Stacking sequence dependence of electronic properties in double-layer graphene heterostructures

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1. Introduction

Monolayer graphene invokes considerable interest in electronic application owing to its unique properties such as ultrahigh electronic mobility, anomalous quantum Hall effects, and so on.¹２⁻⁷ These unconventional electronic properties originate from the unusual band structure near the Fermi level of graphene, where the electronic states are well described as massless Dirac electrons, i.e., a zero energy gap with linear π bands crossing at the K point. In the few-layer graphene system, however, the weak interaction between graphene layers changes the electronic properties near the Fermi level.⁸⁻¹² For bilayer graphene, the Bernal AB-stacking graphene, which is more stable than the AA-stacking one, shows a metallic behavior with chiral parabolic dispersions near the K point. For trilayer graphene, there are two types of stacking sequence, i.e., Bernal AB and rhombohedral ABC stacking. Accordingly, their electronic properties under external electric fields and optical conductivity depend on the stacking sequence.¹³-site energies for carbon atoms of graphene layers, the electronic states of the system can be classified into metallic or semiconducting on the basis of the stacking sequence. Moreover, the stacking sequence dependence of the energy band structures of DLGHs is well described using the orbital interaction model.

First-principles calculation has been performed to investigate the stability and electronic properties of double-layer graphene heterostructures (DLGHs). In this system, two graphene layers are separated by hexagonal boron-nitride (h-BN) layers that work as an insulating barrier. Our results show that the stability of the system is determined by the atomicistic configurations between graphene and its adjacent h-BN layer. Among different stacking sequences, AB-stacking is most stable. Since the inserted h-BN layers modulate the on-site energies for carbon atoms of graphene layers, the electronic states of the system can be classified into metallic or semiconducting on the basis of the stacking sequence. Moreover, the stacking sequence dependence of the energy band structures of DLGHs is well described using the orbital interaction model. © 2014 The Japan Society of Applied Physics

2. Calculation method and simulation model

The calculations are performed using density functional theory based Vienna Ab initio Simulation Package (VASP).²³ Core and valence electrons are described with the projector-augmented wave method (PAW).²⁴ The local density approximation (LDA) is used to treat the exchange–correlation functional.²⁵ The plane-wave basis set cutoff is 500 eV and the Brillouin zone is sampled with a 13 × 13 × 1 Monkhorst–Pack mesh. The DLGHs investigated in this paper have the sandwiched structures; h-BN layers are inserted as the spacer between two graphene monolayers. We label the system as G–nBN–G. The number of h-BN layers n is changed from one to three. As the lattice mismatch between graphene and the h-BN monolayer is around 1.8%, the graphene and h-BN layers can be assumed to be commensurate. To ensure negligible interaction between periodic images of the slabs in the stacking direction, a 20 Å vacuum is used. In this study, all the structures are fully optimized including atomic coordinates and supercell. The convergence thresholds for energy and force are 10⁻⁴ eV and 0.01 eV/Å, respectively.

3. Results and discussion

In this work, the stacking sequences are distinguished using the naming convention defined in the paper of Sakai et al.²⁶,²⁷) The capital letters (A, B, and C) and small letters...
... atom positions of graphene and h-BN layer, respectively. For example, the Bernal stacking sequence of bilayer graphene is labeled as AB, and the stacking form of bulk h-BN is aa'. The prime symbol represents exchange of the positions of boron and nitrogen atoms in the adjacent h-BN layers. Figure 1 shows three nonequivalent orientations of graphene on the h-BN monolayer (Ab, Ab', and Aa). Since h-BN layers always have an aa' stacking, a DLGH can have six different stacking sequences with a fixed thickness. Figure 2 shows the six different stacking configurations of G–2BN–G. The corresponding energy band structures are shown in Fig. 3.

Let us try to find out the most stable stacking sequence of DLGHs. To clarify the relative stability among different stacking sequences for a fixed thickness, we have evaluated the relative differences in the total energy $\Delta E$ for each stacking configuration shown in Table I. $\Delta E$ is defined as the energy difference measured from the energy of the most stable structure for a fixed $n$. The structure with $\Delta E = 0$ corresponds to the most stable one.

| G–1BN–G | $\Delta E$ (meV) | G–2BN–G | $\Delta E$ (meV) | G–3BN–G | $\Delta E$ (meV) |
|---------|-----------------|---------|-----------------|---------|-----------------|
| AbA     | 0               | Abb'C   | 0               | Abb'A   | 0               |
| AbC     | 19.1            | Abb'B   | 18.7            | Abb'bC  | 18.6            |
| AbB     | 22.4            | Abb'B   | 21.9            | Abb'bB  | 22.0            |
| AbA     | 29.0            | Abb'bC  | 38.1            | Ab'bA   | 37.4            |
| Ab'B    | 41.3            | Ab'bB   | 42.0            | Ab'b'B  | 41.4            |
| AaA     | 44.8            | Aaa'A   | 44.1            | Aaa'aA  | 45.1            |

