Bandgap Opening of Bilayer Graphene by Dual Doping from Organic Molecule and Substrate

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ABSTRACT: The lack of a bandgap limits the application of pristine graphene in logic circuits and photonic devices. Breaking the inversion symmetry in bilayer graphene (BG) by charge transfer doping is a promising way to open a bandgap. In this work, a sizable bandgap is created in BG by the opposite doping from organic molecule and substrate. Our first-principles calculations have quantitatively identified that BG is n-doped in the N,N-dimethyl-p-phenylenediamine/BG (DMPD/BG) system while it is p-doped in the tetracyanoethylene/BG (TCNE/BG) system. The opposite p-doping from amorphous SiO$_2$ substrate with O$_2^-$ on its surface (a-SiO$_2$-p) increases the bandgap of DMPD/BG from 106 to 253 meV. Similarly, the bandgap of TCNE/BG is enhanced from 98 to 211 meV by the opposite n-doping from Si-terminated 4H-SiC(0001) with a C buffer layer (C-SiC-n). Moreover, the molecular level of DMPD and a-SiO$_2$-p related states locate below the opened bandgap, while the molecular levels of TCNE and C-SiC-n induced states lie above the bandgap. The increased bandgap without the intergap states should really improve the on/off current ratio of BG-based electronic devices. Meanwhile, the high carrier mobility is largely maintained due to the weak interaction at the interface. Thus, this work provides the scientific basis for further development in BG-based electronic devices.

1. INTRODUCTION

Since graphene was discovered by Novoselov et al. through the micromechanical cleavage from graphite, it has attracted considerable attention for fundamental investigations and potential applications due to its intriguing structural, electronic, and transport properties. In particular, owing to its two-dimensional honeycomb structure and atomic π orbitals normal to the sheet, the conduction and valence bands touch at the Dirac points in the six corners of the hexagonal Brillouin zone, and the low-energy excitations are massless Dirac fermions near the Dirac points. These properties lead to extremely high carrier mobility ($\mu$) up to $2 \times 10^6$ cm$^2$/V s in graphene, which associated with the long phase coherence length makes graphene an ideal material for future nanoelectronics. However, due to the absence of a bandgap, pristine graphene devices have a low on/off current ratio and thus cannot be switched off effectively. Thus, creating a bandgap in graphene to increase the on/off current ratio is at the heart of its application for logic circuits and photonic devices.

Up to now, several methods have been suggested to open a bandgap in mono- or bilayer graphene (BG), such as lateral quantum confinement, hydrogenation, and breaking the inversion symmetry in BG. Lots of studies on graphene nanostructures have demonstrated that a sizable bandgap can be expected only if their sizes are less than 10 nm in at least one dimension. Nevertheless, the reliable fabrication of such small structures with smooth edges, well-defined shapes, and controlled edge configurations is still a challenge. Additionally, $\mu$ in graphene nanostructures is limited by the strong edge scattering. By changing the hybridization state of C atoms from sp$^2$ to sp$^3$, hydrogenation of graphene removes the conducting π bands and opens a large bandgap, which however drastically reduces $\mu$. In contrast, breaking the inversion symmetry in BG is a more promising way to generate a bandgap, which can be realized by applying an external electric field normal to the graphene sheet or by charge transfer doping from adsorbed organic molecules or metallic atoms. For the case of the former, to achieve a high on/off current ratio in BG-based field effect transistor, a large bias needs to be applied to the top and bottom gates both. From a device design point of view, the control of a transistor’s electrical conductivity by single gate is more facile. On the other hand, the gate bias is usually confined by the limited strength of gate dielectric stacks. Fortunately, the charge transfer doping by organic molecules or metallic atoms can produce an interlayer electric field, leading to a significant bandgap opening in a similar way as applying a gate bias. Generally, the distribution of metallic atoms on graphene surface is inhomogeneous due to their clustering, which brings charged impurities and causes serious reduction of $\mu$. This clustering can be avoided by molecular doping due to the repulsion among the charged organic molecules. Meanwhile, since the adsorption of organic molecules does not significantly impair the π-bonding networks of graphene, the

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high \( \mu \) value can be largely maintained. Therefore, the bandgap opening in BG by charge transfer doping from organic molecules has been extensively investigated in experiments, although the corresponding theoretical work is less.

