

Tuning semiconducting property of bilayer graphene by ionic molecules

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1. Introduction

Ever since the first exfoliation in 2004, graphene has been keeping a premier position not only in the field of the low-dimensional sciences but also in the electronic device engineering due to its unique structural and electronic properties. However, graphene is a metal with a pair of linear dispersion band at the Fermi level, so that they are not utilized in logical electronic devices. Therefore, it is important to tune the electronic structure and to get a semiconducting graphene. Several efforts have been made to control the band-gap of graphene, such as electric field or chemical doping. In this work, we propose a new and easy recipe to get an semiconducting graphene and to control the conducting properties of resultant semiconducting graphene by applying the ionic materials to two surfaces of graphene. Our first-principles calculations show that bilayer graphene sandwiched by the anion and cation molecules is a semiconductor with 0.3 eV band-gap due to the strong local dipole field induced by cation-anion pair. Furthermore, we can control the semiconducting carrier type of bilayer graphene sandwiched by ionic molecules: i-type (intrinsic), n-type or p-type by changing pair of cation and anion molecules.

2. Methods

All theoretical calculations have been performed based on the density functional theory. We use the local density approximation (LDA) to express exchange-correlation energy. The valence wave function is expanded in terms of the plane wave basis set with the cutoff energy of 25 Ry [1]. We considered a slab model in which bilayer graphene sandwiched by three different pairs of anion and cation of ionic molecules, as shown in Fig. 1. Here, we used 6x6 lateral periodicity of graphene. To avoid the spurious dipole interactions with the image slabs, we adopt the effective screen medium method [2] and a 12-Å vacuum region.

3. Results and Discussion

Figure 2a shows the electronic energy band of bilayer graphene sandwiched by tetrafluoroborate (BF_4^-) anion and 1-ethyl-3-methyl pyrrolidinium cation (S1 structure). It

should be noted that the K point (Dirac point) are folded into the Γ point because of 6x6 lateral periodicity of graphene. We find that finite energy gap of 0.3 eV between conduction and valence bands around the Γ point. This gap value is larger than those obtained by extremely high external electric field [3] or chemical doping [4]. Furthermore, in this case no state of ionic molecules lies within the band gap of bilayer graphene. Thus, bilayer graphene sandwiched by cation and anion molecules is an intrinsic semiconductor.

To clarify the physical origins of band-gap opening, we analyzed the electrostatic potential profile in detail. Figure 2b shows the average electrostatic potential along the z axis (normal to the graphene layer) of bilayer graphene sandwiched by the tetrafluoroborate (BF_4^-) anion and 1-ethyl-3-methyl pyrrolidinium cation. We found that there is a difference (5 eV) in the averaged value of electrostatic potential at the cell boundaries of anion and cation molecules, that originates from the dipole of anion-cation pair. This results induces a local electric field at the bilayer graphene. The onsite energy difference between two graphene layers is about 0.75 eV, leading to the finite gap as in the case of applied external electric field [3].

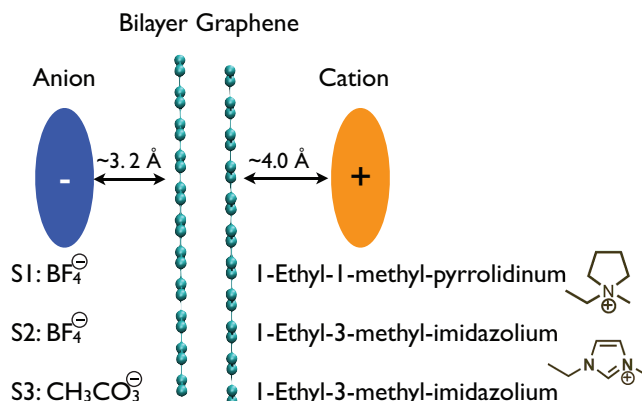


Fig. 1 A structural model of bilayer graphene sandwiched by anion and cation molecules: (S1) tetrafluoroborate (BF_4^-)/1-ethyl-1-methyl pyrrolidinium, (S2) tetrafluoroborate (BF_4^-)/1-ethyl-3-methyl imidazolium, and (S3) methylcarbonate (CH_3CO_3^-)/1-ethyl-3-methyl imidazolium.

