Towards single-gate field effect transistor utilizing dual-doped bilayer graphene

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ABSTRACT

In this work, based on experimental possibilities, our first-principles calculations predict a sizeable bandgap opening in bilayer graphene (BLG) by n-doping from decamethylcobaltocene (DMC) and p-doping from functionalized amorphous SiO2 gate dielectric. With DMC monolayer on BLG and the maximum O2/C0 on the surface of a-SiO2 gate dielectric, the dual-doped BLG presents a bandgap of 390–394 meV and a Dirac level shift of 59 to 52 meV. The former is very close to the technical requirement of 400 meV, while the latter properly lies in the accessible range of the gate voltage of 300 meV. The high carrier mobility largely remains with the on/off current ratio satisfying the technical requirement of 10^4/10^7. The external electric field is not needed in this technique, which avoids a complex fabrication step for preparing a dual-gate structure and a substantial reduction in carrier mobility and on/off current ratio induced by adding an extra gate.

1. Introduction

Modern digital logic is based on Si complementary metal-oxide-semiconductor (CMOS) technology, where the logic gates consist of Si metal-oxide-semiconductor field effect transistors (MOSFETs). For decades, making MOSFETs smaller has been the key to improve the digital logic [1]. However, MOSFET scaling is approaching its limits due to the physical limitation of Si as well as the short-channel effects [2,3]. Thus, the CMOS-based technology has been forecasted to end by 2022 [4]. To continue the development in this field, a suitable substitute of Si is necessary as the channel material of field effect transistors (FETs). Graphene, a two-dimensional sheet of C atoms tightly packed into a honeycomb lattice, has attracted considerable attention since its discovery in 2004 [5]. According to the scaling theory, a FET with a thin barrier and a thin gate-controlled region will be robust against the short-channel effect down to very short gate lengths [6]. Therefore, the possibility of making channels at atomic layer thick is considered as the most attractive feature of graphene for use in FETs [7]. Moreover, graphene has an extremely high carrier mobility (μ) up to 2 × 10^5 cm^2 V^{-1} s^{-1} [8,9]. Both impressive properties make graphene a promising channel material for high-speed FETs. However, due to the absence of a bandgap, the pristine graphene-based FETs have a very low on/off current ratio (I_{on}/I_{off}) between 10^4 and 10^7, which requires the semiconducting channel with a sizeable bandgap close to 400 meV or more [4,7]. Additionally, for graphene FETs, the shift of the Dirac level (E_D, the energy level in the middle of the bandgap opened in graphene) should be within the gate voltage accessible range, where the typical FETs exhibit 300 meV shifts at...
100 V gate voltage [12]. Although the sizeable bandgaps larger than 400 meV have been opened by lateral quantum confinement [13–16], heteroatom doping [17,18], and covalent functionalization of graphene [19,20], the conical bands of graphene disappear and \( \mu \) value is drastically reduced due to the strong scattering from edges for lateral quantum confinement and from heteroatoms for heteroatom doping, and the removal of \( \pi \) electrons for covalent functionalization. To maintain high \( \mu \) values, the structure of graphene should be intact, and the interface interaction between graphene and other materials should be weak. Up to now, two feasible schemes have been proposed to open bandgaps in graphene without degrading its high \( \mu \) value. One is breaking the equivalence between the A and B sublattices of single-layer graphene (SLG), which has been achieved by the adsorption of aromatic molecules [21], depositing SLG on hydrogenated or fluorinated hexagonal BN [22], sandwiching SLG between hexagonal BN or partially hydrogenated SLG [23,24], and the epitaxial growth of SLG on SiC substrate [25]. Although the \( E_D \) shift is small, the opened bandgap is unfortunately lower than 270 meV without an external electric field [21–25]. Another is destroying the inversion symmetry of bilayer graphene (BLG), by applying an external electric field perpendicular to BLG [11,26–28] or by charge transfer doping from the single-side adsorption of organic molecules or metallic atoms [10,29–35]. In the former case, the largest bandgap opening is confined to 250 meV due to the limited strength of gate dielectric stacks [11,26–28]. Moreover, a dual-gate structure is required to apply an external electric field [11,28], which increases the complexity and the cost of FETs. Also, the addition of an extra gate results in a substantial reduction of \( \mu \) and \( I_{on}/I_{off} \) values in graphene FETs [36]. In details, if this deduction is denoted as the ratio of single-gate/dual-gate, the corresponding ratios for \( \mu \) values of graphene hole (\( \mu_h \)) and electron (\( \mu_e \)) are 6.75/1 and 9.02/1, respectively; while the corresponding ratios for \( I_{on}/I_{off} \) values are 3.04/1 and 1.81/1 under negative and positive gate voltage, respectively [36]. From a device design point of view, it is desirable to control a FETs electrical conductivity by a single gate. Fortunately, the charge transfer doping from organic molecules or metallic atoms can generate an interlayer electric field, leading to a significant bandgap opening for single-gate applications [10,29–35]. In general, the clustering of metallic atoms always happens on the graphene surface, which brings out charged impurities and leads to serious reduction of \( \mu \) value [37]. On the contrary, this clustering can be avoided by molecular doping due to the intermolecular repulsion [29,30,32]. So far, the bandgap opening of BLG by single-side molecular doping is usually lower than 230 meV [29–32]. Although the bandgap can be further increased through enhancing doping, the \( E_D \) shift may exceed the accessible range of the gate voltage.

