AA bilayer graphene on Si-terminated SiO_2 under electric field*

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The AA-stacked bilayer graphene/α-SiO_2 (001) interfaces with Si terminated atoms are studied in the presence of an electric field F with different intensities by first principles. AA-stacked bilayer graphene is slightly mis-oriented on SiO_2 substrate without electric field and the band gap is 0.557 eV. However, as F increases, the AA-stacked bilayer graphene has its layers gradually vertically shifted with each other and, finally, transfers into AB-stacked bilayer graphene and the band gap reduces to 0.252 eV under 0.015 Hartree.

Keywords: interface, graphene, oxide

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1. Introduction

Graphene has recently attracted extensive attention due to its potential replacement of traditional Si in future nano-scale electric devices and also due to its use in detectors, sensors, photoelectrons, etc.[1–3] Bilayer graphene (BLG) is more suitable for devices. For instance, IBM has successfully improved the BLG working frequency from 24.7 GHz to 100 GHz and has highlighted that BLG structures showed excellent electrical noise in devices with more than one layer of graphene.[4–6] Three kinds of substrates are dominant: metals (Ni, Ir, etc.), SiC, and SiO_2. Among all graphene device experiments, the overwhelming majority of substrartes are α-SiO_2 because it is cheap and compatible with the present IC process and is easy to obtain and clean. The experiential thickness of SiO_2 is defined as 300 Å or 100 Å for easy observation of graphene.[7] Our previous study[8] pointed out that the atomic structure of one layer graphene slightly changes: when electric field (F) is less than 0.02 Hartree, (1 Hartree = 27.21138 eV/Å), and above 0.02 Hartree the F promotes to form C–O covalent bond in the surface and destroys the excellent electron transport properties of grapheme, respectively. Kang *et al.*[9] comparatively pursued the investigation into Si and O terminated SiO_2/graphene interface to study the charge transfer from substrate due to surface dangling bonds. Shemella and Nayak[10] focused on the H-passivation of a graphene/SiO_2 interface. In the present paper, we evaluate the AA-stacked BLG on α-SiO_2–Si terminated, especially the effects of an external electric field on the BLG/α-SiO_2 interface.

2. Calculations

All the density functional theory calculations are performed using the DMOL^3 code.[11] The generalized gradient approximation (GGA) with the revised Perdew–Burke–Ernzerhof (RPBE) functional is employed as the exchange and correlation function.[12] The energy cutoff is 600 eV for geometry optimization. In the simulation, a three-dimensional periodic boundary condition is taken. For the whole system, a 2×2 supercell of two layers of carbon atoms on SiO_2 with a vacuum width of 2.5 nm is built. The distance between the two layers of carbon atoms is set to be 0.34 nm, which is the same as that of graphite. The Monkhorst–Pack grid k-point is set to be $12 \times 12 \times 1$. In order to investigate the effects of electric field on the atomic configuration, electronic structure, electron distribution of the bilayer system, an external electric field normal to the layer is applied. The ten-layer SiO_2 with terminated silicon atoms is set to be the substrate underlying AA-stacked bilayer graphene. The SiO_2 surface is relaxed before BLG is added on its surface to release the surface dangling bands. The three bottom layers of SiO_2 are fixed during calculations. The whole system contains 10 oxygen atoms, 5 silicon atoms, and 16 carbon atoms.

3. Results and discussion

Firstly, to confirm the validity of our simulation method, the structure parameters of graphite and diamond are calculated and listed in Table 1. The results are in accordance with those of the earlier local-density approximation (LDA) and GGA calculations. The C–C lengths are slightly underestimated when compared with the experimental values. So, in

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the following, we adopt this simulation method to investigate the bilayer graphene/SiO_2 interface.

Table 1. Values of lattice constants a and c of graphite and diamond.

