Electronic structure of B- or N-doped graphene

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In this study, we investigate atomic and electronic structure of graphene with substitutional impurities such as boron or nitrogen atom using density functional theory (DFT) calculations. To investigate the effects of substitutional impurities in graphene, we consider a (6x6) supercell of graphene in our calculations. For detailed electronic properties of graphene, we compare the energy band structure of B- or N-doped graphene with that of pristine graphene.

INTRODUCTION

Graphene is a single atomic layer of carbon atoms corresponding to one layer of graphite. In other words, graphene consists of carbon atoms which are tightly packed into a two-dimensional honeycomb lattice and it is a basic building block for graphitic materials of all other dimensionalities.

In this study, we investigate atomic and electronic structure of graphene with substitutional impurities. We choose boron and nitrogen atoms as substitutional impurities, because they are very similar to the carbon atoms in some aspects. For example, they also undergo sp^2 hybridization like carbon atoms and their atomic radius is nealry the same as carbon atoms.

Graphene have a lot of unique and interesting properties. Especially, it is a gapless semiconductor having a linear dispersion around the Fermi level [1]. Here, we study the variation of energy band structure of graphene depending on the kind and number of doping atoms in reference to previous works [2].

CALCULATION METHODS

In this study, we have performed density functional theory (DFT) calculations within generalized gradient approximation (GGA) for exchange-correlation (*xc*) functional. We obtain atomic and electronic structure of doped graphene using LCAODFTLab simulator in Nanophysics EDISON web site [3] which is supported by SIESTA package based on DFT.

For investigation of electronic structure, a (6x6) supercell of graphene is used in our calculations with a vacuum region of about 10 Å which is enough to neglect the interlayer interaction of graphene, and one or two boron or nitrogen is doped in pristine graphene. For the Brillouin-zone integration, we used the (6x6x1) grid in the Monkhost-Pack scheme.

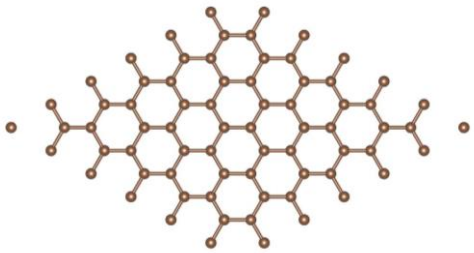

Fig. 1. Atomic structure of a (6x6) supercell of graphene

RESULTS & DISCUSSION

We have studied the atomic and energy band structure of doped graphene by changing one or two carbon atoms into boron or nitrogen atoms. In this study, we basically use a (6x6) supercell of pristine graphene which is shown in Fig.1. For comparison with the band structure of doped graphene, we calculate the energy band structure of pristine graphene. Our calculations show the linear dispersion band structure around the Fermi level as shown in Fig.3(a) and it is well matched with previous experimental and theoretical studies. Here, we calculate the band structure of doping graphene, expecting that the number of electrons affect the energy band structure of graphene.

First, we substitute one carbon atom (C) with a boron (B) or nitrogen (N) atom as shown in Fig.2.

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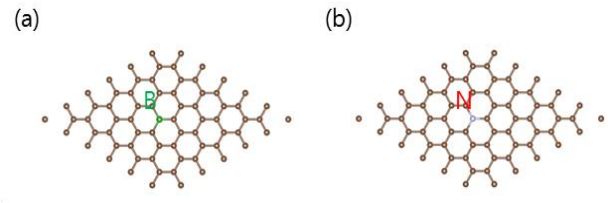

Fig. 2. Atomic structure of (a) B- and (b) N-doped graphene

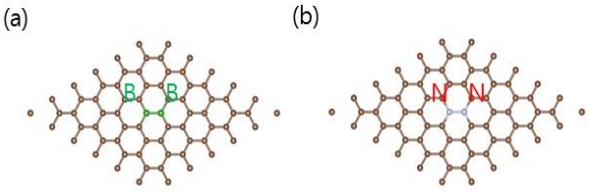

Fig. 4. Atomic structure of (a) two boron atoms (BB) (b) two nitrogen atoms (NN) -doped (6x6) supercell of graphene.

We investigate the energy band structure of B- or N-doped graphene as shown in Fig.3(a) and 3(b). Because boron is a chemical element with atomic number 5, it has one less electron than carbon atom. Our calculations show that the linear energy band is shifted downward by about 0.5 eV from the Fermi level as shown in Fig. 3(b) due to electron-deficient character of boron atom. As a result, B-doped graphene represents p–type characteristics.

In contrast, since nitrogen is a chemical element with atomic number 7, it has one more electron than carbon atom. In this case, the linear energy band is shifted upward by about 0.6 eV from the Fermi level as shown in Fig. 3(c). Thus, N-doped graphene represent n-type characteristics because of electron-rich character of nitrogen atom.

Finally, we substitute two carbon atoms in a (6x6) supercell of pristine graphene with two other elements. First, two boron atoms (BB) are doped in graphene as shown in Fig. 4(a). Compared to pristine graphene, BB-doped graphene is two electron deficient one.

