Band-gap modification by radial deformation in C, BN, and BC_3 nanotubes

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Abstract We investigate the band-gap modification by collapsing deformation in C, BN, and BC_3 nanotubes through first-principles pseudopotential calculations. Semiconductor-metal transitions occur when zigzag C and armchair BC_3 nanotubes undergo collapsing deformation, while in zigzag BN tubes, a variation of band gaps from 5 to 2 eV is found. On the other hand, the band gaps of armchair BN and zigzag BC_3 nanotubes are insensitive to collapsing deformation. Our findings can be used to design new nanotube-based functional devices.

1 Introduction

It is well known that C nanotubes exhibit a variety of electronic properties ranging from metals to small- and large-gap semiconductors [1]. It was recently shown that the electronic structure of C nanotubes can be modified by radial deformations [2,3]. Semiconducting C nanotubes turn into metals under collapsing deformations, while deformations open the gaps of metallic armchair tubes if all mirror symmetries are broken. In composite $B_xC_yN_z$ nanotubes, the band gaps are determined by alloy compositions [4]. Because of the ionic bonds, BN nanotubes have the largest band gap of about 5 eV, almost independent of tube diameter and helicity [5]. Since the increase of C composition reduces the ionic characteristics of bonds, BC_3 tubes have small band gaps of about 0.5 eV [6].

In this work, we study the electronic structure of collapsed C, BN, and BC_3 nanotubes based on the first-principles pseudopotential method. We demonstrate that collapsing deformations severely modify the band gaps of the nanotubes, which allow tuning of band gaps for device applications.

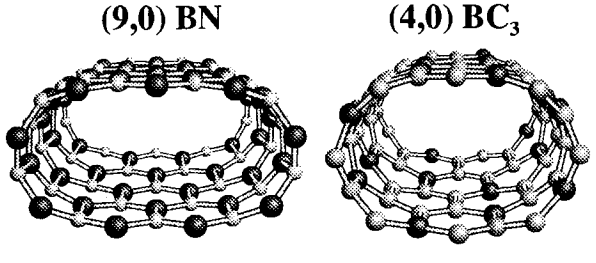

Fig. 1 Ball-and-stick models for collapsed (9,0) BN and (4,0) BC_3 nanotubes. The opposing layer-layer distances are 4.5 and 5.0 Å, respectively.

2 Calculational method

We perform extensive first-principles pseudopotential [7] calculations within the local-density-functional approximation (LDA) for collapsed C, BN, and BC_3 nanotubes. To obtain collapsed single-wall nanotubes, as depicted in Fig. 1, we calculate the Hellmann-Feynman forces acting on ions and use the quasi-Newton method [8] to optimize the geometries of BN and BC_3 tubes. For C nanotubes, we use Tersoff's empirical potential [9]. In the relaxation process, we impose a constraint that atoms are only allowed to move between two walls, the separation of which is defined as the interlayer distance d in collapsed tubes.

The total energies of nanotubes increase as the interlayer distance decreases because of the strain accumulated in the curved regions. We estimate pressures required to collapse nanotubes from the total energy vs interlayer distance curve; a pressure of about 10 GPa is needed to reduce d down to 3.4 Å.

3 Results and discussion

For the zigzag (9,0) C nanotube, the tube diameter is 7.2 Å, and the band gap is 0.09 eV in its perfect form. If this tube is flattened, the band gap gradually decreases, and is completely removed at $d = 5.3$ Å. The analysis of charge densities indicates that the band gap is closed by the lowering of the hybridized singlet state near the band gap under deformation. For the (13,0) and (18,0) C tubes with diameters of 10.5 and 14.3 Å, respectively, the hybridized singlet states are also lowered by collapsing deformation, resulting in an insulator-metal transition near $d = 5$–6 Å.

For metallic armchair C tubes, the band-gap modification follows the mirror-symmetry selection rules. An armchair tube with the rolling index (n,n) has n mirror planes containing the tube axis, with two linear bands characterized by π and π^*, which are even and odd under mirror symmetry operations. If radial deformations break all the mirror symmetries, the π and π^* states are no longer the eigenstates, and the band gap is opened by a mixing of the degenerate π and π^* bands at the Fermi level. Our LDA calculations show that the band gaps are less than 10 meV for $d > 4.0$ Å, while they increase to about 0.2 eV for further deformations. On the other hand, if one mirror symmetry is preserved under deformation, metallic conductions still exist in armchair nanotubes.