For molecular doping, the deposition of organic molecules is usually at single-side, limiting the bandgap opening of BLG. If an opposite doping is introduced into BLG at another side, two layers are needed to carry different types of charges, which can significantly increase the interlayer electric field and thus the opened bandgap. Moreover, the \( E_D \) shift can be reduced, which has been proven by a dual molecular doping of BLG [12,38,39]. Up to now, the reported bandgap opening by dual molecular doping is less than 310 meV [12,38–40]. In a conventional FET, one side of the channel always contacts with the gate dielectric. From a technical viewpoint, it is more meaningful to introduce an additional doping from a functionalized gate dielectric. Both experiments and theoretical calculations have revealed that \( O_2 \) can bind to the 3-fold-coordinated Si atoms at the widely used amorphous SiO\(_2\) (a-SiO\(_2\)) surface to form O\(_2\)\_Si, which brings about a strong p-doping of BLG [10,40,41]. To realize the strongest p-doping of BLG, the O\(_2\) adsorption sites at a-SiO\(_2\) surface should be maximally created. Once the p-doping is identified, an n-type molecular dopant with adequately low ionization energy should be deposited on the other side of BLG. Note that deca-methylcobaltocene (DMC) with a D\(_{5h}\) symmetry is a promising candidate. Under this symmetry, DMC has an electronic state of \( ^2\Sigma_1g \) and an electronic configuration of \( (a_1g)^2(a_2u)^2(e_1g)^4(e_u)\)\(^4\)\( (a_1g)^2(e_2g)^4(e_1u) \) [42], where one electron fills the high-energy \( e_1u \) orbital. This leads to a remarkably low solid-state ionization energy for DMC (3.3 eV) [43], which is even smaller than that of Ca atom. In particular, DMC has been successfully used as an efficient n-dopant in organic electronic materials and devices [43].

In this contribution, we investigate the electronic properties of BLG by p-doping from functionalized a-SiO\(_2\) gate dielectric and n-doping from DMC. First-principles density functional theory (DFT) calculations demonstrate a large bandgap opening of 390–394 meV in this dual-doped BLG with a proper Dirac level shift by −59 to −52 meV. Moreover, a single-gate FET based on this dual-doped BLG shows a high \( \mu \) value and an \( I_{on}/I_{off} \) ratio within \( 10^4 \) and \( 10^5 \), facilitating its application in CMOS-like logic.

### 2. Experimental

It is well known that, as a widely used gate dielectric, a-SiO\(_2\) can be obtained by thermal oxidation of Si wafer in a wet environment. The gotten a-SiO\(_2\) layer is coated with hydroxyls [44–46]. The maximal concentration of hydroxyls can reach (4.9 ± 0.5)/nm\(^2\) (arithmetical mean), which includes isolated, geminal, and vicinal ones [45]. If O\(_2\) is adsorbed on the vicinal 3-fold-coordinated Si atoms, the outside O atoms of two adjacent O\(_2\) may combine to form one O\(_2\). The remaining O atoms will covalently interact with BLG [47], which seriously decreases the \( \mu \) value. Namely, the vicinal adsorption sites are useless. Therefore, a vacuum pretreatment at 673 K is necessary. With this pretreatment, the vicinal hydroxyls disappear through a dehydration reaction by forming siloxane bridges [45]. Following this, the O\(_2\) adsorption sites can be created by removing the residual hydroxyls with a multi-step thermochemical method [48]. Here, the O\(_2\) adsorption sites are composed of 3-fold-coordinated (93.2%) and 2-fold-coordinated (6.8%) Si atoms [45]. Note that O\(_2\) may also be built when O\(_2\) is adsorbed on the 2-fold-coordinated Si atoms at a low concentration [47]. Finally, the a-SiO\(_2\) gate dielectric with maximal O\(_2\) concentration (about (2.34 ± 0.5)/nm\(^2\)) [45] could be produced by the adsorption of dry O\(_2\). The cell parameters of the functionalized a-SiO\(_2\) gate dielectric are chosen to match the 4 × 4 supercell of BLG. In the cell, there are two O\(_2\), which corresponds to a concentration of 2.39/\( nm^2 \) and relates to the experimental possibilities discussed.
above. For simplicity, all O₂ adsorption sites are considered as the 3-fold-coordinated Si atoms. The details to build the functionalized a-SiO₂ gate dielectric are given in Supplementary data.