Structures	Values /Å	Our work/Å	Experiment/Å	LDA/Å	GGA/Å
Graphite	a	2.446	2.46[a)]	2.445[c)]	2.465[c)]
	c	6.422	6.67[a)]	6.712[c)]	6.640[c)]
Diamond	a	3.534	3.57[b)]	3.529[c)]	3.578[c)]

[a)] Ref. [13], [b)] Ref. [14], [c)] Ref. [15]

The atomic structures of AA-stacked BLG/α-SiO_2 interfaces under diverse F are shown in Figs. 1 and 2. The corresponding structure data are listed in Table 2. Horizontally, without an external electric field, the bilayers slightly misalign, each with an angle of 92.201°. Recently, the misorientation is plausible and reported from the X-ray analysis of multilayer graphene on SiC.[16] As F increases, the top layer shifts toward the right and the bottom layer moves toward the left to form the misaligned AA-stacked BLG. The angle in the Fig. 1 obviously indicates the trend, the corresponding concrete values are summarized in Table 2. When $F = 0.015$ Hartree, the angle between the segments is 119.73°, which is very near to 120° in Bernal structure. In other words, the AA-stacked bilayer graphene almost completely transfers into AB-stacked BLG, the top view pictures are shown in Fig. 2. The electronic properties and, consequently, the optical, vibrational, and transport properties have strong correlation with the (mis)orientation of the successive layers. So far, the transfer from our simulation means that AA-stacked BLG under electric field is less stable than AB-stacked BLG, which is in reasonable agreement with the experimental data about AA-stacked structure, which has been reported to be energetically unfavorable to the simple AA graphite existing theoretically.[17] The total energy barrier from AA to AB-stacked BLG is 2.34 eV. The respective energy barriers are 0.10 eV, 0.53 eV, and 1.71 eV from (a) → (b), (b) → (c), and (c) → (d) in Fig. 1.

Vertically, the nearest C–C distance and the spacing between two layers decline as F increases as shown by the last two columns in Table 2. The vertical distance between surface oxygen and BLG (d_0) increases from 3.304 Å to 3.368 Å with F increasing from 0 to 0.015 Hartree. It can be found that the top layer graphene moves from top to bottom. The bottom layer slightly moves up and brings up with the surface atoms on the SiO_2 surface. The surface oxygen atoms move away from the BLG bottom layer and Si–O first layer bonds increase with an increase in F. Hence, as F increases, electron accumulation along the interface region generates a force pointing to the interface, while the top layer of BLG moves downwards and atoms on SiO_2 surface and BLG bottom layer move upwards.[8]

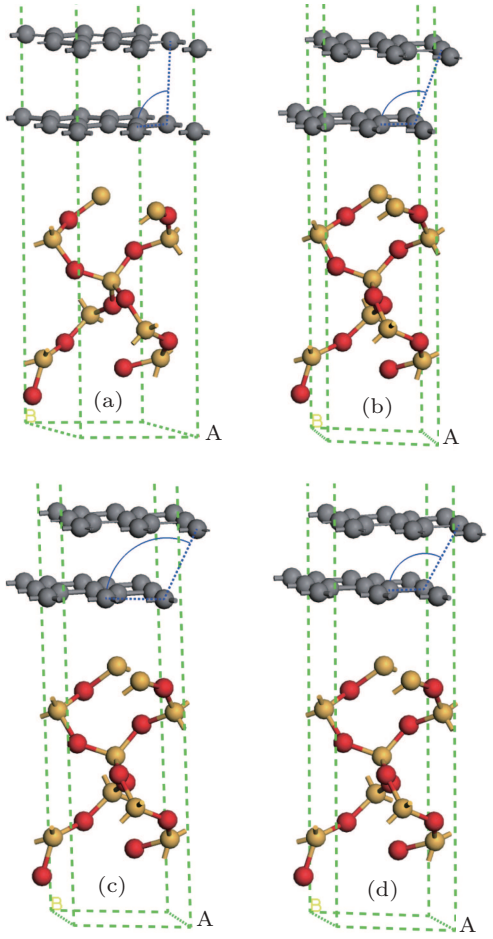


Fig. 1. (color online) Side face atomic stacking BLG/SiO_2–Si interfaces under $F = 0$ Hartree (a), 0.005 Hartree (b), 0.01 Hartree (c), and 0.015 Hartree (d). The gray, red, and yellow symbolize C, O, and Si atoms.