For molecular doping, organic molecules are usually deposited on the top graphene layer only, and thus the bandgap opening is limited. If an opposite doping is introduced into BG through the bottom layer, the two layers should carry different types of charge. As a result, the interlayer electric field can be significantly enhanced, which should increase the bandgap opened originally by charge transfer doping from organic molecules. Actually, with all atoms on the surface, the properties of graphene are strongly influenced by not only the adsorbed organic molecules but also the supporting substrate. It has been revealed by ultraviolet angle-resolved photoemission spectroscopy and theoretical calculations that epilayer graphene layers on SiC(0001) suffer from intrinsic n-type doping.\(^{22,23,24}\) Contrarily, graphene on the widely used amorphous SiO\(_2\) (a-SiO\(_2\)) substrate is p-doped, when the O\(_2\)/H\(_2\) moisture species are adsorbed at the interface between BG and a-SiO\(_2\).\(^{25,26}\) The systematic experiments by Ryu et al. have suggested that O\(_2\) can bind to the 3-fold-coordinated Si atoms at a-SiO\(_2\) surface to form the anion O\(_2^-\), which brings out the p-doping of BG.\(^{27}\) After extended desorption of these gases, BG becomes slightly n-doped.\(^{28}\) Therefore, it should be possible to further increase the opened bandgap of BG by an additional doping from a suitable substrate.

Motivated by the above considerations, we use first-principles method to investigate the bandgap opening of BG by dual doping from organic molecule and substrate. Herein, two model systems are considered, namely, N,D-dimethyl-p-phenylendiamine (DMPD) on BG supported by a-SiO\(_2\) substrate with O\(_2^-\) at the interface and tetracyanoethylene (TCNE) on BG supported by SiC(0001) with a C buffer layer, where DMPD and TCNE are the well-known n- and p-type dopants, respectively. The individual effect of organic molecule and substrate on the electronic properties of BG is first investigated. Following this, the joint effects of DMPD and a-SiO\(_2\) substrate [TCNE and SiC(0001) substrate] are considered.

## 2. COMPUTATIONAL METHODS

The first-principles density functional theory (DFT) calculations are performed using the Dmol\(^3\) code, which uses numerical functions on an atom-centered grid as its atomic basis.\(^{29,30}\) The local density approximation (LDA) with the Perdew–Wang (PWC) method is utilized as the exchange-correlation functional.\(^{31}\) Although neither the LDA nor the generalized gradient approximation (GGA) functional fully accounts for van der Waals (vdW) interactions, the LDA has been proven to perform well for the adsorption of molecule on graphene and weakly bound systems.\(^{16,32,33}\) Moreover, the LDA calculation of bandgap opening in BG under external electric field has been shown to be in reasonable agreement with the experimental result.\(^{16}\) The all-electron (AE) core treatment and double numeric plus polarization (DNP) basis set are adopted for the spin-polarized DFT calculations. The AB-stacking BGs are modeled by 5 \( \times \) 5 and 4 \( \times \) 4 supercells, which are used to match a-SiO\(_2\) and SiC(0001) substrates, respectively. A vacuum larger than 18 Å is used to prevent the interaction effect from neighboring cells in the direction normal to the graphene surface. For all calculations, the k-point is set to 5 \( \times \) 5 \( \times \) 1 (6 \( \times \) 6 \( \times \) 1) for 5 \( \times \) 5 (4 \( \times \) 4) supercell, and the global orbital cutoff is 5.0 Å. The optimization of the structures is performed using the delocalized internal coordinate optimization scheme, in which the geometry of the system is described by a set of internal coordinates that consist of the proper combination of all bonds, angles, and torsions. The optimization is an iterative procedure, in which the coordinates are adjusted so that the energy of the structure is brought to a stationary point, i.e., one in which the convergence tolerances of energy, maximum force, and maximum displacement of 1.0 \( \times \) 10\(^{-3}\) Ha (1 Ha = 27.2114 eV), 0.002 Ha/Å, and 0.005 Å are reached, respectively. Note that increasing the k-point to 7 \( \times \) 7 \( \times \) 1 (8 \( \times \) 8 \( \times \) 1) for 5 \( \times \) 5 (4 \( \times \) 4) supercell, the changes in adsorption energy of molecule, binding energy between BG and substrate, and the opened bandgap are only less than 0.1%, 0.1%, and 3.6%, respectively.