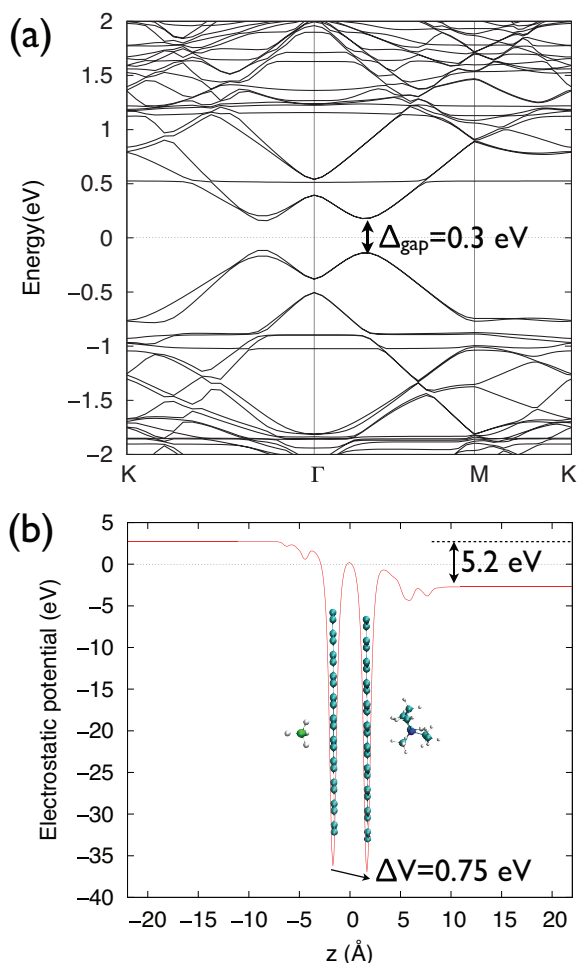


Fig. 2 (a) Electronic energy band, and (b) Average electrostatic potential profile along z axis of bilayer graphene sandwiched by tetrafluoroborate (BF_4^-) anion and 1-ethyl-1-methyl pyrrolidinium cation (S1 structure).

Another interesting issue is how the pair of cation and anion molecules affect on the band-gap or semiconducting property of sandwiched bilayer graphene. Thus, we next investigated the electronic structure of bilayer graphene sandwiched by other anion-cation pairs. Figure 3 shows the energy band of bilayer graphene sandwiched by tetrafluoroborate (BF_4^-) anion/1-ethyl-3-methyl imidazolium cation (S2 structure), and by methylcarbonate (CH_3CO_3^-) anion/1-ethyl-3-methyl imidazolium cation (S3 structure). We find that both sandwiched bilayer graphene also has a semiconductor with a band-gap as in the case of S1 structure. However, the Fermi energy level is shifted into the valence band (Fig. 3a) or the conduction band (Fig. 3b) of bilayer graphene. These results indicate the charge transfer from and to bilayer graphene to the lowest unoccupied molecular (LUMO) state and the highest occupied molecular (HOMO) state of ionic molecules. Thus, the sandwiched bilayer graphenes are both p-type doped or n-type doped semiconductors. In other word, we can tune the carrier type of bilayer graphene semiconductor by controlling the ionic molecule species. Therefore we conclude

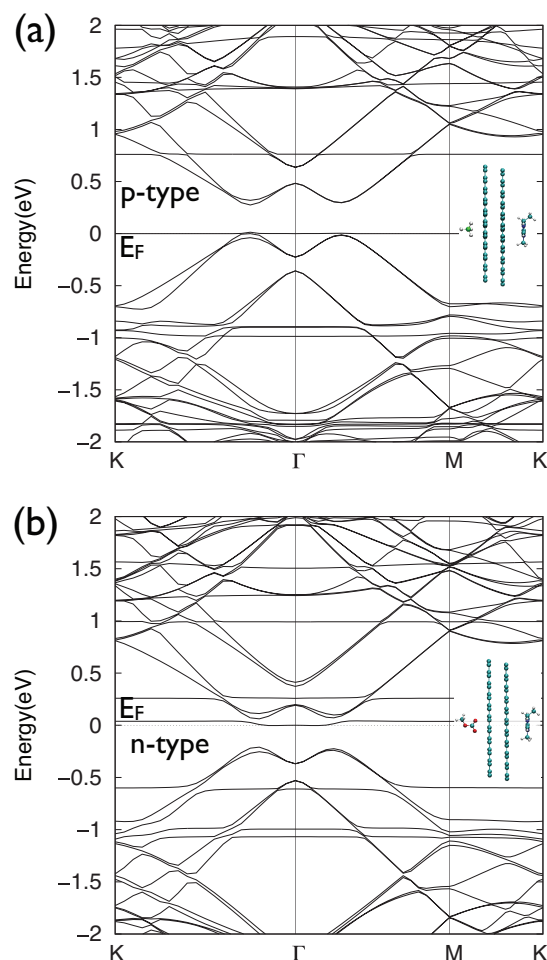


Fig. 3 Electronic energy band of bilayer graphene sandwiched by (a) tetrafluoroborate (BF_4^-) anion and 1-ethyl-3-methyl imidazolium cation (S2 structure), and (b) Methylcarbonate (CH_3CO_3^-) anion and 1-ethyl-3-methyl imidazolium cation (S3 structure).

that the bilayer graphene applied the ionic molecules are applicable for the constituent for the switching electronic devices.

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