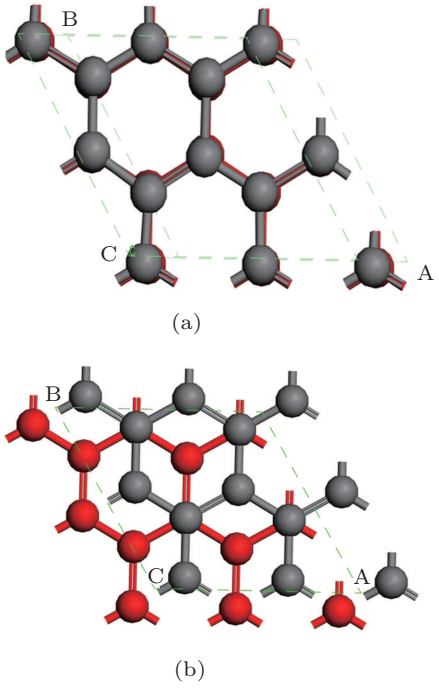


Fig. 2. (color online) Top views of AA-stacked BLG/α-SiO_2 interfaces before (a) and (b) after simulation at 0.015 Hartree, the gray and red symbolize the top and bottom layer. SiO_2 atoms are deleted from the system.

Table 2. Structure parameters under different values of F with d_0 denoting the vertical distance between surface Si and C atom, l_0 the surface Si–O bending length, distance and spacing the nearest C–C distance and vertical distance between top and bottom layer of BLG, respectively.

Electric field/Hartree	d_0/Å	l_0/Å	Angle/(°)	Distance/Å	Spacing/Å
0	3.304	1.691	92.2	3.524	3.521
0.005	3.175	1.693	108.2	3.335	3.168
0.01	3.293	1.690	113.5	3.080	2.825
0.015	3.368	1.691	119.7	2.875	2.496

In Table 2, d_0 is 3.304 Å, which is much larger than the Si–O bond length 1.67 Å of in SiO_2. The interactions between the graphene and substrate are weak Van der Waals. The d_0 increases as F increases. In other words, the interaction between BLG and SiO_2 substrate decreases with the increase of F. Without an electric field, the spacing is 3.521 Å from our simulation, which is consistent with the experimental value. The experimental value for AA-stacked is between 4.7 Å and 4.3 Å while the number of layers is 15.[16] On lithium intercalated AA graphite, the spacing is $\sim$ 3.706 Å.[18] The spacing drops off from 3.521 Å to 2.496 Å when F is 0.015 Hartree. The distance and spacing shortening with the increase of F indicates that the interaction between the top and bottom layer of BLG is enhanced. The original weak interlayer bonding is forced by more overlaps between 2pz orbitals (π states).

Mulliken charge population in terms of F is listed in Table 3, whose values indicate the charges of all atoms. As shown in the table, oxygen and silicon are anion and cation, which correspond to negatively and positively charges, respectively. When $F = 0$, carbon atoms have positive charges and lose some electrons to SiO_2 substrate, which accords with the theory that the substrate induces charged impurities.[19,20] In addition, the external electric field only slightly changes the total electrons from SiO_2 to carbon atoms, as shown by the charge sum of all carbon atoms in Table 3. As F increases, the charges in SiO_2 substrate change slightly. For instance, even the surface silicon atom (No. 13) and sub-surface oxygen atoms, O No.5 and O No.10, have almost no change in charge quantity. The absolute charge quantity of carbon atom increases as F increases. The downward electric field greatly rearranges the charges of C atoms. The top layer and bottom layer can be regarded as cathode and anode, respectively. The built-in electric field is upwards to compensate the external electric field. In the BLG case, charges are more sensitive to electric field, since the charges on C atoms at 0.005 Hartree in our simulation are comparable to those in one layer grephene/SiO_2 at 0.03 Hartree.[8]

