Tunable band gap in half-fluorinated bilayer graphene under biaxial strains

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Abstract
Opening and tuning of the band gap of bilayer graphene (BLG) is of particular importance for its utilization in nanoelectronics. We presented herein the electronic structures of two types of stoichiometrically half-fluorinated BLGs (i.e., C2Fs) as well as those under biaxial compressive and tensile strains. Our results reveal that both C2Fs are semiconductor with large direct band gaps in their unstrained configurations. Under biaxial compressive strains, the band gaps of both C2Fs can be reduced. However, by applying biaxial tensile strains, both C2Fs undergo a direct-to-indirect band gap transition. Electronic nature of the strain-tuned band gaps has been discussed.

Keywords:
Bilayer graphene
Biaxial strain
Tunable band gap
Direct-to-indirect gap transition

Graphene’s unique band structure has led to a host of fascinating phenomena, exemplified by massless Dirac fermion physics [1–3] and anomalous quantum Hall effect [4–7]. Available studies suggest that the valence and conduction bands of graphene exhibit a linear dispersion degenerate near the so-called Dirac point, resulting in the effectively massless Dirac fermion character of the carriers [8]. With one more graphene layer added, BLG has an entirely different (and equally interesting) band structure [9] but still possesses a zero band gap that in some way limits its utilization in modern device physics and nanotechnology.

To date, surface passivation such as hydrogenation [10–14] and fluorination [15–18] has attracted much interest due to its ability to create finite band gaps for single layer graphene (SLG) and BLG, enabling their potential applications in nanoelectronics and nanophotonics. In the case of SLG, it has been reported that the fully fluorinated and hydrogenated SLG could exhibit semiconducting behavior with large direct band gaps of about 3.0 [15–17,19,20] and 3.5 eV [11–13], respectively. Bringing the fluorinated SLG up to the level of technological application, the fluorinated SLG has been proved to be a good counterpart of Teflon [20], a possible channel proving to be a good counterpart of Teflon [20], a possible channel in design and optimization of the graphene-based devices [9]. Such wide strain-tunable band gaps of the C2Fs, if realized, will promise their highly flexible application in these areas and especially the ultraviolet photodetectors [31]. Additionally, the direct-to-indirect band gap transition in the C2Fs is also expected to provide some guidance in their optoelectronic applications.

The present calculations have been performed by using the Vienna ab initio simulation package (VASP) [32,33], which is based on the density functional theory, the plane-wave basis and the projector augmented wave (PAW) representation. The exchange–correlation functional is treated within the local density approximation (LDA) [34,35]. The wave functions are expanded by plane waves with a kinetic energy cutoff of 450 eV. The Brillouin zone integrations are approximated by using a special k-point sampling of the Monkhorst–Pack scheme [36] with a 15 × 15 × 1 Γ-centered grid. All the calculations are modeled by a (1 × 1) unit cell (consisting of four C and two F atoms, half-fluorinated) with a vacuum...
space of 20 Å in Z-direction to avoid the interactions between adjacent BLGs (see also Fig. 1). All the atomic configurations are fully relaxed until the Hellmann–Feynman forces on all the atoms are smaller than 0.01 eV/Å. Our spin-polarized calculations show that C2F is rather insensitive to the spin-polarized effect, therefore, all of the following calculations are based on the non-spin-polarization scheme.

Despite the electronic energy gap is of great importance for BLG to be exploited in nanoelectronics and nanophotonics, switching off the conductivity to a desirable level remains challenging in epitaxial graphene [37]. In this regard, it is of particular interest to investigate the electronic properties of AB-C2F and AA-C2F modulated by applying biaxial strains. The calculated band structures of the two unstrained C2Fs, and those modulated by applying biaxial strains are summarized in Fig. 2a and b, where the valence band maximums (VBMs) of both unstrained C2Fs are chosen as the reference energies (i.e., 0 eV), respectively. In Fig. 2, the D- and E-points are just the energy levels of the lowest conduction bands of AB-C2F at Γ and M points, respectively. It is shown from Fig. 2 that both unstrained AB-C2F and AA-C2F are analogous in their band structures and exhibit direct band gaps. What is more, their band structures are still analogous to each other when they are loaded with biaxial strains, either compressive or tensile. By applying biaxial strains, the band gaps of AB-C2F and AA-C2F are found to be gradually diminished and transformed from semiconductor to metal at the compressive strain around 17% (see left two panels of Fig. 2a and b, respectively). However, by applying biaxial tensile strain, the band gaps of both C2Fs are found to be scarcely changed in magnitude but undergo the direct-to-indirect transition (see right two panels of Fig. 2a and b, respectively).

In order to have a microscopic understanding of the changes of the band gaps under biaxial strains, the partial densities of states (PDOS) of AB-C2F under −10%, 0% and 10% biaxial strains are given in Fig. 3a–c, respectively. Moreover, the evaluated band and k-point partial decomposed charge densities at the specified points (e.g., D, VBM, E points in Fig. 2) of the unstrained AB-C2F are presented in Fig. 3d–f, respectively. For the unstrained AB-C2F, as can be seen from Fig. 3d and e, the conduction band minimum (CBM, i.e., the D-point) is dominated by the pₓ–pᵧ antibonding states of Cₓ–F atoms and interlayer Cₓ–Cₓ atoms. However, VBM is mainly contributed by the pₓ–pᵧ bonding states of C–C atoms in each graphene layer and by those of F–F atoms in each Fluorine layer, with no s- or p-states involved (see Fig. 3b and e). Therefore, the VBM of AB-C2F is mainly sensitive to interactions between the x-y planar electronic orbitals while the CBM is only sensitive to the interactions between the electronic orbitals in the Z-direction. Indeed, from Fig. 3a–c, it is revealed that the energy of D-point is almost indifferent to the biaxial compressive strain, which is attributed to the flexibility of the Cₓ–F and interlayer Cₓ–Cₓ bonds along the Z

