Interlayer distances and band-gap tuning of hexagonal boron-nitride bilayers

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We report on relationships between interlayer distances and electronic structures of hexagonal boron-nitride (h-BN) bilayers based on first-principles density-functional calculations. The energy-band structures and the band-gap values are calculated under uniaxial compressive strains along the direction perpendicular to the h-BN bilayer sheets. It is found that the band gap can be tuned by applying compressive strains uniaxially. More specifically, the band-gap value decreases with decreasing the interlayer distances between two layers of the h-BN bilayer. The behaviors of the band gaps under uniaxial strains are explained in terms of the energy-band structures.

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1. Introduction

Since the discovery of graphene, two-dimensional atomic-layered materials have received much interest in the field of basic nanoscience and applicable nanotechnology.1–3 In particular, hexagonal boron-nitride (h-BN) atomic layers have been also studied vigorously because they exhibit unique and important properties including large band gap and high photo-emission efficiency.4–6 In view of the practical applications, it is also expected to be a good candidate for deep ultraviolet optoelectronic device materials.7,8 In particular, the interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials9 and exchange–correlation effects are treated using the local density approximation (LDA) parameterized by Perdew and Zunger.10–12 The length of the supercell along the direction perpendicular to the h-BN bilayer is set to be 20 Å (1 Å = 0.1 nm). It is reported that the LDA calculations give comparable results with generalized gradient approximation (GGA) calculations including van der Waals (VDW) interactions for relative energetics and interlayer distances of multi-layered materials such as the h-BN bulk, the graphite, and the graphene/h-BN hybrid structures.13,14

Applying strains is the effective method to tune the electronic properties of low dimensional nano-materials.12–17 The Fermi velocity of graphene varies with depending on the directions of the uniaxial strains.12 The mechanical strains can tune the energy-band structures of monolayer and bilayer of MoS2.14 The electronic properties of h-BN atomic layers are also tunable under biaxial strains.15–17 These reports are, on the other hand, focused on the effects of in-plane strains of atomic layers. To best of our knowledge, there are only few theoretical reports regarding effects of uniaxial strains on electronic properties of h-BN bilayers along the direction perpendicular to the atomic layers.

In this paper, we report electronic properties of h-BN bilayers under uniaxially compressive strains along the direction perpendicular to the bilayers, based on a first-principles total-energy calculation within the framework of the density-functional theory. The energy-band structures and the band-gap widths are calculated when compressive strains are uniaxially applied. It is found that the band gap diminishes with increasing the compressive strains. In addition, we also discuss the relationship between the energy band structures and the uniaxial strains.

2. Computational methods

First-principles electronic-structure calculations have been carried out in the framework of the density-functional theory.13,19 The interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials10 and exchange–correlation effects are treated using the local density approximation (LDA) parameterized by Perdew and Zunger.21,22 The length of the supercell along the direction perpendicular to the h-BN bilayer is set to be 20 Å (1 Å = 0.1 nm). It is reported that the LDA calculations give comparable results with generalized gradient approximation (GGA) calculations including van der Waals (VDW) interactions for relative energetics and interlayer distances of multi-layered materials such as the h-BN bulk, the graphite, and the graphene/h-BN hybrid structures.23,24

The wave functions are expanded in a plane-wave basis and the kinetic-energy cutoff is taken to be 60 Ry (1 Ry = 8.72 × 10−18 J). The atomic positions are optimized until the Hellmann–Feynman force acting on each atom becomes less than 0.05 eV/Å (1 eV = 1.602 × 10−19 J). Two-dimensional Brillouin-zone integration is performed with 16 × 16 sampling k-points. Computations have been performed using the Tokyo Ab Initio Program Package (TAPP).25

3. Results and discussion

We start with studying the stabilities of the unstrained h-BN bilayer sheets. There are five different atomic structures regarding stacking patterns, as shown in Fig. 1. In the case of AA stacking patterns, there are two types of stacking patterns (AA1 and AA2). In the case of the AB stacking patterns, there are three types of patterns (AB1, AB2, and AB3). For AA1 stacking pattern