To model a-SiO\(_2\) substrate with O\(_2^-\) on the surface, we first build a periodic cell for bulk a-SiO\(_2\) with the experimental density of 2.20 g/cm\(^3\). The cell parameters of a \( a \) and b are both 12.30 Å, which match the 5 \( \times \) 5 supercell of BG, and the length of c is 15.57 Å. The bulk a-SiO\(_2\) is simulated by classical molecular dynamics following the procedure in ref 34. The relevant simulations are carried out using the Vashishta force field as implemented in the GULP code.\(^{35,36}\) Then, the simulation of a-SiO\(_2\) surface begins by removing the periodic boundary condition along the c direction. Following this, the surface slab is annealed from high temperature. As a widely used gate dielectric, a-SiO\(_2\) is usually obtained by thermal oxidation of Si substrate. The gotten a-SiO\(_2\) layer is hydrophilic and coated with hydroxyls.\(^{28,29}\) Here, the surface concentration of hydroxyls is chosen as 4.58 \( \times \) 10\(^{14}\) cm\(^{-2}\), corresponding to the experimental result of 4.60 \( \times \) 10\(^{14}\) cm\(^{-2}\).\(^{37}\) Then, one O\(_2\) molecule is adsorbed on the 3-fold-coordinated Si atom at one side of the slab, which represents the surface O\(_2^-\) concentration of 7.63 \( \times \) 10\(^{13}\) cm\(^{-2}\) at the same level of the experimental estimation of 10\(^{13}\) cm\(^{-2}\).\(^{27}\) It has been demonstrated that water vapor does not dope graphene noticeably, although it stabilizes O\(_2^-\) and promotes the doping from O\(_2^-\).\(^{8,27}\) Thus, the adsorption of water on a-SiO\(_2\) substrate is not considered for simplicity. In the following text, this modeled a-SiO\(_2\) slab is denoted as a-SiO\(_2\)-p substrate.

Theoretical DFT calculations have demonstrated that the graphene layers on Si-terminated 4H-SiC(0001) are n-doped.\(^{26}\) Because of the strong covalent bonds formed between the first graphene layer and Si-terminated 4H-SiC(0001), the first layer lacks the graphitic band structure and acts as a buffer layer. In realistic situation, the 6\( \sqrt{3} \) \( \times \) 6\( \sqrt{3} \)R30 substrate cell is almost commensurate with 13 \( \times \) 13 graphene cell, which is too large for realistic DFT calculations. As done in ref 26, we also adopt a 2\( \sqrt{3} \) \( \times \) 2\( \sqrt{3} \)R30 substrate cell to accommodate the 4 \( \times \) 4 supercell of BG, which needs a 7.9% stretch of BG. This approximation has been checked to have no qualitative effect on the electronic structure.\(^{26}\) The 4H-SiC(0001) slab contains four SiC layers, and the bottom two layers are constrained. Moreover, Si atoms in the bottom SiC layer are saturated with H atoms. In the following text, the Si-terminated 4H-SiC(0001) with a C buffer layer is denoted as C-SiC-n substrate.

When organic molecules are adsorbed on a freestanding (supported) BG, the adsorption energy, \( E_{\text{ads}} \), can be calculated by

\[
E_{\text{ads}} = E_{\text{gra(s gra)}} - E_{\text{mol}} - E_{\text{total}}
\]

where \( E_{\text{gra(s gra)}} \), \( E_{\text{mol}} \), and \( E_{\text{total}} \) are the energies of the freestanding (supported) BG, single organic molecule, and total
adsorption system, respectively. Under this definition, the adsorption configuration with a more positive $E_{\text{ads}}$ value should be more energetically favorable. Furthermore, the binding energy between BG and substrate, $E_{\text{bio}}$, can be obtained by:

$$E_{\text{bi}} = E_{\text{ads}} + E_{\text{f-gra(s-gra)}} - E_{\text{total}}$$ (2)

where $E_{\text{ads}}$ and $E_{\text{f-gra(s-gra)}}$ are the energies of substrate and BG adsorbed with molecule, respectively. If there is no special indication, all models are optimized and all energies are calculated with fixed lattice constants, since the largest difference between lattice constants with and without cell optimization is only less than 2.0%.