(a, b, and c) represent the relative stacking positions of graphene and h-BN layer, respectively. For example, the Bernal stacking sequence of bilayer graphene is labeled as AB, and the stacking form of bulk h-BN is aa'. The prime symbol represents exchange of the positions of boron and nitrogen atoms in the adjacent h-BN layers. Figure 1 shows three nonequivalent orientations of graphene on the h-BN monolayer (Ab, Ab', and Aa). Since h-BN layers always have an aa' stacking, a DLGH can have six different stacking sequences with a fixed thickness. Figure 2 shows the six different stacking configurations of G–2BN–G. The corresponding energy band structures are shown in Fig. 3.

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Table I. Relative differences of the total energy $\Delta E$ for G–nBN–G ($n = 1–3$). $\Delta E$ is defined as the energy difference measured from the energy of the most stable structure for a fixed $n$. The structure with $\Delta E = 0$ corresponds to the most stable one.

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Let us try to find out the most stable stacking sequence of DLGHs. To clarify the relative stability among different stacking sequences for a fixed thickness, we have evaluated the relative differences in the total energy $\Delta E$ for each stacking configuration shown in Table I. $\Delta E$ is defined as the energy difference measured from the energy difference of the total energy for each configuration measured from that of the most stable structure for a fixed thickness of DLGH. We can see that the most stable structure in each thickness group favors Ab-stacking between graphene and its adjacent h-BN layer except G–2BN–G. The Ab-stacking sequence is that the carbon atoms on one of two sublattices are above boron atoms, and carbon atoms on the other sublattice are above the centers of the BN hexagonal rings. According to this definition, b'C-stacking is equivalent to bA-stacking. Therefore, the most stable configuration in G–2BN–G is Abb'C, where both layers of graphene are also Ab-stacking with their adjacent h-BN layers. The DLGHs with Aa or Aa' stacking sequence, which are least stable, have 40 meV higher total energy than the most stable structure.

The stability of DLGHs can also be embodied by the interlayer distance between graphene and its adjacent h-BN layer. We find that the average interlayer distances between the graphene and the h-BN layer are 3.24 Å for Ab-stacking, 3.46 Å for Ab'-stacking, and 3.52 Å for Aa-stacking. This fact denotes that the shorter interlayer distance gives the larger stability of DLGHs owing to the stronger interaction. Since Ab-stacking is most stable, the interaction between boron and carbon atoms is favorable. This fact is consistent with the results of the graphene/h-BN bilayer superlattices.

The energy band gaps of G–nBN–G are shown in Table II. First, we discuss the band structures of G–2BN–G and G–3BN–G. In these two cases, the band gaps can be classified into two types: (1) larger band gaps of more than 37 meV and (2) very tiny band gaps of less than 10 meV. To clarify the mechanisms of the two types of band gap, we investigate the effects of interlayer interaction and stacking sequence on the band structures of heterostructures. In the DLGHs, the two graphene layers are separated by h-BN layers, therefore, graphene interacts with h-BN directly. Previous studies showed that this interaction causes a difference in on-site energies for carbon atoms between two sublattices, which induces a small band gap. Since
G–1BN–G has a much stronger interlayer interaction between graphenes than other cases, its electronic band structure will be discussed later.

In addition to the interlayer interaction, the stacking sequences crucially affect the electronic states near the Fermi energy. Let us consider the configuration Abb'A as an example (see Fig. 2). The corresponding energy band structure is shown in Fig. 3(d). As for the top (bottom) graphene layer, the carbon atoms on two different sublattices are located above (below) the boron (nitrogen) atoms and the centers of hexagonal h-BN rings, respectively. Therefore, the electrostatic potential of the top and bottom graphene layers in the Abb'A heterostructure is different. In accordance with this fact, the energy dispersion related to the top (bottom) graphene layer shifts about 0.07 eV downward (upward) as can be seen in Fig. 3(d). In contrast, for Abb'C, as the carbon atoms on two different sublattices in the top (bottom) graphene layer are located above (under) the boron atoms and centers of h-BN hexagonal rings, both the layers of graphene have the same electrostatic potential. Therefore, the energy dispersion related to the top and bottom graphene layers overlaps at almost the same place, as can be seen in Fig. 3(b).

