Interface effect on structural and electronic properties of graphdiyne adsorbed on SiO_2 and h-BN substrates: A first-principles study*

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We use the first-principles calculation method to study the interface effect on the structure and electronic properties of graphdiyne adsorbed on the conventional substrates of rough SiO_2 and flat h-BN. For the SiO_2 substrate, we consider all possible surface terminations, including Si termination with dangling bond, Si terminations with full and partial hydrogenation, and oxygen terminations with dimerization and hydrogenation. We find that graphdiyne can maintain a flat geometry when absorbed on both h-BN and SiO_2 substrates except for the Si termination with partial hydrogenation (Si-H) SiO_2 substrate. A lack of surface corrugation in graphdiyne on the substrates, which may help maintain its electronic band character, is due to the weak Van der Waals interaction between graphdiyne and the substrate. Si-H SiO_2 should be avoided in applications since a covalent type bonding between graphdiyne and SiO_2 will totally vary the band structure of graphdiyne. Interestingly, the oxygen termination with dimerization SiO_2 substrate has spontaneous p-type doping on graphdiyne via interlayer charge transfer even in the absence of extrinsic impurities in the substrate. Our result may provide a stimulus for future experiments to unveil its potential in electronic device applications.

Keywords: graphdiyne, electronics applications, interface effect, spontaneous doping

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1. Introduction

Graphene[1] as a perfect two-dimensional (2D) material has attracted tremendous research interest in the last decade. The drawback is the lack of a sizable energy band gap which hinders its applications in nanoelectronics. New types of 2D materials, such as transition metal dichalcogenides,[2,3] black phosphorene,[4,5]and graphdiyne,[6] have emerged as potential alternatives which are both stable and semiconducting. Among them, graphdiyne is a new type of 2D carbon allotrope, which has both sp and sp^2 hybridizations, with its two adjacent hexagons connected by a diacetylenic linkage (–C≡C–C≡C–). Graphdiyne (GDY) was successfully synthesized on a copper surface in 2010 by Li *et al.*[6] Unlike graphene having no band gap, GDY is found to be a natural semiconductor[6] with electrical conductivity up to 2.516×10^4 S·m^{-1}. First-principles calculations[7–10] show that GDY has a direct band gap of about 0.5 eV. More interestingly, its in-plane electron and hole mobilities can be up to 10^5 cm^2·V^{-1}·s^{-1} and 10^4 cm^2·V^{-1}·s^{-1} at room temperature according to the calculations,[9] which are almost 100 times as large as those of the silicon. As a monolayer material, the short-channel effects in GDY are expected to be greatly suppressed like those in graphene.[11] Therefore, GDY as a very promising candidate for electronic applications has attracted tremendous attention ever since its debut. However, little attention has been paid to the effect of the substrates, which actually play an essential role in electronic applications, except for some studies performed on the interfacial properties of GDY on metal substrates.[12]

As is well known, semiconducting GDY has to be deposited on a dielectric layer for electronic applications such as field effect transistor (FET). It is therefore essential to understand and control at nanoscale the interaction between GDY and the dielectric layer. Encouragingly, a large number of attempts have been made to synthesize GDY substructures[13–16] on different substrates. These substrates can also be directly used as the dielectric layer for a logic gate. So far, rough silicon dioxide (SiO_2) and flat hexagonal boron nitride (h-BN) substrates are two representative dielectric layers widely used.[17,18] However, it is not fully understood how these substrates interact with GDY and modify its electronic properties, which urgently calls for an accurate theoretical investigation.

In this work, we study the interlayer effect on the structural and electronic properties of GDY deposited on both SiO_2 and h-BN substrates. By looking into different conceivable interface configurations, we find that the structure of GDY is quite insensitive to the interface configurations, except the partially hydrogenated Si terminal of the SiO_2 substrate. However, the electronic properties are very sensitive to the interface environment. It is interesting that we can achieve p-type dop-

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ing simply by depositing GDY on the O_2-dimerised surface along (0001) direction of α-quartz SiO_2. The self-doping effect can be attributed to the charge transfer between GDY and the substrate even without external impurities. Whereas, the band character of GDY is maintained when the SiO_2 substrate with Si-polar and O-polar terminations is fully hydrogenated. In contrast, h-BN as the substrate has no obvious effect on the structural and electronic properties of GDY.

2. Computational methods

The first-principles calculations were performed based on the density-functional theory (DFT) and the projector augmented wave (PAW) pseudopotential method[19] implemented in the Vienna *ab-initio* simulation package (VASP)[20] within the Perdew–Burke–Ernzerhof (PBE)[21] generalized gradient approximation. The Van der Waals (VdW) interaction between the layers was calculated by using Grimme's DFT-D2[22] correction to the PBE functional. The wave functions were expanded in a plane-wave basis set with cutoff energy of 500 eV. The periodical slab model was used to simulate the interaction between graphdiyne and SiO_2 or h-BN. In order to avoid the interaction between the periodical slabs, they were separated by more than 15 Å vacuum, and the back sides of the SiO_2 slabs were all passivated by hydrogen. The cell parameters of free-standing graphdiyne and the (0001) surface of SiO_2 are $a = b = 9.477$ Å, $\gamma = 120^\circ$ and $a = b = 5.06$ Å, $\gamma = 120^\circ$, respectively. The graphdiyne of 6.7% uniform tension was used to match the 2×2 SiO_2 slabs. Here $5 \times 5 \times 1$ k-points were used. In the mean time, Bader charge analysis[23] was performed to estimate the charge transfer between the layers. As for graphdiyne supported by h-BN, which has a crystal 2D atomic structure, the influence of stacking should not be ignored. Therefore, eight representative stackings were considered in the GDY/h-BN system, 4×4 supercell h-BN was used to match the lattice constant of graphdiyne, while the mismatch was about 6%. The graphdiyne layer and the substrates were all allowed to relax until the Hellmann–Feynman force on the atoms was less than 0.01 eV/Å, except that the lowest three layers of the SiO_2 slabs were fixed.

