



First principle study of unzipped boron nitride nanotubes

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ABSTRACT

Systematic first principle calculations have been used to explain the dangling bonds behaviour in the rolling up of a boron nitride nanoribbon (BNNR) to construct a single-walled boron nitride nanotube (BNNT). We found in armchair BNNR two degenerate dangling bonds split and move up to higher energies due to symmetry breaking of system. While in zigzag BNNR changing the topology of system does not affect on metallic features of the band structure, but in unzipped BNNT case a metallic–semimetallic phase transition occurs. Considering the width dependent electronic properties of hydrogen passivated armchair BNNRs, exhibit zigzag behaviour of energy gap in agreement with previous results.

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1. Introduction

Recently method to fabricate graphene nanoribbons (GNRs) using unzipping carbon nanotubes [1,2] not only offers a new way of producing GNRs, but also introduces a new relation between two-dimensional structures and rolled up cases of them. Due to promising applications in nanoelectronic and spintronic devices two-dimensional structure of carbon atoms, including graphene and graphene nanoribbons (GNRs), have been studied extensively [3–8,15–18]. The investigation of the electronic states of GNRs brings it out that the edge shape leads to different electronic states near the Fermi energy [8,9].

However, thin and long strips of hexagonal boron nitride (BN) layer, boron nitride nanoribbons (BNNRs), have still not been considered widely. The large ionicity of two-dimensional BN structures leads to novel electronic properties different from graphene and make them new potential applications for nano-devices. In contrast to metallic graphene, which shows the characteristic degeneracy of π and π^* states at the Fermi level, the BN sheet is a wide direct band gap semiconductor. Since the two atoms in the unit cell of BN graphitic sheets are not identical the degeneracy of the π and π^* states is removed.

The successive fabrication of BN nano-devices demands the elucidation of edge effects on the electronic properties of BNNRs. The study of BNNRs with bare zigzag edges reveals that they are magnetic semiconductors with an energy gap that decreases slightly

with the ribbon widths [10]. The ground states of both the fully bare ZBNNRs and the ZBNNRs with a bare nitrogen and a hydrogen terminated boron edge, also, are half-metallic [11]. Density functional theory calculations exhibit that the energy gap of BNNRs changes slightly with width, but a transverse electric field reduces it considerably [12]. Additionally, the band gaps of armchair and zigzag BNNRs do not converge to the same value even when the BNNRs width increases [13]. Studying the stability of hydrogen terminated BNNRs using DFT framework, exhibits five kinds stable edges for the ZBNNRs and three kinds for ABNNRs [14].

An interesting question to consider is, whether a semiconductor BNNT is still semiconductor when it is unzipped into BN nanoribbon. It has not yet reported the changing of edge states due to rolling up a BNNR to make BNNT or unzipping of BNNT to create BNNR. The important point is how the topology affects quantum mechanical states, especially in a periodic surface embedded in the three-dimensional space. The main purpose of this Letter is to describe edge states near the Fermi level and elucidate their altering in BNNR rolling up process. We answer to a question of how the band structure for flat surface could be related to that for the curved one. Reaching this goal we have studied bare and hydrogen passivated zigzag and armchair BNNRs utilizing first principle band structure calculations. The Letter organized as follows. In Section 2 we introduce method of calculation. In Section 3 our results and discussion are presented. Finally, Section 4 is conclusion.

2. Computational method

We have used first principles full potential linearised augmented plane-wave density functional theory as implemented in

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the WIEN2k code [19]. For the exchange and correlation terms the generalized gradient approximation (GGA) is used following Ref. [20]. For boron and nitrogen atoms the $1s$ state is the core state while $2s$ and $2p$ are the valance states. Muffin-tin radii for boron and nitrogen are considered 1.3 a.u. and 1.31 a.u. respectively, and in H-BNNRs for hydrogen it is 0.7 a.u. In our calculations, for systems without hydrogen the cut-off parameter is $R_{mt} * K_{max} = 7$ where R_{mt} is the smallest atomic sphere radius in the unit cell and K_{max} is the plane-wave cut-off, and for the H-BNNRs it is 3.0.

Calculation are performed in the super-cell approximation, with 10 Å distance in the x direction and 8 Å distance in the y direction, for avoidance of interaction between nanoribbons. Since in the super-cell approach, the super-cells are periodically repeated in the space, the resulting band structure can be explained using the reduced Brillouin zone corresponding to the super-cell. All valence and conduction bands are described by the wave vectors belonging to this Brillouin zone. Reduced Brillouin zone is smaller than crystalline BNNT one. The total number of k points in the reduced Brillouin zone (BZ) is 28. In calculation of equilibrium positions we have used reverse-communication trust-region Quasi-Newton method. The force tolerance is 0.1 (mRy/bohr). For zigzag and armchair BNNRs and partially rolled states between them, we have calculated the band structure and energy gap after relaxation of the system. In the next section we present our results.

3. Results and discussion

BN sheet is two-dimensional one atom thick layer where boron and nitrogen atoms arranged in honeycomb lattice. The BN sheet is semiconductor with energy gap $E_g = 4.3$ eV, which is characterized by two types of bonds. First type are in-plane, occupied σ and unoccupied σ^* bonds. Second type are the normal to the BN sheet, occupied and unoccupied π and π^* bonds. In the BN sheet the electronegativity of nitrogen is more than boron hence the π electrons are more distributed around nitrogen rather than boron, showing wide gap semiconductor features which is clear from Fig. 1. Fig. 1 shows the local density of states of π band (due to $2p_z$ orbital) at the nitrogen and boron sites in the BN sheet. Number of occupied π states at nitrogen sites are much more than boron and they are separated from conduction band by a 4.3 eV energy gap.