3. RESULTS AND DISCUSSION

3.1. DMPD and TCNE on a Freestanding BG. Figure 1a (1b) shows 8 (6) high-symmetry adsorption configurations for DMPD (TCNE) on the freestanding BG in the $5 \times 5$ supercell. The corresponding $E_{\text{ads}}$ and distance between molecule and the top graphene layer $d_m$ are given in Table 1. For DMPD adsorbed on the freestanding BG in the $5 \times 5$ supercell, the most stable configuration is B-4 (denoted as DMPD/BG system), in which the benzene ring of DMPD locates over the bridge site of the top graphene layer (see Figure 1a). As shown in Table 1, it has $E_{\text{ads}}$ value of 0.914 eV, which is 0.002–0.082 eV larger than those of other configurations. While for TCNE on the freestanding BG in the $4 \times 4$ supercell, the most stable configuration is H-1 (denoted as TCNE/BG system), where the central C–C bond of TCNE is above the hollow site of the top graphene layer (see Figure 1b). The corresponding $E_{\text{ads}}$ value is 0.826 eV, being 0.031–0.091 eV larger than those of other configurations (see Table 1). Moreover, the $E_{\text{ads}}$ value of TCNE/BG system is reasonably lower (higher) than other simulated $E_{\text{ads}}$ values at lower (higher) coverage, since the larger intermolecular repulsion force at higher coverage increases $E_{\text{total}}$ and thus decreases $E_{\text{ads}}$. For all considered configurations, DMPD is absorbed above the top graphene layer at about 3.160–3.263 Å, whereas for TCNE, the value is 3.067–3.150 Å, and $d_m$ is 3.176 and 3.067 Å for DMPD/BG and TCNE/BG systems, respectively. There are not chemical bonds between DMPD (TCNE) and the top graphene layer, and their interactions are in different length scales, including Coulombic and longer range dipolar interactions. Thus, these adsorptions lead to little structure distortion in BG.

To understand the effect of molecular adsorption on the electronic structure of BG, the band structures of DMPD/BG and TCNE/BG systems are calculated and shown in Figures 2a,b. After the adsorption of organic molecules, the charge asymmetry between two graphene layers can build up an interlayer electric field and result in bandgap opening. As shown in Figures 2a,b, $E_g$ of 106 and 98 meV are generated in BG for DMPD/BG and TCNE/BG systems, respectively. Moreover, the adsorptions of DMPD and TCNE have little effect on the parabolic bands of BG. The bandgap opening can also be found for other configurations. For DMPD adsorbed on the freestanding BG in the $5 \times 5$ supercell, $E_g$ lie in the range of 88–154 meV, while for TCNE on the freestanding BG in the $4 \times 4$ supercell, the values are among 84–119 meV (see Table 1).
molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of molecules and the Fermi level ($E_F$) of the pristine BG.\(^{38}\) The calculated HOMO of DMPD is 1.129 eV higher than the $E_F$ of the pristine BG, while the LUMO of TCNE is 0.980 eV lower than the $E_F$. Therefore, there is electron transfer from DMPD to BG, and DMPD acts as a donor. In contrast, the electron transfer occurs from BG to TCNE, and TCNE works as an acceptor. To equilibrate the potentials of the HOMO of DMPD and the $E_F$ of the pristine BG, the $E_F$ of DMPD shifts downward and intersects the conduction band of BG, while that of TCNE moves upward and crosses the valence band of BG (see Figures 2a,b). To confirm this, the HOMO of DMPD/BG system and LUMO of the TCNE/BG system at the $\Gamma$ point are calculated. As shown in Figures 2c,d, the HOMO of DMPD/BG system and LUMO of the TCNE/BG system locate on DMPD and TCNE, respectively. Note that the mixing of the BG band and molecular level makes them discrete, as shown in Figures 2a,b. The discrete graphene band and molecular level can also be found when organic molecules are adsorbed on monolayer graphene.\(^{39}\)

As discussed by Bengtsson, a slab with adsorbates on only one side can develop a dipole moment.\(^{44}\) When the periodic boundary conditions are imposed on the dipole moment, an artificial electric field is introduced, which may affect the simulation results.\(^{44}\) To verify that our vacuum space is large enough to avoid this effect, we calculate $E_{F_{\text{ads}}}$ and $E_F$ values of DMPD/BG and TCNE/BG systems at different vacuum spaces from 18 to 22 Å with increments of 2 Å. As shown in Table 2, $E_{F_{\text{ads}}}$ and $E_F$ values of the DMPD/BG (TCNE/BG) system are insensitive to the vacuum space within error ranges of 0.2% (0.2%) and 1.9% (3.9%), respectively, suggesting that the results well converge with the vacuum of 18 Å.