For the zigzag (9,0) BN tube, we find a reduction of the band gap from 3.5 to 2 eV as d decreases to 3.0 Å. When this tube is further collapsed to $d = 2.0$ Å, the gap is decreased to 1.0 eV. It is known that zigzag BN tubes with diameters larger than 9.5 Å have a very stable gap of about 5.5 eV [5], independent of tube diameter and helicity. Thus, we suggest that collapsing deformation allows tuning of energy gaps in the range of 5–2 eV under transverse pressure of about 10 GPa. As deformation increases, the charge densities of the minimum conduction band state are significantly overlapped in the curved regions, which lowers the minimum conduction band state, similar to zigzag C tubes. In contrast, the band gaps of armchair BN tubes are little affected by collapsing deformations. When the (5,5) BN tube is collapsed to $d = 5.0$ Å, a band gap of 4.2 eV is found, quite similar to that of the perfect tube. In this tube, we find neither a charge transfer from the flattened layers to the curved regions nor a development of the overlap of charge densities in the curved regions.

For collapsed armchair BC_3 nanotubes, flattening deformation induces a gap closure, while the gaps of zigzag tubes are quite insensitive to deformation. From the analysis of charge densities, we find that only armchair tubes exhibit the overlap of charge densities in the curved regions, thus, the band gaps are significantly modified. This distinct behavior is attributed to the different characteristics of the lowest conduction band and highest valence band states, as compared to C and BN tubes. Because the B atom has one less valence electrons, the π bands of a single BC_3 sheet are partially filled. Thus, the lowest conduction band state has π character, which is insensitive to deformation in zigzag tubes, while the top of the valence bands has σ character.

We summarize the results of calculations for the electronic structure of collapsed nanotubes in Table 1. We find that flattening deformation induces an insulator-metal transition in zigzag C and armchair BC_3 nanotubes. Based on these electronic properties, a nanotube-based quantum dot is proposed, as schematically drawn in Fig. 2(a); a semiconducting nanotube is locally flattened, and the collapsed region with metallic conduction behaves as a quantum dot. When zigzag BN nanotubes with large gaps are deformed, an optical device like Fig. 2(b) is expected.

Table 1 Band-gap modifications by flattening deformations in C, BN, and BC_3 nanotubes

tube	type	modification
C	zigzag	insulator-metal transition 0.5 eV $\Longrightarrow$ 0 eV
	armchair	metal-insulator transition 0 eV $\Longrightarrow$ 0.2 eV
BN	zigzag	large-gap to small-gap transition 5 eV $\Longrightarrow$ 2 eV
	armchair	stable gap of about 5 eV
BC_3	zigzag	stable gap of about 0.5 eV
	armchair	insulator-metal transition 0.5 eV $\Longrightarrow$ 0 eV

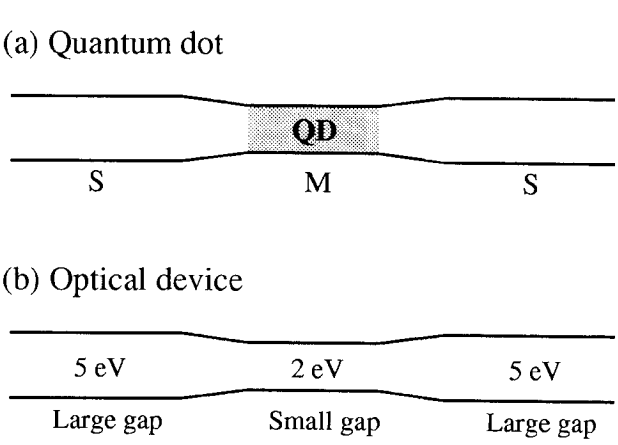

Fig. 2 Nanotube-based functional devices utilizing collapsing deformation. (a) The flattened metallic (M) region sandwitched between two semiconducting (S) tubes behaves as a quantum dot. (b) A large-gap BN nanotube is locally deformed.

4 Conclusions

In conclusion, we have investigated the band-gap modification by flattening deformation in C, BN, and BC_3 nanotubes through the first-principles pseudopotential calculations. For zigzag BN tubes, an appreciable variation of the band gap from 5 to 2 eV is found, while for zigzag C and armchair BC_3 tubes with small gaps, flattening deformation induces the insulator-metal transition. Such modifications of the band gaps can be used to design functional electronic and optical devices.

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