

Adsorption of carbon atoms on graphene/MgO(111)

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In this study, we investigate the electronic and atomic structure of graphene on O-terminated MgO(111) using density functional theory (DFT) calculations. To suggest a possible direction for future band gap engineering of graphene on MgO(111), adsorption of carbon atoms on graphene/MgO(111) is studied by considering the several adsorption sites. Details in adsorption properties of carbon atoms on graphene/MgO(111) are analyzed in terms of energy band structure.

INTRODUCTION

As graphene which consists of carbon atoms with honeycomb structure is a two-dimensional material, it has been attracting much interest with its unique properties; especially, graphene is a gapless semiconductor having a linear dispersion around the Fermi level. For application of graphene in future engineering, it is very important to understand the interaction between graphene and various oxide substrates. So far, there have been many experimental and theoretical investigations of graphene growth on the supporting substrates such as silicon carbide (SiC) and silicon dioxide (SiO₂).

Previously, the direct graphene growth on the MgO(111) surface has been studied concerning the origin of band gap in experiments [1,2]. They reported a significant band gap opening of about 0.5 to 1 eV in 2.5 monolayer graphene, which is deposited on MgO(111) surface, using low energy electron diffraction (LEED).

In connection with the experimental results [1,2], we have investigated the electronic structure of graphene on MgO(111) with the density functional theory (DFT) calculations to understand growth of graphene on MgO(111) [3]. However, we did not find the band gap opening due to a tiny density-of-state at the Fermi level. For realization of a band gap opening, we consider adsorption of carbon atoms on graphene adsorbed on O-terminated MgO(111) surface with the several adsorption sites. From our calculations, we analyze atomic and electronic structure of graphene on MgO(111) with adsorbed carbon atoms.

CALCULATION METHODS

In this study, we have performed spin-polarized DFT calculations within generalized gradient approximation (GGA) for exchange-correlation (*xc*) functional, as implemented in the SIESTA package.

To obtain total energy and the energy band structure of graphene on MgO(111) surface, we use the LCAODFTLab simulator in Nanophysics EDISON website which is supported by SIESTA package.

As an oxide substrate, O-terminated polar MgO(111) surface is used for interaction with graphene, since oxygen atom is more reactive than magnesium atom. Six atomic layers of MgO(111) are modeled by a rhombus periodic slab with a (2x2) surface supercell. Then, a (4x4) supercell of graphene is considered on the O-terminated MgO(111) surface with a vacuum region of about 13 Å. To change the electronic structure of graphene, some carbon atoms are adsorbed on the top, bridge and hollow sites. All atomic coordinates are fully relaxed until the forces are less than 0.025 eV/Å, except the bottom layers of MgO. For the Brillouin-zone integration, we use the (3x3x1) grid in the Monkhost-Pack scheme.

RESULTS & DISCUSSION

As MgO(111) is polar surface, we have investigated atomic and electronic structure of monolayer graphene on O-terminated MgO(111) using DFT calculations. Previously, we found that strong chemical bonds are formed between monolayer graphene and O-terminated surface due

to strong interaction. Our calculations showed a tiny density-of-states at the Fermi level for monolayer graphene on O-terminated MgO(111) surface instead of the band gap opening [3].

In this study, adsorption of several carbon atoms on graphene/MgO(111) is considered to control the band gap. For investigation of atomic and electronic structure, we put a carbon atom at the top, bridge, and hollow sites of graphene. As shown in Figure 1, six kinds of adsorption sites are considered: two top sites, two bridge sites, and two hollow sites. Adsorption sites are determined by relative location of carbon atoms in graphene on MgO(111): Adsorption site T_1 is located on the carbon atom of graphene which forms covalent bonds with oxygen atoms of the top layer of MgO(111), as shown in Figure 1.

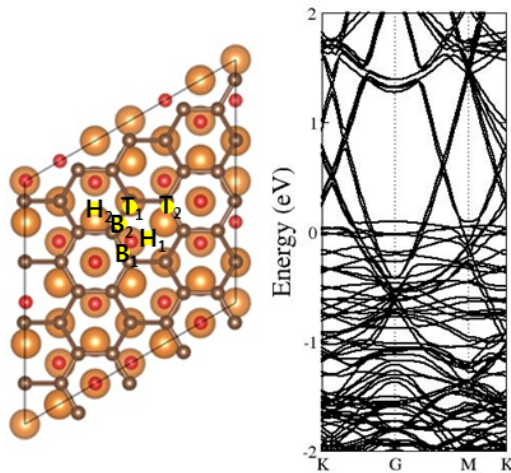


Fig. 1. Adsorption sites of carbon atoms on monolayer graphene/MgO(111) and energy band structure of graphene on O-terminated MgO(111). Two top sites (T_1 and T_2), two bridge sites (B_1 and B_2) and two hollow sites (H_1 and H_2) are considered in this study.