In this work, the Bernal-stacking BLG is modeled by 4 × 4 supercell, in which the adsorption of one DMC represents a concentration of 1.19/nm². In the single crystal of DMC, its (001) surface with a DMC monolayer has a concentration of 1.15/nm² [49]. Thus, the 4 × 4 BLG plus one DMC nearly corresponds to a DMC monolayer on BLG.

The spin-unrestricted DFT calculations are performed within the DMol³ code [50]. The local density approximation (LDA) with Vosko–Wilk–Nusair (VWN) method is employed as the exchange–correlation functional [51]. The LDA functional has been demonstrated to perform well for molecular adsorption on SLG or BLG and weakly bound systems [21–23,29,30,32,38,40,44,47], such as those considered here. Moreover, the LDA calculation of bandgap opening in BLG under an over, the LDA calculation of bandgap opening in BLG under an 23,29,30,32,38,40,44,47, such as those considered here. More-

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3. Results

To investigate the properties of the functionalized a-SiO₂ gate dielectric with the maximal O₂ concentration, we build thirty small models, as shown in Fig. 1, where each one can be regarded as a sample of the gate dielectric. These models are denoted by a-SiO₂-n, where n is the serial number (see Fig. 1). For a-SiO₂-n, the adsorbed O₂ can draw 0.28–0.49 e from a-SiO₂ gate dielectric to form O₂, as shown in Fig. 2a. As a result, their bond lengths (l₀,₀) increase from 1.21 to 1.31–1.40 Å. Note that in Fig. 2a and b, two Q₀₂ and l₀,₀ values at each n are shown, which separately denote the measured results of two O₂ molecules in each a-SiO₂-n model.

The average values of the charge of O₂ (Q₀₂), l₀,₀, and W for all a-SiO₂-n are ~0.41 e, 1.35 Å, and 6.72 eV, respectively (see Fig. 2). Owing to the inhomogeneity of a-SiO₂, we take these average values to calculate the properties of the systems considered in the following.

After the functionalized a-SiO₂ gate dielectric is prepared, BLG is mechanically exfoliated from the highly oriented pyrolytic graphite and then transferred onto the gate dielectric. Here, we choose a-SiO₂-26 to investigate the electronic properties of BLG on the functionalized a-SiO₂ gate dielectric, because the Q₀₂, l₀,₀, and W values of a-SiO₂-26 are close to average ones (see Fig. 2). Fig. 3a presents the optimized structure for BLG supported on a-SiO₂-26, being denoted as BLG/ a-SiO₂-26 system. The E₀₂ between BLG and a-SiO₂-26 is 0.989 eV per supercell (i.e., 0.031 eV per C atom of the bottom graphene layer), which is at the same level of SLG physisorbed on Al, Cu, Ag, Au, and Pt(111) [55]. Although the initial distance (d₀) between BLG and a-SiO₂-26 is set to 1.50 Å, it increases to 2.80 Å after geometry optimization, which again suggests the weak interface interaction between BLG and a-SiO₂-26. This quite differs from the case of BLG on O-terminated a-SiO₂, where the C–O covalent bonds are established at the interface (see Fig. S1, Supplementary data).