It is found that the band gap (E_g) changes with F. When $F = 0$, the E_g is 0.557 eV. This value was reported to be 0.26 eV for epitaxially grown bilayer graphene on SiC.[13] When F is 0.01 Hartree and 0.015 Hartree, E_g changes into 0.056 eV and 0.252 eV, respectively. The variation is due to the atomic structure change. The AB-stacked E_g is less than AA-stacked E_g from our simulation.

Table 3. BLG graphene charges under different strengths of electric field.

No.	Atom	0	0.005 Hartree	0.01 Hartree	0.015 Hartree
1	O	–0.344	–0.347	–0.348	–0.345
2	O	–0.818	–0.818	–0.817	–0.817
3	O	–0.822	–0.824	–0.824	–0.822
4	O	–0.755	–0.754	–0.755	–0.754
5	O	–0.788	–0.79	–0.788	–0.787
6	O	–0.811	–0.81	–0.811	–0.81
7	O	–0.437	–0.434	–0.435	–0.435
8	O	–0.829	–0.828	–0.826	–0.825
9	O	–0.796	–0.796	–0.797	–0.797
10	O	–0.757	–0.757	–0.756	–0.755
11	Si	1.604	1.603	1.605	1.604
12	Si	1.643	1.642	1.643	1.642
13	Si	0.793	0.811	0.792	0.789
14	Si	1.521	1.521	1.521	1.52
15	Si	1.607	1.608	1.606	1.605
16	C	0.002	0.052	0.133	0.244
17	C	0.003	0.058	0.131	0.237
18	C	–0.026	0.041	0.117	0.225
19	C	0.012	0.072	0.141	0.244
20	C	0.003	0.059	0.171	0.314
21	C	–0.001	0.056	0.173	0.315
22	C	–0.001	0.052	0.159	0.305
23	C	–0.007	0.022	0.167	0.316
24	C	0.001	–0.055	–0.072	–0.022
25	C	0	–0.055	–0.074	–0.027
26	C	0	–0.054	–0.225	–0.514
27	C	0.001	–0.056	–0.073	–0.026
28	C	0	–0.054	–0.225	–0.517
29	C	0.001	–0.054	–0.23	–0.544
30	C	0	–0.056	–0.075	–0.033
31	C	0	–0.055	–0.227	–0.528
Sum	C atoms	–0.012	–0.027	–0.009	–0.011

While the F increases to 0.02 a.u. the simulation cannot be converged, indicating that the whole system is unable to remain stable at 0.02 Hartree. However, we reported that one layer graphene reacted with SiO_2 substrate to form C–O covalent bond while F reached 0.03 Hartree, which indicates that one layer graphene on α-SiO_2 remains stable at 0.03 Hartree.[8] The BLG on α-SiO_2 is less stable than one layer graphene on α-SiO_2. In the BLG case, the SiO_2 substrate has no chance to approach to and react with the carbon atoms in the bottom graphene layer. The F arranges and separates the electrons along two layers and form a cathode (bottom layer) and an anode (top layer). The surface silicon atoms are positive to attract the top layer carbon atoms and to be repelled by the bottom layer C atoms in BLG. The distance between the

two layers drops off to 2/3 at 0.015 Hartree. More charges accumulate along the two layers, which means the generation of the great build-in static electric field within BLG. At the same time, the compelling force between surface silicon atoms and bottom carbon atoms enhances and pushes up the BLG. Finally, the built-in F becomes rather large, which results in the uneven BLG structure. On the other hand, the atoms on the top layer repel the SiO_2 surface atoms and avoid the reaction between the BLG atoms and surface SiO_2 atoms. The substrate becomes less controllable to BLG under biased F. This is the reason why the BLG experimental 1/f noise is extremely better than graphene monolayer noise.[5] This offers an exciting chance for using a low-noise and low power nano-device.