### 3.2. BG Supported on $a$-SiO$_2$-p and C-SiC-n Substrates

When a BG is supported on $a$-SiO$_2$ substrate, there are graphene corrugations due to the partial conformaion to the underlying substrate.\(^{45}\) Since the size of the supercell that is tractable in DFT calculations is too small to capture any long-range corrugations, we consider a flat BG structure. Figures 3a,b show the optimized structures for BG supported on $a$-SiO$_2$-p and C-SiC-n substrates, respectively, which are denoted by BG/$a$-SiO$_2$-p and BG/C-SiC-n systems. The distances between the bottom graphene layer and the substrate are 3.014 and 3.205 Å for BG/$a$-SiO$_2$-p and BG/C-SiC-n systems, respectively, where the former denotes the distance between the bottom graphene layer and the centroid of surface hydroxyls and O$_2^\cdot$ of $a$-SiO$_2$-p substrate. Moreover, for BG/$a$-SiO$_2$-p and BG/C-SiC-n

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**Table 2. $E_{\text{F_{ads}}}$ and $E_F$ Values of DMPD/BG and TCNE/BG Systems with Different Vacuum Spaces**

<table>
<thead>
<tr>
<th>system</th>
<th>vacuum (Å)</th>
<th>$E_{\text{F_{ads}}}$ (eV)</th>
<th>$E_F$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMPD/BG</td>
<td>18</td>
<td>0.9136</td>
<td>105.7</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.9122</td>
<td>107.1</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>0.9116</td>
<td>107.8</td>
</tr>
<tr>
<td>TCNE/BG</td>
<td>18</td>
<td>0.8264</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.8253</td>
<td>100.7</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>0.8245</td>
<td>102.4</td>
</tr>
</tbody>
</table>
between BG and the substrate is calculated to be 1.553 and 1.762 eV per supercell (i.e., 31.06 and 55.06 meV per C atom of the bottom graphene layer), respectively. They are at the same level of graphene physisorbed on Al, Cu, Ag, Au, and Pt(111).46 Since the interactions between BG and the two substrates are weak, the bands of BG can be clearly identified for both BG/α-SiO₂-p and BG/C-SiC-n systems (see Figures 3c,d), similar to the case of graphene on above metal surfaces.

For the BG/α-SiO₂-p system, α-SiO₂-p substrate accepts total 0.420 e per supercell from the bottom (0.284 e) and top (0.136 e) graphene layers, which makes BG p-doped. This is consistent with the upshift of the Raman G band and positive charge neutrality point in experiments.8,14,17,27,28 Other DFT calculations have shown that graphene is p-doped when it is physisorbed on O-terminated SiO₂(0001) substrate.47,48 However, the most stable state is actually the chemisorption but not the physisorption. In the BG/α-SiO₂-p system, the C atoms that contact with H atoms of surface hydroxyls gain electrons, while those that contact with O atoms of surface hydroxyls and O₂⁻ lose electrons. Moreover, the charge transfer takes place mainly between BG and O₂⁻. For gaseous O₂, the calculated bond length is 1.212 Å. After O₂ is adsorbed on the 3-fold-coordinated Si atom, it draws 0.525 e from α-SiO₂ substrate to form the anion. Because of the repulsion between the two charged O atoms, the bond length increases to 1.338 Å. Finally, O₂⁻ accepts 0.334 e from the adsorbed BG, and the bond length increases further to 1.444 Å due to the enhanced repulsion. While for BG/C-SiC-n system, C-SiC-n substrate donates total 0.344 e per supercell to the bottom (0.236 e) and top (0.108 e) graphene layers, leading to n-doping of BG. Differing from the case of BG/α-SiO₂-p system, all C atoms of BG in BG/C-SiC-n system accept electrons from C-SiC-n substrate. Actually, after BG is adsorbed on C-SiC-n substrate, 4H-SiC(0001) gives additional 0.139 e to the C buffer layer, implying that the electrons of BG are completely gotten from 4H-SiC(0001) through the C buffer layer.

Here, the charge transfer and doping effect can be illustrated by the related work functions (W).28,46 For the pristine BG, the calculated W value is 4.84 eV, being consistent with the experimental result of 4.69 ± 0.05 eV.39 While for α-SiO₂-p (C-SiC-n) substrate, W = 6.97 (3.13) eV, which is 2.13 (1.71) eV larger (smaller) than that of the pristine BG. To equilibrate the E_F of BG and α-SiO₂-p substrate, electrons are transferred from the former to the latter, which shifts the E_F of BG downward. As a result, the E_F of the BG/α-SiO₂-p system lies below the Dirac level of BG, as shown in Figure 3c. This is similar to the case of graphene physisorbed on Au and Pt(111).46 It has been reported that the clean α-SiO₂ covered with hydroxyls has a lower W than the pristine BG.38 Therefore, the larger W of α-SiO₂-p substrate and the p-doping of BG in this case can be attributed to the formation of O₂⁻. In contrast to the BG/α-SiO₂-p system, electrons are transferred from the C-SiC-n substrate to BG in the BG/C-SiC-n system, driving the E_F of
BG upward. Consequently, the $E_g$ of the BG/C-SiC-n system locates above the Dirac level of BG (see Figure 3d), which is like the case of graphene on Al, Ag, and Cu(111).