Fig. 3b shows the band structure for BLG/a-SiO₂-26 system. Because of the weak interface interaction, the characteristic bands of BLG can be clearly identified and take on a typical Mexican-hat shape, similar to the case of BLG physisorbed by organic molecules [30,32,38,40]. Below the Fermi level (Eₐ), there are four flat bands intersecting the conduction band of BLG, which are mainly contributed by p-electrons of O₂ (see Fig. S2, Supplementary data). The Mulliken population analysis shows that a-SiO₂-26 accepts totally 0.40 e per supercell from the bottom (0.33 e) and the top (0.07 e) graphene layers (see Table S1, Supplementary data), making BLG p-doped. The charge transfer (about 75%) occurs essentially between O₂ and BLG, implying that the p-doping of BLG can be attributed to the formation of O₂. In light of the tight binding model, the interlayer electric field is estimated by Fᵢ ≈ ΔEₓ/ (ed), where ΔEₓ denotes the bandgap generated in BLG at the K point, and dᵢ is the interlayer distance of BLG [30,32]. For BLG/a-SiO₂-26 system, Fᵢ of BLG is estimated to be 0.11 V/Å, which opens a bandgap (Eₐ) of 240 meV in BLG (see Fig. 3b). This Eₐ value is much larger than that of BLG on a-SiO₂ with lower O₂ concentration [10,40]. In addition, due
to the p-doping effect, the $E_D$ of BLG lies above the $E_F$ of BLG/α-
SiO$_2$-26 system, and their difference ($\Delta = E_D - E_F$) is 376 meV, which exceeds the accessible range of the gate voltage of 300 meV, being like the case of other heavy doping on BLG [12,30]. To confirm the above results, BLG/α-SiO$_2$-8 and BLG/α-SiO$_2$-30 systems are also studied, where $Q_{O_2}$, $I_{O-O}$, and $W$ values of α-SiO$_2$-8 and α-SiO$_2$-30 are close to the average ones too (see Fig. 2). Similar results can be found among BLG/α-SiO$_2$-8, BLG/α-SiO$_2$-26, and BLG/α-SiO$_2$-30 systems (see Fig. 3 and S3, and Table S1, Supplementary data). The slight

Fig. 1 – Optimized structures of thirty small α-SiO$_2$ gate dielectric models with O$_2$ concentration of 2.39/nm$^2$. The red, yellow, and white balls denote O, Si, and H atoms, respectively. (A colour version of this figure can be viewed online.)
differences among them are induced by their distinct charge distributions of BLG (especially for the bottom layer) (see Fig. S4, Supplementary data).

To reduce $\Delta$ value and increase $E_g$ value, DMC is considered to be deposited onto the top graphene layer, before which the source and drain electrodes can be produced by evaporating metal on the top graphene layer using hard masks. Fig. 4a shows the structure of DMC molecule, which consists of a Co atom sandwiched between two methyl-substituted cyclopentadienyl groups. For the deposition of DMC on the top graphene layer, three adsorption sites are considered, namely, DMC on the bridge (the center of a C–C bond, B), the hollow (the center of a C hexagon, H), and the top (the top of a C atom, T) sites of the top graphene layer (see Fig. 4b). Fig. 5a gives a schematic of such single-gate FET, where BLG serves as the channel. Fig. 5b presents the optimized structures of four high-symmetry adsorption configurations for DMC on BLG supported by $a$-SiO$_2$-26 (denoted as DMC/BLG/$a$-SiO$_2$-26 system), where two different orientations of DMC at T site are distinguished by T-1 and T-2. The intermolecular distance of DMC in four configurations is about 3.38 Å, which nearly corresponds to a monolayer of DMC on BLG. The $E_{ad}$ values of DMC are almost identical for all four configurations at 1.736–1.740 eV, relating with the similar distances between the top graphene layer and the centroid of DMC (see Table 1). This implies that the adsorption of DMC is site-insensitive and a homogeneous DMC monolayer can form on BLG. In addition, $E_{bi}$ between BLG and $a$-SiO$_2$-26 increases from 0.989 eV to 1.277–1.281 eV after the adsorption of DMC (see Table 1).
Fig. 5c exhibits band structures for B, H, T-1, and T-2 configurations from DMC/BLG/a-SiO$_2$-26 system, where the bands of BLG are still in the Mexican-hat shape due to the weak interface interactions. The band structure of DMC/BLG/a-SiO$_2$-26 system is insensitive to the adsorption sites yet, corresponding to the similar $E_{ad}$ and $d_m$ values for all four configurations. As shown in Fig. 5c, the four flat bands below the $E_F$ are related to a-SiO$_2$-26 (see Fig. S5, Supplementary data). Compared with BLG/a-SiO$_2$-26 system, the four bands move up relative to the $E_D$ (see Figs. 3b and 5c). Above the $E_F$, the flat bands that span the valance band of BLG are associated with the adsorption of DMC (see Fig. S5, Supplementary data). The slight splitting of these flat bands is due to the spin-polarized nature of DMC [30]. For DMC/BLG/a-SiO$_2$-26 system, DMC donates 0.60–0.61 e, the top graphene layer accepts 0.43 e, the bottom graphene layer gives 0.26–0.27 e, and a-SiO$_2$-26 attains 0.44 e per supercell (see Table 1), where the electron–hole recombination of 0.17–0.18 e takes place through BLG. The larger electron acceptance of a-SiO$_2$-26 in this system can explain the increased $E_{bi}$ value. Corresponding to the large electron donation of DMC, the distance between two cyclopentadienyls decreases from 3.34 to 3.27 Å, and the spin polarization of DMC seriously weakens. Because the two layers of BLG carry opposite charges, $F_i$ is significantly enhanced to 0.28 V/Å. As results, a sizeable $E_g$ of 390–394 meV is opened in BLG for DMC/BLG/a-SiO$_2$-26 system (see Fig. 5c), which is very close to the technical requirement of 400 meV [7]. Furthermore, as the electron donation of DMC
is larger than the electron acceptance of α-SiO₂-26, BLG is finally n-doped. However, since the n-doping from DMC is largely counteracted by the p-doping from α-SiO₂-26, the n-doping of BLG in DMC/BLG/α-SiO₂-26 system is much weak. Namely, the $E_p$ shift is successfully reduced. As shown in Table 1, $\Delta$ is −59 to −52 meV for DMC/BLG/α-SiO₂-26 system, which properly lies in the gate voltage accessible range of 300 meV [12].

