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Structural evolution, tunable electronic and magnetic properties of bare and semi-hydrogenated two-dimensional cubic boron nitride nanosheets

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ABSTRACT

By first-principles calculations, we study the layer number (n) dependent structural evolution, electronic and magnetic properties of two-dimensional bare and semi-hydrogenated (1 1 1)-oriented cubic boron nitride (c-BN) nanosheets. After energy optimization, there is a threshold of $n = 7$ for maintaining the cubic phase of the bare BN nanosheets. The hydrogenation on either B-end or N-end surface sites would be helpful for stabilizing the c-BN nanosheets with small n, and the structural relaxations on both two outermost surface sides are asymmetric due to different electronegativity between B and N atoms. The bare nanosheets are ferrimagnetic metallic and further turn into ferrimagnetic semiconductor after semi-hydrogenation.

1. Introduction

The modern semiconducting technology requires dimensional scaling in the deeper nanoscale of several or tens nanometers, and it is highly indispensable to design and search novel materials and/or structures with tunable properties for the advancement of semiconductor science. The investigation of graphene [1] has stimulated interests in atomically thin nanosheets of various layered materials, including the boron nitride (BN) system. In addition to the 0- and 1-dimentional BN nanostructures [2–5], 2-dimensional (2D) single layered (SL), multilayered (ML) graphene-like hexagonal BN (h-BN) nanosheets have been extensively synthesized and characterized [6,7]. However, no ML cubic BN (c-BN) nanosheets have been directly observed thus far. Although Guo et al. systematically investigated the layer number (n) dependent full-hydrogenated (FH) [8] and full-fluorinated ML (1 1 1)-oriented c-BN nanosheets [9], there are still issues yet to be investigated: (i) Why can not ML c-BN nanosheets be found in experiments? (ii) How can the c-BN phase be stabilized depending on n? (iii) What would happen when semi-hydrogenation (SH) is performed on the ML c-BN nanosheets? Here, the present work aims to explore the theoretical basis of the n-dependent intrinsic properties including structural, electronic and magnetic characteristics of c-BN nanosheets without and with hydrogenation on either B-end or N-end side.

2. Computational methods

The first-principles calculations were carried out based on spin-polarized density functional theory implemented in the CASTEP code [10]. The exchange-correlation potentials were treated by the generalized gradient approximation [11] parameterized by the PBE functional. In the calculations, the original 2D c-BN structures were cleaved from bulk c-BN crystals perpendicularly to the [1 1 1] direction with various layer numbers n. Each (1 1 1) BN monolayer consists of two sub-planes. The outermost surfaces with B atoms and N atoms are named as B-end and N-end surfaces, respectively. Both 2×2 and 4×4 supercells have been employed for all the infinite 2D BN (1 1 1) sheets, and the calculated results from both supercells are nearly the same. Here, we name the 2D sheets without hydrogenation as bare BN nanosheets. Since SH was performed only on the outermost sub-planes of either B-end or N-end to passivate the dangling bonds, the number of H atoms is 4 (1 6) for SH per 2×2 (4×4) supercell. The calculations of FH BN nanosheets were also proposed for comparison.

3. Results and discussion

Energy-minimization calculation for the bare SL c-BN (i.e. $n = 1$) reveals that the originated buckled c-BN (1 1 1) plane becomes flat,

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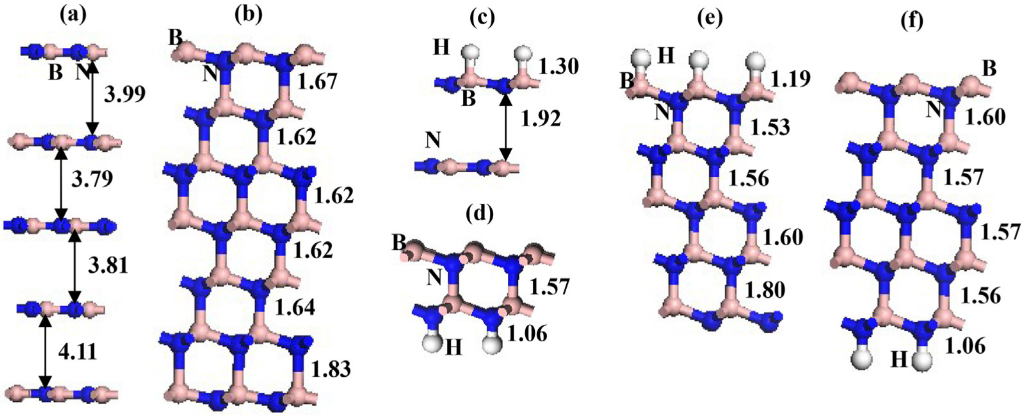