Because of this charge transfer and doping effect, $E_g$ values of 187 and 141 meV are produced in BG for BG/a-SiO$_2$-p and BG/C-SiC-n systems, respectively, as shown in Figures 3c,d. Again, the vdW-corrected GGA functional gives similar $E_g$ values of 193 and 144 meV for BG/a-SiO$_2$-p and BG/C-SiC-n systems, respectively. It has been reported experimentally that $E_g$ of about 260 meV can be created in the BG/C-SiC-n system. The smaller simulated $E_g$ value may be induced by the underestimation of LDA and GGA calculations on $E_g$.

To better understand the substrate related states near the $E_g$, we calculate the HOMO of the BG/a-SiO$_2$-p system and HOMO, HOMO−1, HOMO−2, HOMO−3, and HOMO−4 of the BG/C-SiC-n system at the Γ point. Here, the HOMO of the BG/a-SiO$_2$-p system at the Γ point corresponds to the flat band that crosses the valence band of BG, while the HOMO, HOMO−1, HOMO−2, HOMO−3, and HOMO−4 of the BG/C-SiC-n system at the Γ point correlate with the five bands that intersect the conduction band of BG near the $E_F$ (see Figures 3c,d). As shown in Figure 4a, the HOMO of the BG/a-SiO$_2$-p system at Γ point locates mainly on O$_2^−$ and is contributed by p-electrons, suggesting that the a-SiO$_2$-p substrate induced state near $E_g$ is primarily from O$_2^−$. For the BG/C-SiC-n system, the HOMO and HOMO−1 distribute on the C atoms of the buffer layer, while the HOMO−2, HOMO−3, and HOMO−4 lie on the C−C bonds of the buffer layer and the C−Si bonds between the buffer layer and 4H-SiC(0001) (see Figure 4b). Similarly, they are all contributed by p-electrons. This suggests that the C-SiC-n substrate related states near $E_g$ are from the C buffer layer and surface Si atoms of 4H-SiC(0001).

### 3.3. DMPD (TCNE) on BG Supported by a-SiO$_2$-p (C-SiC-n) Substrate.

Figures 5a−b display the optimized structures for DMPD on BG supported by a-SiO$_2$-p substrate and TCNE on BG supported by C-SiC-n substrate, respectively. The adsorption sites are the same as those of DMPD/BG and TCNE/BG systems (see B−4 in Figure 1a and H−1 in Figure 1b). The corresponding $E_{	ext{ad}}$ data of DMPD and TCNE are 0.984 and 0.770 eV, which are larger and smaller than those of DMPD/BG and TCNE/BG systems, respectively. In addition, the $E_{	ext{ad}}$ between BG and the substrate increases to 1.623 and 1.850 eV for DMPD/BG/a-SiO$_2$-p and TCNE/BG/C-SiC-n systems, respectively. The adsorption sites are the same as those of DMPD/BG and TCNE/BG systems (see B−4 in Figure 1a and H−1 in Figure 1b). The corresponding $E_{	ext{ad}}$ data of DMPD and TCNE are 0.984 and 0.770 eV, which are larger and smaller than those of DMPD/BG and TCNE/BG systems, respectively. Note that the smaller $E_{	ext{ad}}$ of TCNE for the TCNE/BG/C-SiC-n system is produced by the approximate stretch of BG. If this stretch is also considered for the TCNE/BG system, $E_{	ext{ad}}$ of TCNE decreases from 0.826 to 0.682 eV, which is smaller than that for the TCNE/BG/C-SiC-n system. Therefore, in a realistic situation, $E_{	ext{ad}}$ of TCNE for the TCNE/BG/C-SiC-n system should be larger than that for the TCNE/BG system. For DMPD/BG/a-SiO$_2$-p and TCNE/BG/C-SiC-n systems, $d_{\text{ad}}$ are 3.184 and 3.022 Å, while the distances between the bottom graphene layer and the substrate are 3.112 and 3.204 Å, respectively.