For comparison purposes, the electronic properties of DMC/BLG/α-SiO₂-26 system are also calculated using the generalized gradient approximation (GGA) functional of the Perdew–Burke–Ernzerhof (PBE) [56] with a dispersion correction devised by Grimme [57], before which the geometry optimization is first performed. As shown in Table 1, the calculated charge transfer and $E_g$ values are consistent with those calculated by the LDA functional. Such agreement between the LDA and the vdW-corrected GGA functional has also been found in other weakly bound systems [30,40]. Although LDA values calculated by the LDA functional are larger than those calculated by the vdW-corrected GGA functional, their differences from the both methods are all small and properly lie in the accessible range of the gate voltage of 300 meV.

In this work, the sizeable $E_g$ opening and proper $E_p$ shift are achieved without any external electric field. Thus, a single gate, as shown in Fig. 5a, does not require the complicated fabrication step for preparing a dual-gate structure and avoids the reduction of $\mu$ and $I_{on}/I_{off}$ values associated with the deposition of an extra gate [36]. It is noteworthy that the standard DFT calculations with the local exchange–correlation potentials might underestimate the $E_g$ value. Therefore, we also calculate the $E_g$ value of BLG in DMC/BLG/α-SiO₂-26 system by the hybrid sX-LDA functional in the CASTEP code [58]. This hybrid sX-LDA functional has been used to calculate the electronic properties of graphene-related materials with accuracy comparable to GW [59]. A test calculation by the hybrid sX-LDA functional gives $E_g$ value of 5.68 eV for the h-BN sheet, which is very close to the experimental result of 5.69 eV [60]. Due to the site insensitivity of $E_g$ values for DMC/BLG/α-SiO₂-26 system and the large computational cost of the hybrid sX-LDA functional, we only calculate $E_g$ value for the B configuration of DMC/BLG/α-SiO₂-26 system, where the Norm-conserving pseudopotential is used and the Brillouin zone is sampled by 2 × 2 × 1 k-points with the energy cutoff of 600 eV. The $E_g$ value of B configuration calculated is 455 meV, which is 16% larger than that calculated by the LDA functional. To the authors’ knowledge, the $E_g$ value of 390–394 meV from the LDA functional or that of ~455 meV from the hybrid sX-LDA functional is now the largest one opened in graphene without degrading its high $\mu$ value [10–12,21–35,38–40,47]. Note that a sizeable $E_g$ of 408 meV has been reported by applying a strong electric field (0.8 V/A) normal to SLG on a functionalized BN bilayer where a dual-gate structure is needed [22]. However, the applied electric field has largely exceeded the breakdown strength of hexagonal BN (about 0.08 V/A) [61] and is thus difficult for actual applications.