In the energy band structure of BB-doped graphene, the linear energy band is shifted by about 0.5 eV below the Fermi level, representing p-type characteristics which is shown in Fig. 5(a). Interestingly, the band gap (~0.17 eV) is opened in this case.

Second, two nitrogen atoms (NN) is doped in graphene as shown in Fig.4(b). NN-doped graphene has two more electrons than pristine graphene. In this case, the linear energy band structure of NN doped graphene is shifted by about 0.5eV above the Fermi level and the band gap (~0.13 eV) is also opened as shown in Fig. 5(b).

Third, we change two carban atoms into boron and nitrogen atoms as shown in Fig.6. Boron atom is one electron deficient and nitrogen atom is one electron rich element, compared to carbon atom. Then, we expect that if we substitute two carbon atoms with one boron and one nitrogen atoms, the total number of electrons in doped graphene is the same as that in pristine graphene. Therefore, we might assume that the energy band structure of the doped case is similar to that of pristine graphene.

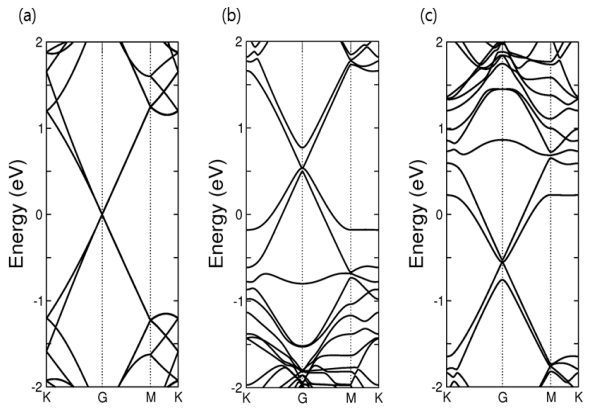

Fig. 3. Energy band structure of (a) pristine graphene, (b) B-doped graphene and (c) N-doped graphene. Fermi level is set to 0 eV in all band structures.

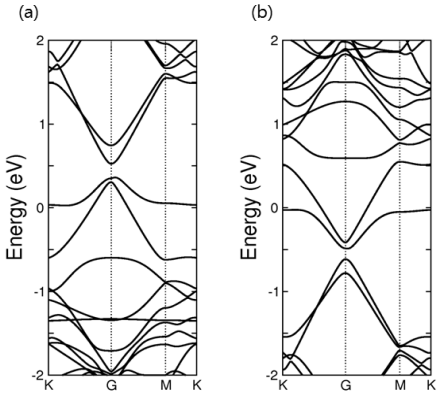

Fig. 5. Energy band structure of (a) two boron atoms (BB) and (b) two nitrogen atoms (NN)-doped graphene

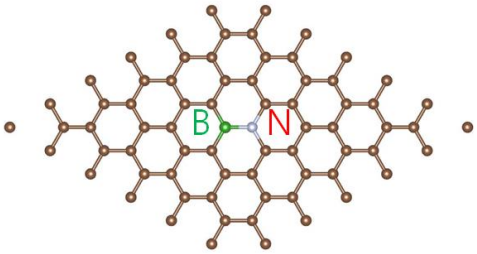

Fig. 6. A (6x6) Supercell of graphene which change two carbon atoms into boron and nitrogen atom.

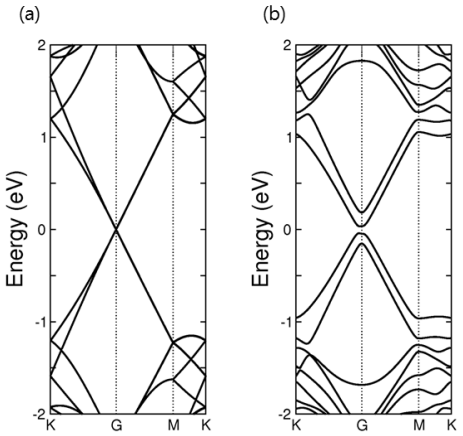

Fig. 7. Energy band structure of (a) pristine graphene and (b) BN-doped graphene

However, there are distinct differences in energy band structure between pristine graphene and BN-doped graphene. The Fermi level of BN-doped graphene is nearly the same as that of pristine graphene. But the small band gap (~0.08 eV) is opened as shown in Fig.7(b) and the linear energy band at the Dirac point is splitted because of the effect of doping atoms.

CONCLUSION

We investigated the effect of impurity substitution such as boron or nitrogen in pristine graphene using density functional theory (DFT) calculations. In this study, we compared differences in electronic energy band structure between pristine graphene and doped graphene.

As a result, the Fermi levels of B-doped and BB-doped graphene are shifted downward, and those of N-doped and NN-doped graphene are shifted upward depending on the number of electrons involved in energy band structure. For the two-atom substitutional cases, the band gap is opened.

ACKNOWLEDGEMENT

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