For the DMPD/BG/a-SiO$_2$-p system, the Mulliken population analysis shows that DMPD donates 0.365 $e$, the top graphene layer accepts 0.167 $e$, the bottom graphene layer gives 0.257 $e$, and a-SiO$_2$-p substrate attains 0.455 $e$ per supercell. It is clear that the top and bottom graphene layers are n- and p-doped, respectively. Because the $W$ difference (2.13 eV) between a-SiO$_2$-p substrate and the pristine BG is larger than the energy difference (1.129 eV) between the HOMO of DMPD and the $E_g$ of the pristine BG, the p-doping from a-SiO$_2$-p substrate should be stronger than n-doping from DMPD. As a result, BG in the DMPD/BG/a-SiO$_2$-p system is finally p-doped, which can be reflected by the lower $E_g$ of the DMPD/BG/a-SiO$_2$-p system than the Dirac level of BG (see Figure 5c). However, the p-doping from a-SiO$_2$-p substrate is partially overcome by n-doping from DMPD, the p-doping of BG in DMPD/BG/a-SiO$_2$-p system is weaker than that in the BG/a-SiO$_2$-p system. This corresponds to the smaller down-shift of the $E_g$ relative to the Dirac level of BG in this system than that in the BG/a-SiO$_2$-p system (see Figures 3c and 5c). Moreover, since the p-doping from a-SiO$_2$-p substrate causes the $E_g$ of the BG/a-SiO$_2$-p substrate lower than that of the pristine BG, the energy difference between the HOMO of DMPD and the $E_g$ of the BG/a-SiO$_2$-p system is smaller than that between the HOMO of DMPD and the $E_g$ of the pristine BG. Therefore, compared to DMPD in the DMPD/BG system, DMPD in the DMPD/BG/a-SiO$_2$-p system should donate
more electrons. Additionally, the downshift degree of the molecular level of DMPD in the DMPD/BG/a-SiO₂-p system should be larger than that in the DMPD/BG system. Namely, the introduction of p-doping into BG from a-SiO₂-p substrate makes the molecular level of the DMPD/BG system shift downward. As shown in Figures 2a and 5c, the molecular level of DMPD that originally intersects the conduction band of BG in the DMPD/BG system crosses the valence band of BG in the DMPD/BG/a-SiO₂-p system. To confirm this, the HOMO and HOMO-1 of the DMPD/BG/a-SiO₂-p system at the Γ point, which corresponds to the two flat bands just below the $E_F$ (see Figure 5c), are given in Figure 6a. As shown in Figure 6a, more HOMO distributes on O₂⁻, while less HOMO lies on DMPD. For HOMO-1, the opposite is the case. Moreover, they are both contributed by p-electrons. It is obvious that both the molecular level of DMPD and the O₂⁻ related state locate below the opened bandgap of BG. As discussed in section 3.1, the n-doping of BG from DMPD results in higher $E_F$ in the DMPD/BG system than that in the pristine BG, which implies a smaller W value of the DMPD/BG system (4.57 eV) than that of the pristine BG (4.84 eV). Therefore, the W difference between a-SiO₂-p substrate and DMPD/BG system is larger than that between a-SiO₂-p substrate and the pristine BG, and a-SiO₂-p substrate should accept more electrons in the DMPD/BG/a-SiO₂-p system, which accounts for the increased $E_F$ value. Although DMPD donates and a-SiO₂-p substrate accepts more electrons, the top graphene layer accepts and the bottom graphene layer donates fewer electrons, where the electron–hole recombination (0.198 e) takes place through BG. However, since the top and bottom graphene layers carry opposite charges, the interlayer electric field should be significantly enhanced. As a result, the introduction of p-doping into BG from a-SiO₂-p substrate increases $E_F$ of BG in the DMPD/BG system from 106 to 253 meV (see Figures 2a and 5c). The increased $E_F$ without intergap molecular level should enhance the on/off current ratio, as observed in recent experiments. For the DMPD/BG/a-SiO₂-p system, a slightly smaller $E_F$ value of 248 meV is obtained from the vdW-corrected GGA functional.