Figure 1. Side views of the optimized geometric structures of (1 1 1)-oriented BN nanosheets with various layer number (n). The structures of bare BN nanosheets with $n = 5$ (a), $n = 7$ (b). Semi-hydrogenation on B-end side and N-end side with $n = 2$ (c and d) and $n = 5$ (e and f), respectively. The corresponding bond lengths (in Å) of B—H, N—H and B—N are labeled. The B, N, and H atoms are shown in pink, blue and white, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

similar to the previous report [12]. The sp^3 bond angle α (109.47°) of B—N—B and N—B—N becomes 120° for sp^2 bond, as well as the bond length of B—N (1.56 Å) in c-BN is contracted to 1.45 Å (in h-BN). For the structural evolution of the ML c-BN nanosheets with $n = 2$–6, for example as indicated in Fig. 1a for $n = 5$, all the original buckling layers transform into flat layers. These structural evolutions suggest that the c-BN nanosheets with $n < 7$ prefer to relax and reconstruct to form h-BN phase. The result can explain to a certain degree why ML buckled c-BN-like nanosheets could not be experimentally observed so far. Once $n \geq 7$, the buckling c-BN configurations are nearly maintained, as shown in Fig. 1b taking $n = 7$ as an example. It is calculated that the B—N bond lengths in the intralayers are in the region of 1.50–1.56 Å, which are close to that of bulk c-BN (1.56 Å). Interestingly, the bond lengths in the interlayers are enlarged from the innermost layer ($d \sim 1.62$ Å) to the outermost (~1.67–1.83 Å), and slightly extended larger than that of bulk c-BN. Furthermore, the bond lengths in the interlayer near the N-end side (1.83 Å) are much larger than that near the B-end side (1.67 Å), showing an asymmetric feature on the two sides (Fig. 1b). As known that B atoms on the surface of c-BN prefer to be tri-coordinated inducing an inward relaxation to the bulk [13], by which sp^3 hybridized structure with less relaxation of the surface layers can be easily maintained as a consequence. Meanwhile, due to the strong localized unbonded electrons induced by the larger electronegativity of N atoms, the outermost layer with N-end has a tendency of forming sp^2 hybridized structure with less buckling feature. In addition, the different surface atomic coordination imperfections [14] from N and B cause the surface layer relaxation with different degrees of lattice expansion, which are associated with the varying bond energy of those dangling bonds. The relaxation on B- and N-end sides is therefore strongly related to the ionic character of the B—N bonds, which leads to the asymmetric optimized structure and the small threshold layer number ($n = 7$) to keep the c-BN phase. This result is significantly different to the structural evolution of the 2D diamond nanosheets with highly covalent C—C bonds, where the relaxation is symmetric on both sides and the threshold for the cubic phase kept is $n = 12$ [15]. Furthermore, for some wurtzite III–V (i.e., AlN, GaN, and InN) compound with stronger ionic bonds [16,17] or diamond structural IV (i.e., Si and Ge) semiconductors with relatively weak covalent bonds [18] comparing to diamond, it is favorable for maintaining the cubic structure consisting of buckling (1 1 1) layers with a relatively lower threshold layer number n.

The stability of the optimized bare c-BN nanosheets is measured by the calculated formation energy (FE, in eV/atom) as a function of layer number n. The FEs follow the equation of $FE = (E_{\mathrm{cal}} - E_{\mathrm{BN}})/(N_{\mathrm{B}} + N_{\mathrm{N}})$, where E_{cal} and E_{BN} are the total energies per unit cell after and before energy optimization, N_{B} and N_{N} are the numbers of B and N atoms per unit cell. As plotted in Fig. 2, the value of FE is negative because E_{cal} is smaller than E_{BN}. The absolute data of FE are large at small n and decreased monotonously with the increase of n. With larger n (≥ 7), the FE has a saturation tendency and it stabilized at about 0.031–0.035 eV/atom. Thus, the 2D c-BN phase is easier to be maintained at $n \geq 7$, on the contrary, h-BN is energetically favorable at $n < 7$.

It is well known that surface hydrogenation has become an important route to modulate the structure and properties of the various 2D nanosheets, such as graphene [19], diamond [20] and c-BN [8]. In our calculations, we denote SH on B-end site as H—BN and on N-end site as BN—H. Fig. 1c–f shows the calculated structures of the H—BN (Fig. 1c and e) and BN—H (Fig. 1d and f) nanosheets with $n = 2$ and $n = 5$, respectively. Indeed, the hydrogenation plays a key role in stabilizing cubic structure of BN nanosheets with smaller threshold n ($n = 2$ for BN—H and 5 for H—BN) with respect to that for their bare counterpart. The hydrogenation would delocalize the distribution of electrons of N or B atoms inducing the formation of sp^3 hybridization. For the ML H—BN, the unhydrogenated N-side is flat when $n \leq 4$, which is consistent with the fact that N-side is favorable to form a planar surface. Moreover, such a buckled

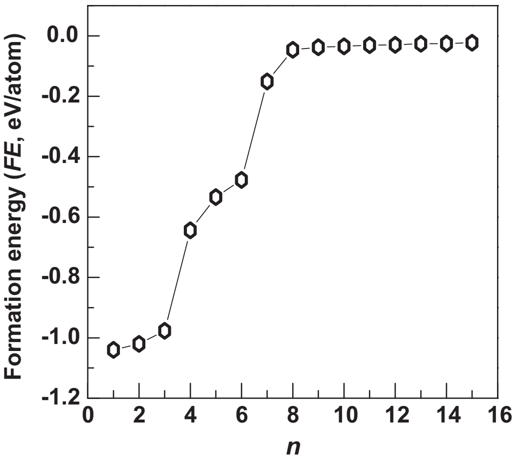

Figure 2. Formation energy for the optimized bare (1 1 1)-oriented BN nanosheets as a function of layer number n.