Using the LCAODFTLab simulator in Nanophysics EDISON website, we obtain the energy band structure of monolayer graphene on MgO(111). As shown in Figure 1, some flat linear bands are located near the Fermi level. From our previous work [3], we infer that flat bands are related with tiny density-of-states of monolayer graphene on MgO(111) near the Fermi level. These flat bands come from the carbon atoms in graphene which do not form covalent bonds with

oxygen atoms in the previous work. To suggest the direction of band gap engineering of graphene on MgO(111), we study of adsorption of a carbon atom on graphene/MgO(111).

Adsorption sites	ΔE
Top 1 (T_1)	2.36 eV
Top 2 (T_2)	1.89 eV
Bridge 1 (B_1)	0 eV
Bridge 2 (B_2)	1.77 eV
Hollow 1 (H_1)	2.48 eV
Hollow 2 (H_2)	2.48 eV

Table 1. Adsorption energy differences for several adsorption sites. B_1 is the most stable adsorption site in our calculations. Adsorption sites are shown in Fig.1.

First, we consider two kinds of top sites as shown in Figure 2. While T_1 site is located on carbon atoms in graphene which form covalent bonds with substrate, the carbon atoms of T_2 site does not form. T_2 is more stable adsorption site than T_1 . Energetically, T_2 is about 0.47 eV more stable, as shown in Table 1. We also obtain energy band structure for T_1 and T_2 in Figure 3. Here, we find that flat bands near the Fermi level is changed by adsorption of carbon atom. Especially, when carbon atom is adsorbed on T_2 site, there are no flat bands near the Fermi level in Figure 3(b).

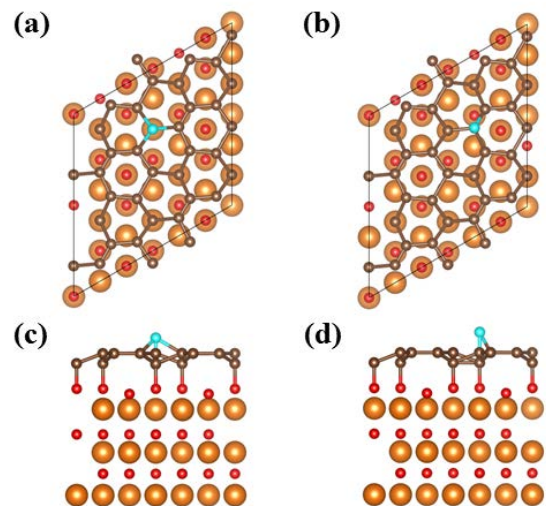


Fig. 2. Carbon atoms adsorbed on top sites of graphene/MgO(111): (a), (c) and (b), (d) are top and side views of T_1 and T_2 structure, respectively.

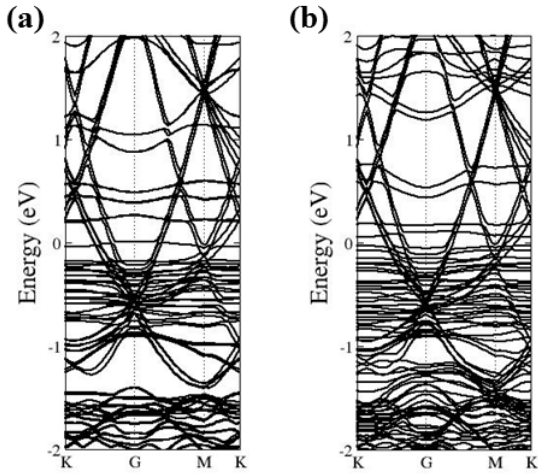


Fig. 3. Energy band structure of carbon atoms which are adsorbed on (a) T₁ and (b) T₂ sites of graphene/MgO(111).

We adsorb a carbon atom on two kinds of bridge sites B₁ and B₂, in Figure 4. In this case, B₁ is farther away from carbon atoms in graphene which have covalent bonds with substrate than B₂. Our calculations show that B₁ is the most stable adsorption sites than others as shown in table 1. Energy band structures of carbon atoms in B₁ and B₂ sites on graphene/MgO(111) are shown in Figure 5. In Figure 5(a) the band structure of B₁ almost unchanged near the Fermi level, while change in the band structure of B₂ is shown in Figure 5(b) compared to the Figure 1.

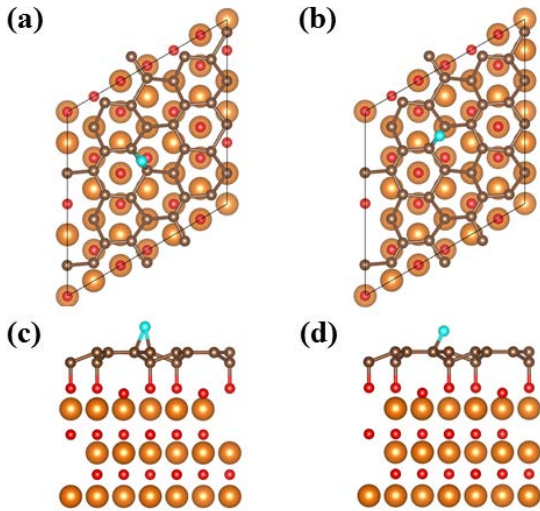


Fig. 4. Carbon atoms adsorbed on bridge sites of graphene/MgO(111): (a), (c) and (b), (d) are top and side views of B₁ and B₂ structure, respectively.

