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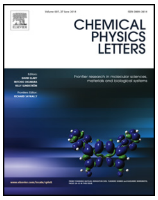

Editor's choice

Band gap modulation of bilayer graphene by single and dual molecular doping: A van der Waals density-functional study

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ABSTRACT

Density functional calculations including long-range dispersion effects demonstrate that non-covalent doping with an electron donor acceptor couple of molecules can open an energy gap in a bilayer graphene. The band gap modulation can be controlled not only by the choice of adsorbed molecules (n-dopant versus p-dopant) but also by their concentration. A deep analysis of the charge transfer reveals that charge redistribution in bilayer graphene is the key issue for gap opening, due to the induced inversion symmetry breaking. The dual molecular non-covalent doping mode can achieve the opening of a gap up to 138 meV.

1. Introduction

Graphene has unique electronic transport [1,2], mechanical [3], and optical [4] properties that exhibit extraordinary potential for nanoelectronic applications [5–8]. However, pristine graphene, in the monolayer (MLG) or bilayer (BLG) states, is a gapless semimetal, thus limiting its applications in electronic nano-devices. Therefore, considerable efforts have been made to open band gaps in MLG or BLG. Both theoretical and experimental studies have demonstrated that a band gap can appear in the Bernal-stacking (AB-stacking) BLG, by breaking inversion symmetry [9–15], by applying an external electric field for instance [16–18], by breaking in-plane symmetry [19], by applying different homogeneous strains to the two layers [20] or by varying the interlayer spacing [21]. Molecular doping is also an alternative by provoking asymmetric charge distribution in graphene layers. In a non-covalent doping process of graphene, the carrier concentration, which is a key feature for electronics, can be controlled by the concentration of the adsorbed molecules, without introducing significant lattice deformation [22–25]. Currently, graphene growth process only allows molecular dopants to be absorbed on the topside of the graphene layers, although intercalation cannot be completely excluded. The bottom layer is usually doped by traditional substrates [26] or by specifically modified ones [27], see Refs. [28–30] for BLG cases.

Theoretically speaking, to yield accurate description of interlayer distances, to correctly describe the non-covalent interaction between graphene layers and charge transfer complexes in the density functional theory (DFT) framework it is mandatory to include nonlocal effects [31]. In previous theoretical reports on BLG doping, van der Waals forces are not explicitly taken into account [12,32], since traditional exchange-correlation functionals missed them. In this work we have used the so called van der Waals density functional (vdW-DF) [33–35], which has been successfully applied on layered [36,37] as well as on some molecular systems [38].

In this study, we report the doping of a Bernal-stacking BLG by several organic electron donor acceptor molecules as function of their adsorption modes. If one type of molecule (acceptor or donor) is adsorbed on a single side of the BLG, it corresponds to a single molecule doping mode. When at the same time, top and bottom layers are in interaction with a n-dopant and p-dopant, respectively, this hypothetical situation is called dual molecules doping mode throughout the article. Despite any experimental results on this specific setting have not been yet reported in the literature, one could imagine a three-steps procedure to realize it. By choosing first an appropriate molecule or atoms (donor or acceptor) that can easily intercalate between graphene layers or between a graphene layer and the substrate [39], and then by soft washing, some dopants should still remain bound on the downside of the BLG, due to larger binding energies. Finally, a dopant's solution with opposite character should be deposited, to transfer charge from/to the upper graphene layer. This setting also mimics in a sense the effect of an applied perpendicular electric field on the BLG by creating a dipole moment on an atomic length-scale. This directly relates to experimental works of Refs. [26,27].

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By using DFT calculations, we report that dual molecular doping can induce the opening of a significant band gap. It can be controlled as well as the carrier concentration, in a wider range by dual mode doping. As a consequence, a fine-tuning through the threshold voltage of the electronic conduction properties, that is a crucial issue for electronics application, is potentially achieved.

2. Method

We have studied a doped BLG system, in AB-stacking only, using periodic boundary condition within the supercell approach, with a vacuum region larger than 1.5 nm to avoid interaction between the periodic images. The calculations have been performed using the VASP code [40] with the Projected Augmented Wave (PAW) [41] pseudopotentials. The vdW-DF [42] functional is used for correlation and PBE for exchange [43]. An energy cutoff of 400 eV and care about *k*-point sampling have been taken to ensure energy convergence below few meV. The *k*-point grids are 3 × 3 × 1 for large cells and 7 × 7 × 1 for the smaller cells. The convergence criterion for calculations is that the force on each atom is smaller than 0.02 eV $Å^{-1}$. The Bader Charge Analysis method is used to estimate the charge transfer, using the program of G. Henkelman's group [44]. BLG is modeled either by a cell containing two (7 × 7) monolayers (98 carbon atoms each layer) or two (4 × 4) monolayers (32 carbon atoms each layer). It allows to discuss concentration's effects, with three possible concentrations: one molecule per 196 carbon atoms (0.51%) see Fig. 1, one molecule per 64 carbon atoms (1.56%) and one donor and one acceptor molecule per 196 carbon atoms (1%). These concentrations correspond to standard experimental settings of graphene molecular doping [45], and allow to avoid interaction between adsorbates within periodic boundary conditions. Three organic molecules, tetracyanoethylene (TCNE), tetrathiafulvalene (TTF), tetrakis(dimethylamino)ethylene (TDAE), are employed as dopant. As in Ref. [24], we have investigated all the possible adsorption sites on the BLG models, in terms of energetic and geometric aspects. They are very similar to the monolayer case, with very small energy differences between adsorption sites. Moreover the charge transfers from the different configurations are almost equal, as reported in a previous study [15]. Thus only structures, which minimize the total energy, are taken into consideration in the following.