For the TCNE/BG/C-SiC-n system, TCNE accepts 0.195 e, the top graphene layer donates 0.029 e, the bottom graphene layer attains 0.205 e, and C-SiC-n substrate gives 0.371 e per supercell. Differing from the DMPD/BG/a-SiO₂-p system, the top and bottom graphene layers are p- and n-doped, respectively. Moreover, BG in this system is n-doped due to the stronger n-doping from C-SiC-n substrate than p-doping from TCNE [the W difference (1.71 eV) between the pristine BG and C-SiC-n substrate is larger than the energy difference (0.980 eV) between the $E_F$ of the pristine BG and the LUMO of TCNE]. This can be confirmed by the higher $E_F$ of the TCNE/BG/C-SiC-n system than the Dirac level of BG (see Figure 5d). Compared to the BG/C-SiC-n system, the n-doping of BG in the TCNE/BG/C-SiC-n system becomes weaker, which can be reflected by the smaller upshift of the $E_F$ relative to the Dirac level of BG in this system than that in BG/C-SiC-n system (see Figures 3d and 5d). Furthermore, since the p-doping from TCNE causes the $E_F$ of TCNE/BG system lower than that of the pristine BG, the $W$ of the former (5.36 eV) is larger than that of the latter (4.84 eV). Hence, the $W$ difference between the TCNE/BG system and C-SiC-n substrate is larger than that between the pristine BG and C-SiC-n substrate. Then, C-SiC-n substrate loses more electrons in the TCNE/BG/C-SiC-n system, explaining the larger $E_F$ value. As found in section 3.2, the $E_F$ of the BG/C-SiC-n system is higher than that of the pristine BG, leading to the larger difference between the $E_F$ of the BG/C-SiC-n system and the LUMO of TCNE than that between the $E_F$ of the pristine BG and the LUMO of TCNE. Therefore, TCNE should gain more electrons in the TCNE/BG/C-SiC-n system relative to the TCNE/BG system. In addition, the upshift degree of the molecular level of TCNE in the TCNE/BG/C-SiC-n system becomes weaker, which can be re-estimated by the smaller upshift of the $E_F$ relative to the Dirac level of BG in this system than that in BG/C-SiC-n system (see Figures 3d and 5d).

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semiconductor Si (1400 cm²/(V s)). Note that $\mu$ of SiO₂-supported BG in experiments is even smaller than that of the DMPD/BG/α-SiO₂-p system, which may be induced by the scattering from defects or impurities at the interface between SiO₂ and BG.

In this work, other molecule concentrations are not examined. However, the qualitative effect of molecule concentration on the bandgap opening is clear. As the molecule coverage increases, the overall charge transfer between molecules and BG becomes more efficient. Then, a larger interlayer electric field can be produced, leading to improved $E_g$ value. When the molecule coverage increases to a certain thickness, $E_g$ should reach maximum. For greater thickness, $E_g$ remains constant, since the charge transfer between molecules and BG becomes saturated. By increasing the deposition time, it is easy to control the thickness of molecules for obtaining the maximum $E_g$ value in experiments. Because the molecule coverage for DMPD/BG/α-SiO₂-p and TCNE/BG/C-SiC-n systems in this study is less than a monolayer, larger $E_g$ values than 253 and 211 meV can be gained by increasing the coverage. Furthermore, DMPD/ BG/α-SiO₂-p and TCNE/BG/C-SiC-n systems can be easily incorporated into field effect transistors experimentally. For the case of the former, α-SiO₂ is thermally grown on a highly doped Si wafer first. Then, a-SiO₂-p substrate can be produced by exposing a-SiO₂ in pure O₂. Following this, BG is mechanically exfoliated from natural graphite flakes and transferred to a-SiO₂-p substrate. The source and drain electrodes can be prepared by directly evaporating Cr and Au on the top graphene layer using hard masks. Finally, DMPD is thermally evaporated onto the top layer to further dope BG. In this field effect transistor, Cr, Au, doped BG, and a-SiO₂/ Si serve as source electrode, drain electrode, channel, and bottom gate, respectively. While for the TCNE/BG/C-SiC-n system, the fabrication of source and drain electrodes is similar to that of the DMPD/BG/α-SiO₂-p system. And TCNE is finally evaporated onto the top graphene layer. Here, the source electrode, drain electrode, channel, and bottom gate are Cr, Au, doped BG, and 4H-SiC(0001), respectively.

4. CONCLUSIONS

In summary, we have used the first-principles DFT calculations to investigate the electronic properties of BG adsorbed with DMPD (TCNE) and supported on α-SiO₂-p (C-SiC-n) substrate. BG is n-doped in the DMPD/BG system, while it is p-doped in the TCNE/BG system. For DMPD/BG and TCNE/BG systems, $E_g$ of 106 and 98 meV are generated, where the molecular levels intersect the conduction and valence bands of BG, respectively. The opposite p-doping from α-SiO₂-p substrate increases $E_g$ of the DMPD/BG system to 253 meV, while the opposite n-doping from C-SiC-n substrate improves $E_g$ of the TCNE/BG system to 211 meV. Moreover, the p-doping from α-SiO₂-p substrate moves the molecular level of DMPD/BG system downward to cross the valence band of BG, whereas the n-doping from C-SiC-n substrate shifts the molecular level of the TCNE/BG system upward to intersect the conduction band of BG. The increased bandgap of BG without intergap molecular level can enhance the on/off current ratio. Meanwhile, the high $\mu$ value is largely maintained due to the weak interaction at the interface.

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