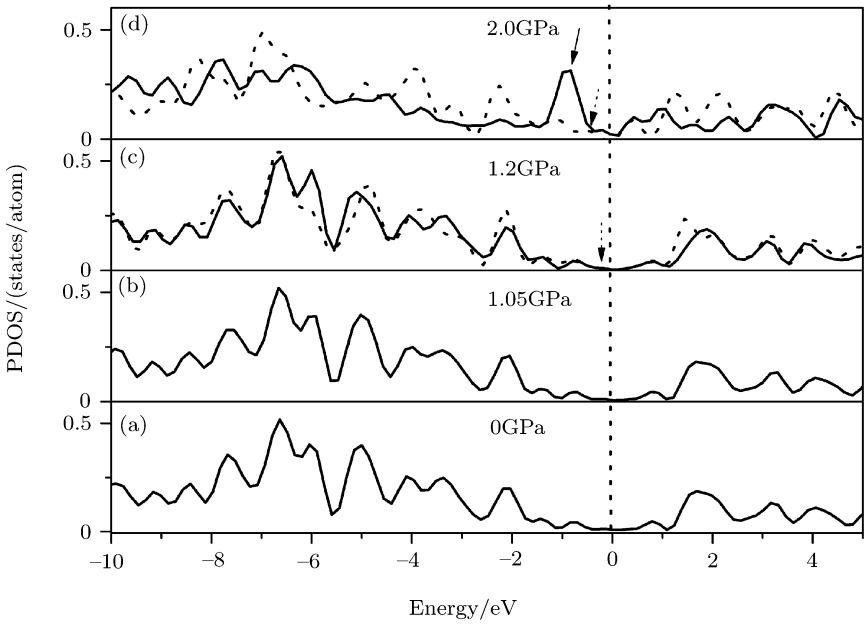


Fig.4. Projected densities of states of (10, 10) nanotube for atoms in the flattened (solid line) and curved (dotted line) zones under pressures: 0 (a), 1.05 (b), 1.2 (c), and 2.0GPa (d).

The curves for PDOS of (10, 0) SWCN for atoms in the flattened and curved zones are shown in Fig.5. One can see that (10, 0) tube has a band gap of 0.8eV near the Fermi level. Similar to the (10, 10) SWCN, the (10, 0) SWCN presents a number of new peaks in the PDOS for atoms in the curved zone. As the pressure increases, these new peaks shift toward the Fermi level, indicating that the sp^3 bonding configuration becomes a dominant one for SWCNs under the hydrostatic pressure. Generally speaking, electronic transport of SWCNs is determined mainly by the density of states in the vicinity of the Fermi level. Consequently, one can tune the electronic transport properties of SWCNs by applying an external pressure. The theoretical results reported here should be of concern in understanding the pressure-induced transition of structural and electronic properties of carbon nanotube in the future.

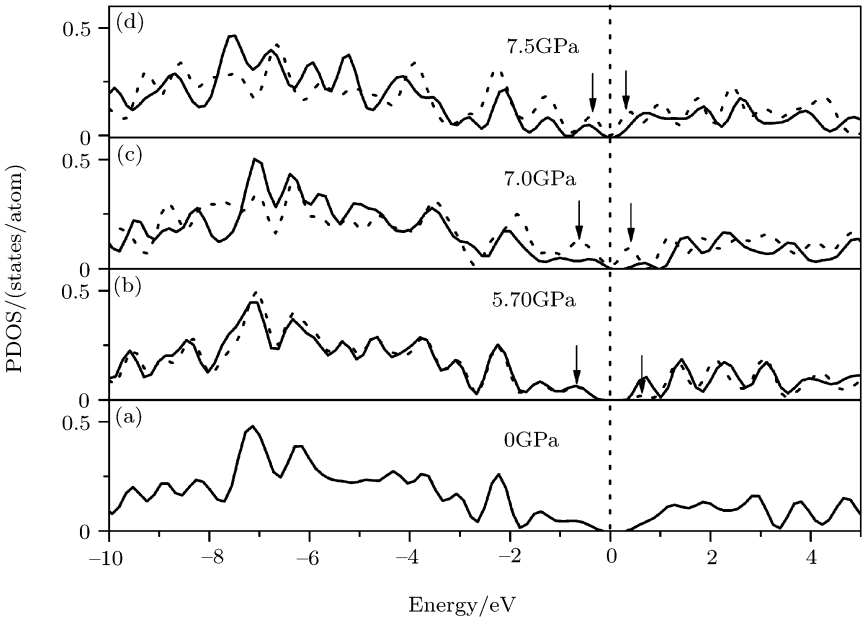


Fig.5. Projected densities of states of (10, 0) nanotube for atoms in the flattened (solid line) and curved (dotted line) zones under pressures: 0 (a), 5.7 (b), 7.0 (c), and 7.5GPa (d).

4. Conclusion

In this paper, we have studied the geometrical structures and electronic properties of individual SWCN under hydrostatic pressures. As pressure increases, (10, 0) and (10, 10) SWCNs experience a hard-to-soft transition at 5.7 and 1.05GPa, respectively. The bulk modulus of soft phase is much smaller than that of hard phase. The band gap of (10, 0) SWCN first increases with pressure at low pressures, and then decreases rapidly above the critical pressure, finally becomes zero at 6.62GPa. The slope $\frac{\Delta E_{\mathrm{g}}}{\Delta P}$ is 0.019eV/GPa below the critical pressure and –1.427 eV/GPa between the critical pressure and 6.62GPa. Moreover, a large pressure can change the charge densities in the flattened and curved zones greatly. Especially, a transition from sp^2 to sp^3 bonding configurations can be clearly seen in the projected density of states.

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