First-principles electronic-structure calculations have been performed to examine electronic properties of hexagonal boron nitride (h-BN) monolayers. The dispersion of the energy bands and the width of the band gaps are calculated under biaxial strains. It is found that the band gap decreases as the tensile strain increases, whereas the band gap increases and then it decreases as the compressive strain increases. The relationship between the energy-band structures and the applied strains is reported to clarify the unique behaviors of the band gaps induced by biaxial strains.

Key-words : h-BN monolayer, Biaxial strains, Energy-band structures, Band gap, First-principles density-functional calculation

1. Introduction

Two-dimensional atomic monolayers have attracted great attention from the viewpoints of fundamental nanoscience and applicable nanoelectronics. Specifically, graphene exhibits extremely high carrier mobility, and is one of the good candidates for nanoelectronics materials such as conduction channels in field-effect transistors. However, it has been reported that graphene-based materials often offer unreliable control of electronic properties due to the lack of band gap of graphene. The hexagonal boron nitride (h-BN) monolayer, a two-dimensional material with a honeycomb lattice, exhibits remarkable properties similar to graphene although it possesses a wide band gap. The strain engineering has been the crucial way to modify the electronic properties of two-dimensional nano-materials. For example, the Fermi velocity of graphene can be changed, depending on the directions of the uniaxial strains.

In this paper, we report effects of the biaxial strain on the electronic properties of the h-BN monolayers based on a first-principles total-energy calculation within the framework of the density-functional theory. We calculate the energy-band structure and the band-gap width under biaxial strains. We find that the band gap diminishes as the tensile strain increases, while the band gap increases and then it decreases as the compressive strain increases. We also discuss the unique behavior of the band gap in terms of the energy-band structures under the biaxial strains.

2. Computational methods

Our calculations are performed based on first-principles electronic-structure methods within the density-functional theory. The interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials and exchange-correlation effects are treated using the local density approximation parameterized by Perdew and Zunger. The length of the supercell along the direction perpendicular to the h-BN monolayer is set to be 20 Å.

The wave functions are expanded in a plane-wave basis and the kinetic-energy cutoff is taken to be 60 Ry (1 Ry = 13.6057 eV). The atomic positions are optimized until the Hellmann–Feynman force acting on each atom becomes less than 0.05 eV Å⁻¹. Two-dimensional Brillouin-zone integration is performed with 16 × 16 k-point sampling. Computations have been performed using the Tokyo Ab Initio Program Package (TAPP).

For the calculations of structural optimizations of the 5% tensile strained, the 5% compressively strained, and unstrained h-BN monolayers, one B atom and one N atom in a unit cell are set to be buckled from a planar sheet as an initial configuration before the structural optimizations are carried out. After the
optimizations, the B and the N atoms are confirmed to reside in a planar sheet.

3. Results and discussion

Before discussing the strain effects on the electronic properties of the h-BN monolayer, we show the atomic structure and electronic energy bands of the unstrained h-BN monolayer sheet. Figure 1 shows the optimized atomic geometry of the h-BN monolayer. Our calculated B-N bond length is 1.43 Å. This is in good agreement with the experimental value of 1.44 Å.7) The energy-band structure of the h-BN monolayer is shown in Fig. 2. The valence-band maximum (VBM) as well as the conduction-band minimum (CBM) is located at the K point, and therefore we can observe that the h-BN monolayer is a wide-gap semiconductor with a direct band gap of 4.6 eV in our LDA calculation. It is noted that the h-BN bulk is a semiconductor with an indirect band gap of 4.0 eV in other LDA calculation.17)

We next examine the biaxial strain effects on the electronic structures of the h-BN monolayer. Figure 3 shows the band gap as a function of the biaxially applied strain $\varepsilon$. Here, strain $\varepsilon$ is calculated as $(l - l_0)/l_0$, where $l$ and $l_0$ are lattice constants of biaxially strained and unstrained h-BN monolayers, respectively. When the tensile strains are applied, the band gap decreases with increasing the strain. In the region of the compressive strain, the behavior of the band gap exhibits unusual behavior: the band gap increases as the compressive strain increases, and reaches the maximum value of about 4.8 eV at $\varepsilon \sim -2\%$. It is surprised that the band gap diminishes when further compressive strains with more than a magnitude of 2% are applied.

To examine this unusual behavior of the band gap, we study the energy gaps between the VBM and the CBM at the K point (K-K gap) and between the VBM at the K point and the CBM at the $\Gamma$ point (K-$\Gamma$ gap). Figure 4 shows the energy gaps at K-K and K-$\Gamma$ points as a function of applied strain. The energy gap between K-K points decreases as the strain increases. On the other hand, it is interesting that the energy gap between K-$\Gamma$ points increases as the strain increases. Thus, the K-K gap line and the K-$\Gamma$ gap line intersect each other at around $\varepsilon = -2\%$ and thereby the band gap has the maximum value of approximately 4.8 eV at $\varepsilon \sim -2\%$.

We also study the electronic band structures of compressively strained and tensile strained h-BN monolayers. In Figs. 5(a) and 5(b), we plot the energy-band structures of 5% compressively and 5% tensile strained h-BN monolayers, respectively. When the 5% compressive strain is applied, the VBM, which is located at the K point, moves upward and approaches to the vacuum level with about 0.2 eV compared with that of the energy band of the unstrained h-BN monolayer. On the other hand, the VBM at the K point moves downward from the vacuum level when the 5% tensile strain is applied. In sharp contrast to the behavior of the VBM, the CBMs (conduction-band minima) at the K and the $\Gamma$ points exhibit unique features. When the 5% tensile strain is applied, the lowest CBM is located at the K point, whereas the lowest CBM is at the $\Gamma$ point when the 5% compression is applied. It is interesting that the CBM at the $\Gamma$ point is almost unchanged without depending on the magnitude of the compressive as well as the tensile strain although the CBM at the K point considerably moves upward to and downward from the vacuum level, depending on the directions of the applied strains. The character of the electron state of the CBM at the K point is

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Fig. 2. Energy-band structure around the fundamental gap of h-BN monolayer. Vacuum level is set to be zero.

Fig. 3. Band gap as a function of biaxial strain $\varepsilon$.

Fig. 4. Energy gaps between the VBM at the K point and the CBM at the K point (K-K gap), and between the VBM at the K point and the CBM at the $\Gamma$ point (K-$\Gamma$ gap) as a function of biaxial strain $\varepsilon$.

Fig. 5. Energy-band structures around the fundamental gap of (a) 5% compressively strained and (b) 5% tensile strained h-BN monolayers. Vacuum level is set to be zero.
qualitatively different from that at the $\Gamma$ point: The electron state at the $K$ point consists of $\pi^*$ state, whereas that at the $\Gamma$ point is composed of a free electron-like state. Thus, the characters of the electron states of the CBMs at the $K$ and the $\Gamma$ points determine the behaviors of the $K-K$ and the $K-\Gamma$ gap lines under applying the strains, respectively.

4. Summary

We have investigated electronic structures of biaxially strained as well as unstrained $h$-BN monolayer using a first-principles density-functional calculation. We have calculated the energy bands and the band gaps of biaxially strained $h$-BN monolayers. We have found that the band gap decreases with increasing the tensile strain, whereas the band gap reaches the maximum value in the region of the compressive strains. We have also revealed that the unusual behavior of the band gap is attributed to the position of the CBM. Thus, the band gaps of the $h$-BN monolayer are tunable by biaxially applying strains.

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