To understand the effect of different stacking sequences on the energy band structure of DLGH, an orbital interaction model is employed. Here we just consider the interaction between the π orbitals of adjacent atoms. According to atom electronegativity, i.e., N > C > B, the energy levels of the orbitals of N, C, and B atoms (\(E_N\), \(E_C\), and \(E_B\)) are \(E_B > E_C > E_N\). In Fig. 4, schematic energy diagram is shown to illustrate the shift of energy levels induced by the interaction between graphene and the h-BN layer. For the h-BN monolayer, at the K point, the top of the valence band is mainly contributed by nitrogen atoms and the bottom of the conduction band is contributed by boron atoms. Therefore, when the carbon atom is located above or below the boron atom, the occupied carbon orbital interacts with the empty boron orbital, leading to the downward shift of the bonding state from the original carbon level. As for the interaction between carbon and nitrogen atoms, the situation is opposite. The empty carbon orbital interacts with the nitrogen orbital, resulting in the upward shift of the antibonding energy state.

The shift of the orbital energy for the carbon atom can be used to explain the band structures of DLGHs. In the case of tetralayer heterostructures, for Aaa'A, Abb'C, and Abb'BC configurations, the top and bottom graphene layers have the same stacking sequence with their adjacent h-BN layers. Therefore, the interaction with the adjacent h-BN layers makes the carbon energy levels move in the same direction. In this situation, as shown in Figs. 3(a) and 3(c), the energy band structures of those heterostructures are similar to that of graphene monolayer on the h-BN layer. For another three heterostructures Abb'A, Abb'B, and Abb'BC, the stackings of the top and bottom graphene layers with h-BN layers are in different ways, which induces the carbon orbital energies of two graphenes to shift towards opposite directions, as shown in Figs. 3(d) and 3(f). Let us take Abb'A as an example. The energy band corresponding to the bottom graphene moves upwards, and the energy band corresponding to the top graphene moves downwards. Around the Fermi level, the energy bands from top and bottom graphenes intersect. At the crossing point, there are small openings of the energy band gap. For Abb'A, it is 8 meV, and for Abb'B, it is 5 meV. We attribute the band-gap opening at the crossing points to the coupling of the top and bottom graphene layers mediated by h-BN layers. For pentalayer heterostructures Abb'bB and Abb'BC where three layers of h-BN are inserted, the band structures are similar to those of Abb'A and Abb'B tetralayer heterostructures. However, the band gaps at the cross points are almost zero, which indicates the much weakened inter-graphene interaction.

Figure 5 shows the energy band structures of G–1BN–G for six different stacking sequences. For G–1BN–G, the coupling between top and bottom graphene layers is stronger...
than those of G–2BN–G and G–3BN–G. As a result, the band structures near the Fermi level become more complex. For AbB, Ab′B, and AbC configurations, their energy band structures become similar to those of Abb′bB, Ab′bb′B, and Abb′C, because of the similar stacking configuration between graphene and its adjacent h-BN layer. The only difference is that the interlayer distance between two graphenes is shorter in trilayer heterostructures, resulting in the larger band gaps owing to the stronger interlayer interaction. For AbA, Ab′A, and AaA configurations, although the stacking sequences between graphene and h-BN are the same as those of Abb′bB, Ab′bb′B, and AaAaA, the band structures are totally different. As shown in Figs. 5(d) and 5(f), there are two types of energy band around the Fermi level. One energy band is approximately linear at the K point, and the other one is nonlinear. We find that this linear energy band is contributed by all four carbon atoms in the unit cell, which is similar to the linear band state existing in the ABA-stacking trilayer graphene.8) For the ABA-stacking trilayer graphene, the linear band states refer to the bonding state of orbitals at both ends via the second neighbor hopping parameter γs. For AbA, Ab′A, and AaA heterostructures, the situation is similar. Only the sandwiched layer is changed from graphene to h-BN, so the second neighbor hopping parameter is different. As for the nonlinear energy band, the energy levels of the carbon atoms with the same electrostatic potential move towards the same direction, because of which they compose one energy band, labeled as Cb, Cb′, Cc, and Cc′. This indicates that the coupling between top and bottom graphene plays a more important role.

From the above results, it is clear that the band structures can demonstrate the difference of the coupling in the two graphene layers. The coupling of the graphene layers is strong in trilayer heterostructures despite the existence of a tunnel barrier of h-BN. As the number of h-BN layers increases, the coupling is weakened.

4. Conclusions

In this paper, first-principles calculation has been performed to investigate the stability and energy band structure of DLGHs, where h-BN layers are inserted between two graphene monolayers. Our results show that the stability and band structures are sensitive to the stacking sequence of DLGHs. It is found that the stability of DLGHs is mainly dependent on the stacking sequence of graphene and its adjacent h-BN layer. Among the three stacking sequences, Ab′-stacking is most stable. In addition, it is found that the interaction between graphene and h-BN affects the electronic properties in two aspects. The first one is the modification of the on-site energy of carbon atoms between two nonequivalent sublattices in the same graphene. The second one is the shifting the band structures of the top and bottom graphene layers, like graphene under an external electric field. Our results provide the fundamental aspects of the electronic states of DLGHs for the application of electronic devices.

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