Based on the electronic properties calculated for DMC/BLG/α-SiO₂-26 system, $\mu$ and $I_{on}/I_{off}$ values of the single-gate FET shown in Fig. 5a can be approximately estimated. To estimate $\mu_e$ and $\mu_h$ values, the effective masses of electrons ($m_e$) and holes ($m_h$) of BLG in DMC/BLG/α-SiO₂-26 system are first calculated by $m = \hbar^2/[2(E(k)/\hbar^2)]$, where $\hbar$ is the reduced Planck constant, $k$ is the wave vector, and $E(k)$ is the dispersion relation. The calculated $m_e$ and $m_h$ values of BLG for DMC/BLG/α-SiO₂-26 system are 1.50–1.89 and 1.28–1.47 times larger than those of the pristine BLG, respectively. On the basis of the relationship of $\mu = ev/\mu$ (v: the scattering time) and the fact of $\mu = 2 \times 10^6$ cm²/V·s for the pristine BLG [8,9], $\mu_e$ and $\mu_h$ in this single-gate FET estimated are (1.06–1.33) × 10⁵ and (1.36–1.56) × 10⁵ cm²/V·s, respectively. The high $\mu$ values relate with the weak interface interactions. A routine experimental measurement for $\mu$ of exfoliated

Table 1 – Summary of the results for DMC/BLG/α-SiO₂-26 system: adsorption energy of DMC ($E_{ad}$), binding energy between BLG and α-SiO₂-26 ($E_b$), distance between the top graphene layer and the centroid of DMC ($d_m$), distance between the bottom graphene layer and the centroid of O₂ on α-SiO₂-26 ($d_a$), charge carried by DMC ($Q_{ad}$), the top graphene layer ($Q_b$), and α-SiO₂-26 ($Q_{b}$), bandgap opened in BLG ($E_g$), difference between the $E_p$ of BLG and the $E_g$ of system (Δ), carrier mobility of graphene electrons ($\mu_e$) and holes ($\mu_h$), and on/off current ratio estimated at room temperature ($I_{on}/I_{off}$).

<table>
<thead>
<tr>
<th>DMC/BLG/α-SiO₂-26</th>
<th>B</th>
<th>H</th>
<th>T-1</th>
<th>T-2</th>
</tr>
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<tbody>
<tr>
<td>$E_{ad}$ (eV)</td>
<td>1.736</td>
<td>1.740</td>
<td>1.736</td>
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</tr>
<tr>
<td>$E_b$ (eV)</td>
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<td>1.281</td>
<td>1.277</td>
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</tr>
<tr>
<td>$d_m$ (Å)</td>
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<td>5.06</td>
<td>5.05</td>
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<tr>
<td>$d_a$ (Å)</td>
<td>2.83</td>
<td>2.83</td>
<td>2.83</td>
<td>2.83</td>
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<tr>
<td>$Q_{ad}$ (e)</td>
<td>0.65 (0.58)</td>
<td>0.51 (0.59)</td>
<td>0.60 (0.58)</td>
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<tr>
<td>$Q_b$ (e)</td>
<td>−0.43 (−0.43)</td>
<td>−0.43 (−0.43)</td>
<td>−0.43 (−0.43)</td>
<td>−0.43 (−0.43)</td>
</tr>
<tr>
<td>$Q_{b}$ (e)</td>
<td>0.27 (0.30)</td>
<td>0.26 (0.29)</td>
<td>0.27 (0.30)</td>
<td>0.27 (0.30)</td>
</tr>
<tr>
<td>$E_g$ (meV)</td>
<td>392 (404)</td>
<td>390 (398)</td>
<td>392 (410)</td>
<td>394 (408)</td>
</tr>
<tr>
<td>$\Delta$ (meV)</td>
<td>−55 (−24)</td>
<td>−59 (−33)</td>
<td>−57 (−21)</td>
<td>−52 (−27)</td>
</tr>
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<td>$\mu_e$ (cm²/V·s)</td>
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<td>$\mu_h$ (cm²/V·s)</td>
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<td>1.36 × 10⁵</td>
<td>1.51 × 10⁵</td>
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<td>$I_{on}/I_{off}$</td>
<td>7.34 × 10⁶</td>
<td>6.79 × 10⁶</td>
<td>7.34 × 10⁶</td>
<td>7.93 × 10⁶</td>
</tr>
</tbody>
</table>

* The data in parentheses are obtained from the vdW-corrected GGA functional within the Grimme scheme.
graphene on a-SiO$_2$-covered Si wafers is $(0.10-0.15) \times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [7]. This difference may come from the corrugations of graphene on a-SiO$_2$, the defects in graphene, the impurities at the interface between graphene and a-SiO$_2$, and so on.