When the translational symmetry of a solid breaks in a certain direction the localized states are generated. Cutting a BN sheet into BNNRs creates the localized states, because a BNNR lacks the two-dimensional periodic boundaries of a BN sheet. The new generated dangling bonds at the nanoribbon edge in cutting process, cause localized states near the Fermi energy. The reported electronic properties of bare carbon ribbons [22], and H-terminated BN and BCN ribbons [23], demonstrating the main role of the edge states on the energy gap of the system. Although the thermal and chemical stability of bare BNNRs have not been considered, their existence is supposed in the surface of nanospheres during electron emission [24].

Now we investigate the electronic properties of partially rolled up BNNR in the creation process of a BNNT and the effect of curvature on the dangling bonds. It is reported for all widths, the zigzag BNNRs are more stable than armchair BNNRs [21]. They claimed the zigzag SWBNNTs with radius greater than 2.0 Å are more stable than zigzag BNNRs and in experimental point of view, first the zigzag BNNRs are created due to their higher energies then the SWBNNTs are formed from them. We investigate this by calculation of binding energy and band structure of partially rolled up BNNR where curvature increases to create a BNNT. In our study, BNNRs with armchair (ABNNR) and zigzag (ZBNNR) shaped edges in the z -direction, as shown in Fig. 6, are categorized by the num-

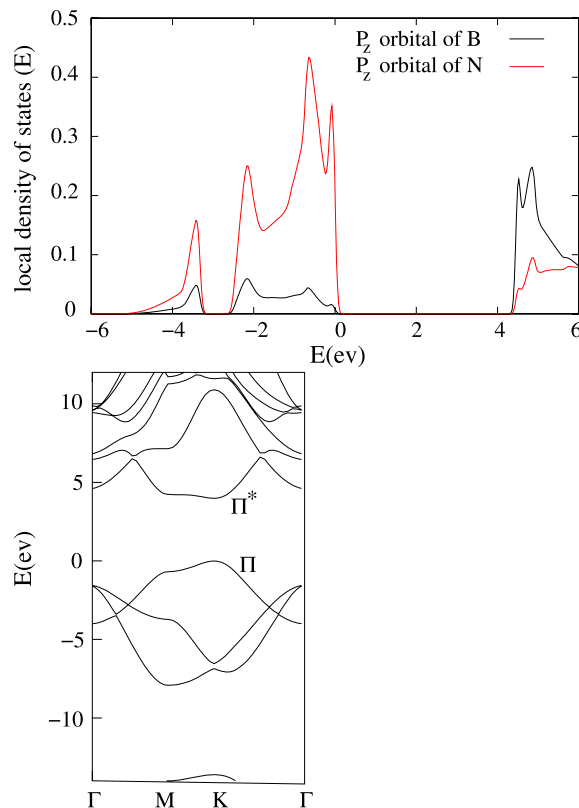


Fig. 1. The local density of states of π band (due to $2p_z$ orbital) at the boron and nitrogen sites in a BN sheet. Number of occupied π states at the nitrogen sites (due to $2p_z$ orbital of nitrogen) are more than boron sites. These full bands separated from conduction band by a 4.30 eV energy gap. Hence system is the wide band gap semiconductor. The Fermi energy of system is set to zero (top). Band structure of a hexagonal BN sheet showing direct wide band gap at the high symmetry K point of Brillouin zone (down).

ber of dimer bonds and zigzag chains in the x -direction, respectively. Periodic boundary conditions are assumed in the z -direction. Fig. 2 illustrates creation process of a (7, 0) zigzag SWBNNT by rolling up of a 14-ABNNR.

To probe the curvature effect on the BNNR electronic properties and dangling bonds, we partially rolled up a 14-ABNNR to create a zigzag (7, 0) SWBNNT. For each curvature cases of this process, we have calculated band structure to analyze the edge states in gap region. Fig. 3(a) illustrates the band structure of a 14-ABNNR, while Fig. 3(b)–(g) and (h) show the band structures of a partially rolled up 14-ABNNRs. Calculated binding energies, and energy gaps in terms of line crack width in BNNR rolling up process are listed in Table 1. By rolling up more and more (increasing the curvature), the two degenerate dangling bands inside of wide gap of BNNR band structure are separated and moved to the higher energies, hence the energy gap is increased by increasing of curvature.

Indeed, the topological transformation of the BNNR and surface curvature have two effects on dangling bonds, first: removing the degeneracy and second: shifting them to the higher energies. By curling BNNR to form BNNT the symmetry is broken and resulting the splitting of σ dangling bonds. Fig. 3 could be considered as the band structure of a unzipped zigzag SWBNNT which illustrates two dangling bonds at the bottom of the conduction band. The maximum gap is $E_g = 3.318$ eV where it belongs to (7, 0) zigzag BNNT. The indirect gap in the BNNR band structure changes to a direct gap in the nanotube band structure. Note that (7, 0) zigzag BNNT is more stable than 14-ABNNR due to its lower binding energy. Calculated binding energies show that by decreasing the crack width, the binding energy decreases too.

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