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We study the electronic structures of the h-BN bilayers under uniaxial strains. Here, the electronic structures of only the AB3 stacked h-BN bilayer are examined because h-BN bilayer with the AB3 stacking becomes the most favorable as discussed above. Figure 2 shows the band-gap change ($\Delta E_g$) as a function of the interlayer-distance change $d$, where $d$ is defined as $a_0 - a$, and $a_0$ and $a$ are interlayer distances of uniaxially strained and unstrained h-BN bilayers, respectively. It can be seen that the band gap diminishes as the interlayer distance decreases. It is interesting that the slopes of the band-gap change between $d = 0$ and 0.5 Å and between $d = 0.5$ and 1.0 Å take considerably different values; the reduction rate between $d = 0.5$ and 1.0 Å is much larger compared with that between $d = 0$ and 0.5 Å. On the other hand, interestingly, the band gap of h-BN bilayer decreases monotonically with increasing the biaxial strains. Thus, the band-gap value changes largely as two layers of h-BN bilayer approach each other, which is caused by the sizable modification of the energy-band structure as will be discussed below.

We also examine the electronic band structures of compressively strained h-BN bilayers. Figures 3(a) and 3(b) show the energy-band structures of h-BN bilayers with interlayer-distance change of $d = 0$ and $d = 0.5$, respectively. In the unstrained h-BN bilayer [Fig. 3(a)], the valence-band maximum (VBM) is located at the K point and the conduction-band minimum (CBM) is located at the M point. The h-BN bilayer is found to exhibit semiconducting property and it has an indirect gap of 4.37 eV in our present calculation, while the h-BN monolayer possesses a direct gap at the K point and its band-gap value is 4.64 eV in our previous LDA calculation. Due to the interaction between two layers of h-BN bilayer, the band gap of the bilayer is considerably reduced compared with that of the monolayer, and the valence bands as well as the conduction bands near the fundamental gap are splitted. Thereby, further reduction of the interlayer distance will modulate the electronic structure of the h-BN bilayer. When two layers of bilayer are located at $d = 1.0$, the band gap considerably decreases by $\sim -0.8$ eV [Fig. 2] and the electronic band structure is strongly modified [Fig. 3(b)]; the CBM moves downward by $\sim -0.8$ eV and the position of the CBM changes to the K point from the M point at $d = 0$. On the other hand, the height of the VBM is almost unchanged and resides near $-6$ eV, but its position moves from the K point at $d = 0$ to the K–Γ direction. Thus, the reduction of the band gap is attributed mainly...
to the sizable modulation of the CBM rather than that of the VBM. It is rather obvious from Fig. 3(a) that at $d = 0$ both the valence-band state and the conduction-band state of each $h$-BN layer are weakly interacting with those of the other layer and consequently there appear nearly degenerate states at both VBM and CBM. On the other hand, with compressive strain at $d = 1.0$ [Fig. 3(b)], these near-degeneracies are fully lifted due to the sizable interlayer interaction. At the same time, the average energy of two interacting VBM states and that of two interacting CBM states both move downwards under compressive strain. In the case of CBM states, this lifting of degeneracy enhances the downward shift of the lowest conduction-band state and gives rise to the total shift of 0.8 eV as mentioned above. However, in the case of VBM states, lifting of degeneracy cancels the downward shift of the highest valence-band state, which therefore shows very little total shift under compressive strain.

4. Summary

We have studied the relationship between the interlayer distances and the electronic structures of $h$-BN bilayers using first-principles density-functional calculations. The energy-band structures and the band gaps of $h$-BN bilayers have been calculated under uniaxial compressions. It is found that the band gap decreases with increasing the compressive strain. It is also found that the reduction of the band gap is caused by modification of the CBM. Therefore, the band gaps of the $h$-BN bilayer are tunable by applying uniaxial compression.

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