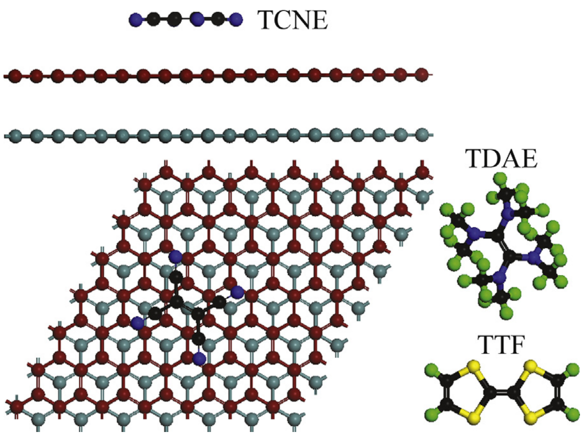

Fig. 1. Schematic view of three molecules adsorbed on a Bernal BLG. For an easier visualization, the carbon atoms of the two layers of BLG are in brown (upper layer) and cyan (bottom layer) respectively, while molecular carbon atoms are in black. Hydrogen atoms are in green, nitrogen in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

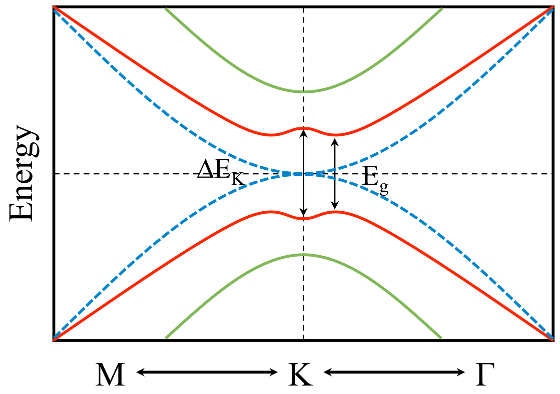

Fig. 2. Schematic band structure model of doped BLG close to the *K* point showing the "Mexican hat" dispersion (red lines). The dashed curves represent the quadratic dispersion of pristine BLG. The black dashed line corresponds to the Fermi level. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Electronic band structure of BLG

Accurate description of the band structure of pristine BLG is a prerequisite for a discussion of doped BLG electronic structures. In the Bernal stacking, pristine BLG band structure near the special K point of the reduced Brillouin zone, shows a quadratic dispersion, see Fig. 2. The $\boldsymbol{\pi}$, $\boldsymbol{\pi}^*$ states and two lower energy bands are split in each valley by interlayer coupling [9,13], as in Fig. 3a which shows the DFT results. Two bands stand for the highest occupied $\boldsymbol{\pi}$ orbitals and the lowest unoccupied $\boldsymbol{\pi}$ orbitals (dashed blue). The corresponding electron and hole effective masses are calculated to be $0.045m_0$ and $0.056m_0$. These values agree very well with previous DFT estimates [15], but overestimate slightly experimental ones [46]: 0.041 and $0.036m_0$, respectively. The bands in green correspond to the two next levels. When the BLG is doped, a gap at the Dirac point *K* can appear (defined as $\boldsymbol{\Delta}E_K$) whereas the minimum separation between the bands is E_g. E_D can be defined as the energy difference between the middle of the band gap at K point and the Fermi level of the system. Thus, E_D, E_g and $\boldsymbol{\Delta}E_K$ are equal to 0 for pristine BLG. Meanwhile, a doped BLG will possess the "Mexican hat" dispersion, the band gap (E_g) is no longer null. Moreover the energy level of the Dirac point can be shifted due to charge transfer.

3.2. Single molecular doping

3.2.1. Electron donor molecule doping

Band structures in Fig. 3c indicate that TTF's adsorption doesn't affect electronic structure of BLG except an upshift of Fermi level with an E_D value of 251 meV. This is in contradiction with the reported band gap of 80 meV [15]. One could first attribute this discrepancy to a concentration effect, since we have 1 TTF molecule per 98 C atoms, when 72 C atoms were used in Samuels' work. However when the concentration is increased, we only observe a larger shift of the Fermi level, without gap opening. So we may attribute this difference, to the different computational settings used and possibly to the exchange-correlation functional choice. The HOMO-derived state of the TTF molecule hybridizes with one of low-energy bands of the former Dirac crossing point. The charge transfer between the TTF molecule and the BLG is small 0.1 and 0.02 e depending on the concentration, as shown in Table 1.

One could expect that a stronger electron donor should be able to open a gap in a BLG. Since TDAE molecule has a low ionization energy that approaches those of alkali atoms [47,48] it should provide more electronic density to the carbon substrate than TTF