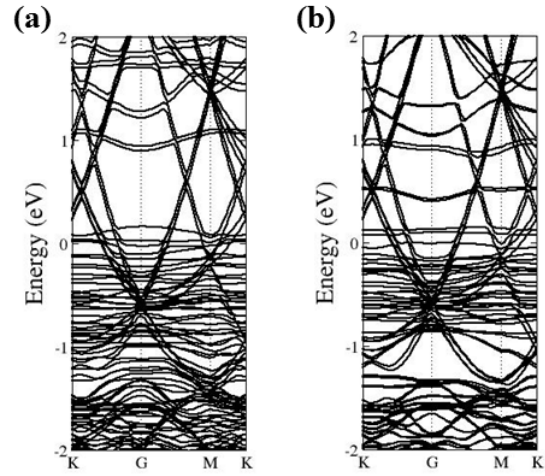


Fig. 5. Energy band structure of carbon atoms which are adsorbed on (a) B₁ and (b) B₂ sites of graphene/MgO(111).

Finally, carbon atoms are adsorbed on two kinds of hollow sites. In this case, carbon atoms are put on the center of carbon ring. Carbon ring below the H₁ site has two carbon atoms which form covalent bonds with MgO(111), while carbon ring under the H₂ site has only one covalent bonded carbon atom. Energetically, there is no energy difference between adsorption of carbon atom on H₁ and H₂ in our calculations. Also, band structures are almost the same near the Fermi level, as shown in Figure 7. In these cases, flat bands are removed near the Fermi level.

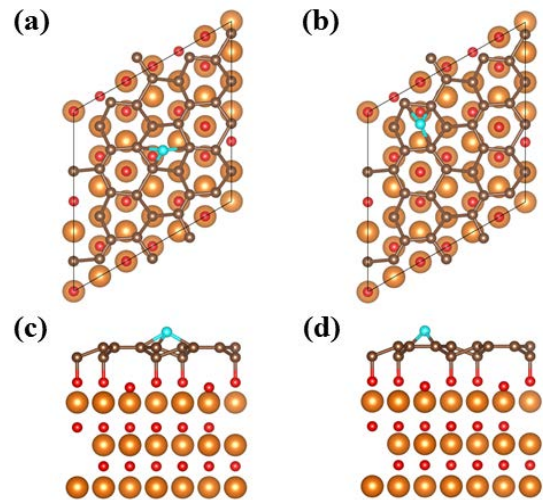


Fig. 6. Carbon atoms adsorbed on hollow sites of graphene/MgO(111): (a), (c) and (b), (d) are top and side views of H₁ and H₂ structure, respectively.

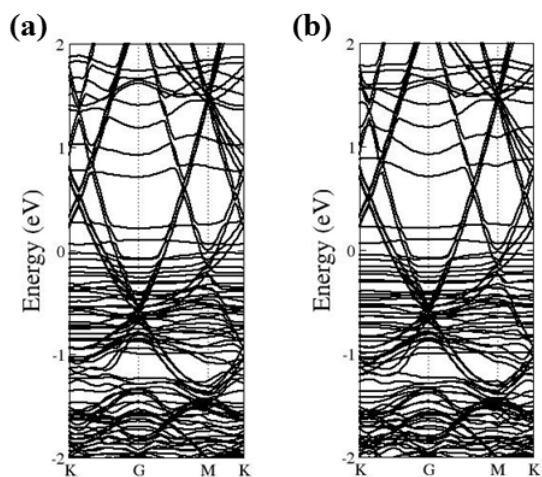


Fig. 7. Energy band structure of carbon atoms which are adsorbed on (a) H_1 and (b) H_2 sites on graphene/MgO(111).

Depending on the adsorption sites, the band structure near the Fermi level can be changed in our calculations. When carbon atoms are adsorbed on the hollow sites (H_1 and H_2) and top site (T_2) on the carbon atoms which do not form covalent bonds with MgO(111), some flat bands are removed near the Fermi level. With this investigations, we may suggest that band gap could be opened in graphene on MgO(111).

CONCLUSION

In this study, we investigated adsorption of carbon atoms on graphene/MgO(111) using DFT calculations to suggest the band gap engineering of graphene/MgO(111). Our calculations show that the band structure of graphene could be changed by adsorption of carbon atoms near the Fermi level depending on the adsorption sites.

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