Table 1

<table>
<thead>
<tr>
<th>C2F</th>
<th>a</th>
<th>dₓ–C</th>
<th>lₓ–C</th>
<th>dₓ–F</th>
<th>lₓ</th>
<th>Eₓ</th>
<th>E₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB-C2F</td>
<td>2.55</td>
<td>1.54</td>
<td>1.54</td>
<td>1.36</td>
<td>0.50</td>
<td>4.04</td>
<td>21.55</td>
</tr>
<tr>
<td>AA-C2F</td>
<td>2.52</td>
<td>1.54</td>
<td>1.55</td>
<td>1.36</td>
<td>0.51</td>
<td>3.94</td>
<td>21.51</td>
</tr>
</tbody>
</table>

Fig. 1. Side and top views of (a) AB-C2F and (b) AA-C2F, with unit cells shown by blue rhombuses. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
direction, since the bonds of C−F and CA−CX can adjust themselves easily along with the biaxial compressive strains. On the other hand, VBM is greatly influenced by the biaxial compressive strain, as seen from Fig. 3e, bonding between the px−py orbitals of C−C atoms in each graphene layer and of F−F atoms in each fluorine layer will be strengthened by the compressive strains. This directly leads to the increase of the band-width of energy band around the VBM and consequently an upward shift of VBM in Fig. 2. Accordingly, the band gap of AB-C2F is gradually reduced along with the increasing compressive strain and transforms from semiconducting to metallic when the compressive strain is large enough (about −17%). However, because of the strong interatomic bonding in the graphene layers, the −17% compressive strain maybe too much than normal and might be unable to be realized in experiment at the moment, therefore, the value of strain −17% presented here is just a theoretical prediction.

Under the biaxial tensile strain, it is suggested that the AB-C2F changes from a direct-gap to an indirect-gap semiconductor, as shown in the right two panels of Fig. 2a. The calculated CBM is located at Λ-point for the unstrained AB-C2F, however, it is transferred to the M-point when the loaded biaxial tensile strain is larger than about 5%. To explain such a phenomenon, the understanding of electronic states at E-point, as highlighted by red1 solid circles in Fig. 2a, is of great importance. Based on our calculations on the site projected wave function character for each band, the

**Fig. 2.** Band structures of (a) AB-C2F and (b) AA-C2F in the unstrained configurations (0%) and those loaded with the biaxial compressive (−17% and −10%) and tensile strains (5% and 10%). The zero energies in (a) and (b) are set to the VBMs of the unstrained AB-C2F and AA-C2F, respectively.

**Fig. 3.** PDOS of the AB-C2F under biaxial strains of (a) −10%, (b) 0%, and (c) 10%, respectively, and the evaluated band and k-point decomposed charge densities for the unstrained AB-C2F at (d) D-point, (e) VBM and (f) E-point (see Fig. 2). The zero energy is set to the VBM of unstrained AB-C2F.

1 For interpretation of color in Figs. 2 and 4, the reader is referred to the web version of this article.
explain why the band gap of AB-C2F is larger than that of AA-C2F. From Fig. 4, by comparing the density of contour lines between the bonded atoms, it suggests that the intralayer sp^3 C–C covalent bonds in both C2Fs are strengthened by the biaxial compressive strains but weakened by the biaxial tensile strains, while the C–F bonds are found to be almost indifferent to the biaxial strains. In summary, first-principles DFT calculations have been performed to study the electronic properties of two C2Fs under different biaxial strains. Results show that both AB-C2F and AA-C2F in their unstrained configurations are semiconducting with large direct band gaps of about 4.04 and 3.94 eV, respectively. Nonetheless, their band gaps are shown to be modulated by applying biaxial strains. That is, the biaxial compressive strains are shown to reduce their band gaps and could transform them from semiconductor to metals. However, under biaxial tensile strains, both C2Fs are found to be able to undergo direct-to-indirect band gap transition. Therefore, it is suggested that the electronic band gap of BLG can be opened through fluorination and tuned simply by applying biaxial strains, which might be of special importance for the utilization of BLG in nanoelectronics and nanophotonics.

Acknowledgments

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References


Fig. 4. Deformation charge densities of the (1210) planes of (a)-(c) AB-C2F and (d)-(e) AA-C2F, with biaxial strains of 10%, 0% and 10%, respectively.

To see the bonding characters in both C2Fs and those loaded with biaxial strains, the corresponding deformation charge densities of the (1210) plane are shown in Fig. 4, where the range and interval of the charge density contours are all the same in the six panels. The deformation charge density is defined as Δρ(Γ) = ρ(Γ) - ∑ρ_{atom}(Γ - R), where ρ(Γ) represents the total charge density of C2F and ∑ρ_{atom}(Γ - R) the superposition of atomic charge densities. Charge accumulation is depicted by orange solid lines, and charge depletion is shown by blue dashed lines. From Fig. 4, it can be seen that the C–C bonds are covalent and the C–F bonds are mainly ionic mixed with covalent for both the unstrained C2Fs and those loaded with biaxial strains. In their unstrained configurations (Fig. 4b and c), the intralayer C–C covalent bonds of AB-C2F and AA-C2F are almost in the same strength, as well as the case of C–F bonds. But the interlayer C–C covalent bonds of the AB-C2F are a bit stronger than those of the AA-C2F, attributed to the shorter interlayer C–C bond lengths in the AB-C2F than those in the AA-C2F (see Table 1). Such bonding characters can also be opened through fluorination and tuned simply by applying biaxial strains, which might be of special importance for the utilization of BLG in nanoelectronics and nanophotonics.