For graphene FETs, the off current is dominated by the thermionic emission of carriers through the Schottky barrier [11,13,39]. There is an approximate relationship between $I_{on}$ and $I_{off}$, namely, $I_{on}/I_{off} \approx \exp(E_g/k_BT)$, where $k_B$ is Boltzmann constant and $T$ is Kelvin temperature [13,62]. Based on the fact that $E_g$ of the narrowest graphene ribbons (2 nm) are about 400 meV and $I_{on}/I_{off}$ up to $10^7$ are obtained from the related FETs [13], the room-temperature $I_{on}/I_{off}$ of this single-gate FET based on DMC/BLG/a-SiO$_2$-26 system estimated is (6.79–7.93) $\times 10^5$. The detailed data relevant to the four configurations of DMC/BLG/a-SiO$_2$-26 system can be found in Table 1.

4. Discussion

For BLG/a-SiO$_2$-26 system, the p-doping effect from a-SiO$_2$-26 can be illustrated by the relative position between the $E_F$ of a-SiO$_2$-26 and that of the pristine BLG [55]. As shown in Fig. 6, the former is 1.77 eV lower than the latter. To equilibrate their potentials, electrons are transferred from the occupied $\pi$ states of BLG to a-SiO$_2$-26, which shifts the $E_F$ of BLG downwards and the related states of a-SiO$_2$-26 upwards. As a result, the $E_F$ of BLG/a-SiO$_2$-26 system locates below the $E_F$ of BLG (see Fig. 3b). Moreover, since the top graphene layer is far away from a-SiO$_2$-26, it donates much fewer electrons than the bottom layer (see Table S1, Supplementary data), which produces $F_I$ and thus opens $E_g$ in BLG.

To better understand the results of DMC/BLG/a-SiO$_2$-26 system, we first explain the n-doping effect from DMC for the system of DMC on freestanding BLG (DMC/BLG), which can be interpreted by the relative position between the highest occupied molecular orbital (HOMO) of DMC in the density of states (DOS) for DMC/BLG system and the $E_F$ of the pristine BLG [30]. The calculated HOMO of DMC in the DOS is 1.92–1.96 eV higher than the $E_F$ of the pristine BLG (see Fig. S6, Supplementary data), which enables efficient transfer of electrons from DMC to the unoccupied $\pi^*$ states of BLG. Hence, the $E_F$ of BLG moves upwards, making the $E_F$ of DMC/BLG system above the $E_F$ of BLG with $\Delta = –401$ to –393 meV (see Fig. S7, Supplementary data).

As discussed above, the $E_F$ of DMC/BLG system is above that of the pristine BLG, leading to the larger $E_F$ difference between DMC/BLG system and a-SiO$_2$-26 than that between the pristine BLG and a-SiO$_2$-26 (see Fig. 6). Accordingly, a-SiO$_2$-26 in DMC/BLG/a-SiO$_2$-26 system accepts more electrons than that in BLG/a-SiO$_2$-26 system. And the upshift degree of a-SiO$_2$-26 related states in DMC/BLG/a-SiO$_2$-26 system is larger than that in BLG/a-SiO$_2$-26 system. Namely, after the deposition of DMC, the flat bands associated with a-SiO$_2$-26 move up relative to the $E_F$ (see Figs. 3b and 5c). As shown in Fig. 6, the difference between the HOMO of DMC and the $E_F$ of the pristine BLG is 0.15–0.19 eV larger than that between the $E_F$ of the pristine BLG and that of a-SiO$_2$-26. Hence, the n-doping from DMC is slightly stronger than the p-doping from a-SiO$_2$-26, which accounts for the little n-doping of BLG in DMC/BLG/a-SiO$_2$-26 system. In other words, the $E_F$ shift is significantly reduced by the adsorption of DMC. Meanwhile, the top graphene layer accepts electrons from DMC, while the bottom one donates electrons to a-SiO$_2$-26 (see Table 1). This greatly increases $F_I$ and thus $E_g$ value in BLG. Actually, there is an extra mechanism for $E_g$ opening of BLG in DMC/BLG/a-SiO$_2$-26 system (i.e., the breaking of the equivalence between the A and B sublattices), besides the breaking of the inversion symmetry of BLG. As shown in Fig. S8 (Supplementary data), the charge distributions of both top and bottom graphene layers are inhomogeneous, which destroys the equivalence between the A and B sublattices of the two layers. To estimate $E_g$ induced by this mechanism in top and bottom graphene layers, the band structures of DMC/SLG and SLG/a-SiO$_2$-26 systems are calculated. The results show that $E_g$ = 5–15 and 28 meV for DMC/SLG and SLG/a-SiO$_2$-26 systems, respectively.