The substrate may influence the graphene properties.[21–24] There are also differences between different interface-terminated atoms. For the O-terminated SiO_2 interface, the structure transformation from AA to AB is found in terms of F. The O surface atoms have a stronger interaction with BLG due to the shorter interlayer distance and more charge populations, whose interface system is more stable than that on Si-terminated SiO_2.

4. Conclusions

In the present paper, the AA-stacked BLG on O-terminated α-SiO_2 under F was transferred into AB-stacked BLG with an increase of F. In addition, as F increases the spacing becomes shorter, and the interlayer bonding and the electrons along the BLG and the built-in electric field and band gap are enhanced.

References

[1] Schwierz F 2010 *Nature Nanotechnology* **5** 487
[2] Geim A K 2009 *Science* **324** 1530
[3] Lin Y M, Dimitrakopoulos C, Jenkins K A, Farmer D B, Chiu H Y, Grill A and Avouris P 2010 *Science* **327** 662
[4] Lin M, Dimitrakopoulos C, Jenkins K A, Farmer D B and Chiu H Y 2010 *Science* **327** 662
[5] Lin Y M and Avouris P 2008 *Nano Lett.* **8** 2119
[6] Lin Y M, Chiu H Y, Jenkins K A, Farmer D B, Avouris P and Alberto V G 2010 *IEEE Electron. Dev. Lett.* **31** 68
[7] Blake P, Hill E W, Castro A H, Novoselov K S, Jiang D, Yang R, Booth T J and Geim A K 2007 *Appl. Phys. Lett.* **91** 063124
[8] Ao Z M, Zheng W T and Jiang Q 2008 *Nanotechnology* **10** 275710
[9] Kang Y J, Kang J and Chang K J 2008 *Phys. Rev. B* **78** 115404
[10] Shemella P and Nayak S K 2009 *Appl. Phys. Lett.* **94** 032101
[11] Delley B 2000 *J. Chem. Phys.* **113** 7756
[12] Hammer B, Hanse L B and NΦrskov J K 1999 *Phys. Rev. B* **59** 7413
[13] Baskin Y and Meyer L 1955 *Phys. Rev.* **100** 544
[14] *Zahlenwerte und Funktionen aus Naturwissenchaften und Technik*, ed. Madelung O and Schulz M 1987 *Landolt-Börnstein, New Series, Group* III, Vol. 22, (Berlin: Springer-Verlag)
[15] Leenaerts O, Partoens B and Peeters FM 2009 *Phys. Rev. B* **80** 245422
[16] Hass J, Feng R, Millan-Otoya J E, Li X, Sprinkle M, First P N, de Heer W A, Conrad E H and Berger C 2007 *Phys. Rev. B* **75** 214109
[17] Charlier J C, Michenaud J P and Gonze X 1992 *Phys. Rev. B* **46** 4531
[18] Dahn J R, Fong R and Spoon M J 1990 *Phys. Rev. B* **42** 6424
[19] Adam S, Hwang E H, Galitski V M and Sarma S D 2007 *Proc. Natl. Acad. Sci. USA* **104** 18392
[20] Zacharia R, Ulbricht H and Hertel T 2004 *Phys. Rev. B* **69** 155406
[21] Li J, Wang L, Feng Z H, Yu C, Liu Q B, Dun S B and Cai S J 2012 *Chin. Phys. B* **21** 097304
[22] Tang C, Wei X L, Tan X, Peng X Y, Sun L Z and Zhong J X 2012 *Chin. Phys. B* **21** 066803
[23] Tang J, Kang C Y, Li L M, Liu Z L, Yan W S, Wei S Q and Xu P S 2012 *Chin. Phys. B* **21** 057303
[24] Wang D C, Zhang Y M, Zhang Y M, Lei T M, Guo H, Wang Y H, Tang X Y and Wang H 2012 *Chin. Phys. B* **21** 038102