To understand the effects of the DMC concentration on $E_g$ and $\Delta$ values of the considered systems, we calculate the electronic properties of DMC/BLG system under the DMC concentration of 0.39, 0.76, 1.19, and 2.38/nm$^2$. As the DMC concentration increases from 0.39 to 1.19/nm$^2$, the electron transfer from DMC to the top graphene layer increases from 0.79 to 1.64 $\times 10^{-2}$ e/C-atom, while that from DMC to the bottom graphene layer changes little and keeps small (see Table 2). As a result, $F_I$ can be enhanced, which increases $E_g$ value from 189 to 244 meV. Moreover, the n-doping of BLG becomes stronger, and $\Delta$ increases from 275 to 401 meV. With the further increase of the DMC concentration from 1.19 to 2.38/nm$^2$, the changes of $E_g$ and $\Delta$ values are small, since the electron transfer from DMC to BLG becomes almost saturated (see Table 2). Based on these results, the effects of the DMC concentration on $E_g$ and $\Delta$ values of DMC/BLG/a-SiO$_2$-26 system are clear, although the relevant electronic properties are not calculated due to the large computational cost. Similarly, as the DMC concentration increases from 0.39 to 1.19/nm$^2$, the electron transfer from DMC to the top graphene layer should become more efficient. Because the bottom graphene layer carries positive charge due to p-doping from a-SiO$_2$-26, $F_I$ can be significantly enhanced, resulting in improved $E_g$ value. As the DMC concentration further increases from 1.19 to 2.38/nm$^2$, $E_g$ value should also change.

Fig. 6 – Relative positions among the HOMO of DMC in the DOS of DMC/BLG system, the $E_F$ of DMC/BLG system, the $E_F$ of the pristine BLG, the $E_F$ of BLG/a-SiO$_2$-26 system, and the $E_F$ of a-SiO$_2$-26. The $E_F$ of the pristine BLG is set to zero.

Please cite this article in press as: Wang TH et al. Towards single-gate field effect transistor utilizing dual-doped bilayer graphene. Carbon (2014), http://dx.doi.org/10.1016/j.carbon.2014.05.048
and gate dielectric. The value estimated is up to 10

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Table 2 – Summary of the results for DMC/BLG system under different DMC concentrations: charge carried by the top graphene layer (Qt) and the bottom graphene layer (Qb), bandgap opened in BLG (Eg), and difference between the ED of BLG and the Eg of DMC/BLG system (Δ).

<table>
<thead>
<tr>
<th>DMC number</th>
<th>BLG supercell</th>
<th>DMC concentration (/nm²)</th>
<th>Qt (e/C-atom)</th>
<th>Qb (e/C-atom)</th>
<th>Eg (meV)</th>
<th>Δ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7 × 7</td>
<td>0.39</td>
<td>−0.79 × 10⁻²</td>
<td>−0.14 × 10⁻²</td>
<td>189</td>
<td>−275</td>
</tr>
<tr>
<td>1</td>
<td>5 × 5</td>
<td>0.76</td>
<td>−1.28 × 10⁻²</td>
<td>−0.16 × 10⁻²</td>
<td>222</td>
<td>−354</td>
</tr>
<tr>
<td>1</td>
<td>4 × 4</td>
<td>1.19</td>
<td>−1.64 × 10⁻²</td>
<td>−0.18 × 10⁻²</td>
<td>244</td>
<td>−401</td>
</tr>
<tr>
<td>2</td>
<td>4 × 4</td>
<td>2.38</td>
<td>−1.65 × 10⁻²</td>
<td>−0.19 × 10⁻²</td>
<td>242</td>
<td>−427</td>
</tr>
</tbody>
</table>

a All results are obtained from the most stable configuration of DMC/BLG system under different DMC concentrations.

5. Conclusions

By using first-principles DFT calculations, we have developed a BLG dual-doped by functionalized -SiO2 gate dielectric and DMC. This dual-doped BLG shows a sizeable band gap at room temperature. Nano Lett 2010;10(2):715–8.

Acknowledgment

We acknowledge the supports from National Key Basic Research and Development Program (Grant No. 2010CB631001).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.05.048.

References