3. Results and discussion

SiO_2 is usually amorphous in experiment, which is hard for one to simulate. Here we choose α-quartz SiO_2, since it is the most stable phase under ambient conditions. The (0001) direction is commonly chosen to construct a substrate. A slab with thickness above 10 Å is used here with one side as the surface and the other side terminated by hydrogen to simulate a semi-infinite substrate. Figure 1(a) shows GDY on five representative SiO_2 substrates ((i) O_2-dimer, (ii) Si-polar, (iii) O-hydrogenated, (iv) Si-hydrogenated, and (v) Si-partially-hydrogenated substrates). The O_2-dimer surface[24] has a covalent bond formed between two surface O atoms both of which are bonded to the same Si atom under the surface; the Si-polar surface has two dangling bonds per surface Si atom; while the Si-hydrogenated (H_2-Si) and the O-hydrogenated (H-O) surfaces are constructed based on the previous two surfaces with all the surface dangling bonds saturated by hydrogen atoms. The Si-partially-hydrogenated (H-Si) surface is based on the (ii) structure with one of the two dangling bonds per surface Si atom hydrogenated and the other retained. On the (i)–(iv) substrates, graphdiyne still has a flat structure, indicating that the structure of graphdiyne is insensitive to these surface configurations. The big vertical separation between graphdiyne and the topmost Si/O atom, for example, 2.80 Å, 3.00 Å, and 3.00 Å on substrates (ii), (iii), and (iv), respectively, suggests a physical adsorption mediated by the Van der Waals interaction. However, substrate (i) leads to a slightly smaller vertical distance (2.50 Å), which may give rise to charge transfer, as discussed later. The situation of the (v) configuration is different, where graphdiyne forms covalent single-bonds with the surface Si atoms with average C–Si bond length of 1.95 Å. In this particular case, the flat structure of graphdiyne could not be maintained. It seems that surface hydrogenation of the SiO_2 substrate can cause a big change of the surface properties.

Different surface configurations naturally give rise to a variety of electronic structures, which are shown in Fig. 1(b). The electronic bands of free-standing graphdiyne and the substrates without and with adsorption are shown in black, blue, and red lines, respectively. The graphdiyne on the top of the fully hydrogenated surfaces (such as the cases (iii) and (iv)) shows almost the same band structure as that of free-standing graphdiyne near the Fermi level, because the energy states of the surface atoms are far below the Fermi level and therefore have no effect on the electronic structure of graphdiyne. In comparison, the un-hydrogenated surfaces play some non-negligible role in the band structure of adsorbed graphdiyne as shown in Fig. 1(b). The Si surface atom with two dangling bonds (case (ii)) and the oxygen dimer (case (i)) both give rise to very localized states and flat bands slightly below/above the Fermi level, however the flat bands have no obvious effect on the graphdiyne's electronic bands. More interesting, the surface oxygen atoms in case (i), which are very reactive, have a very pronounced effect on the electronic bands of graphdiyne. Due to the strong electronegativity of oxygen, hole-doping in graphdiyne occurs. The charge transfer is illustrated in Fig. 1(c) with the yellow charge iso-surface representing the charge accumulation and the cyan one representing the charge depletion. The charge transfer $\Delta\rho$ is defined as $\rho(AB) - \rho(A) - \rho(B)$, where A, B, and AB respectively represent free-standing graphdiyne, the SiO_2 surface,

and graphdiyne absorbed on SiO_2. From Fig. 1(c), we find that graphdiyne adsorption causes charge depletion in graphdiyne and in the meantime charge accumulation in the substrate, especially in the oxygen atoms. In contrast, the partially hydrogenated Si surface, which forms covalent bonds with graphdiyne, totally destroys the band character of graphdiyne, which is different from the other four situations where the band characters of free standing graphdiyne are maintained.

To quantify the charge transfer between graphdiyne and the substrate, Bader charge analysis is used, and the results are shown in Table 1. From Table 1, the largest charge transfer occurs in the GDY/H-Si system, where the covalent bonds are formed between the surface carbon and silicon atoms. A relatively large charge transfer also occurs from graphdiyne to the oxygen-dimer SiO_2 surface. Charge depletion is about 0.6 electron on graphdiyne (18 carbon atoms), which mainly goes to the surface oxygen atoms. For the remaining three substrates, the charge transfer is almost negligible. The results of charge transfer are consistent with the effects of the surface configurations on the band structures as discussed above in Fig. 1.

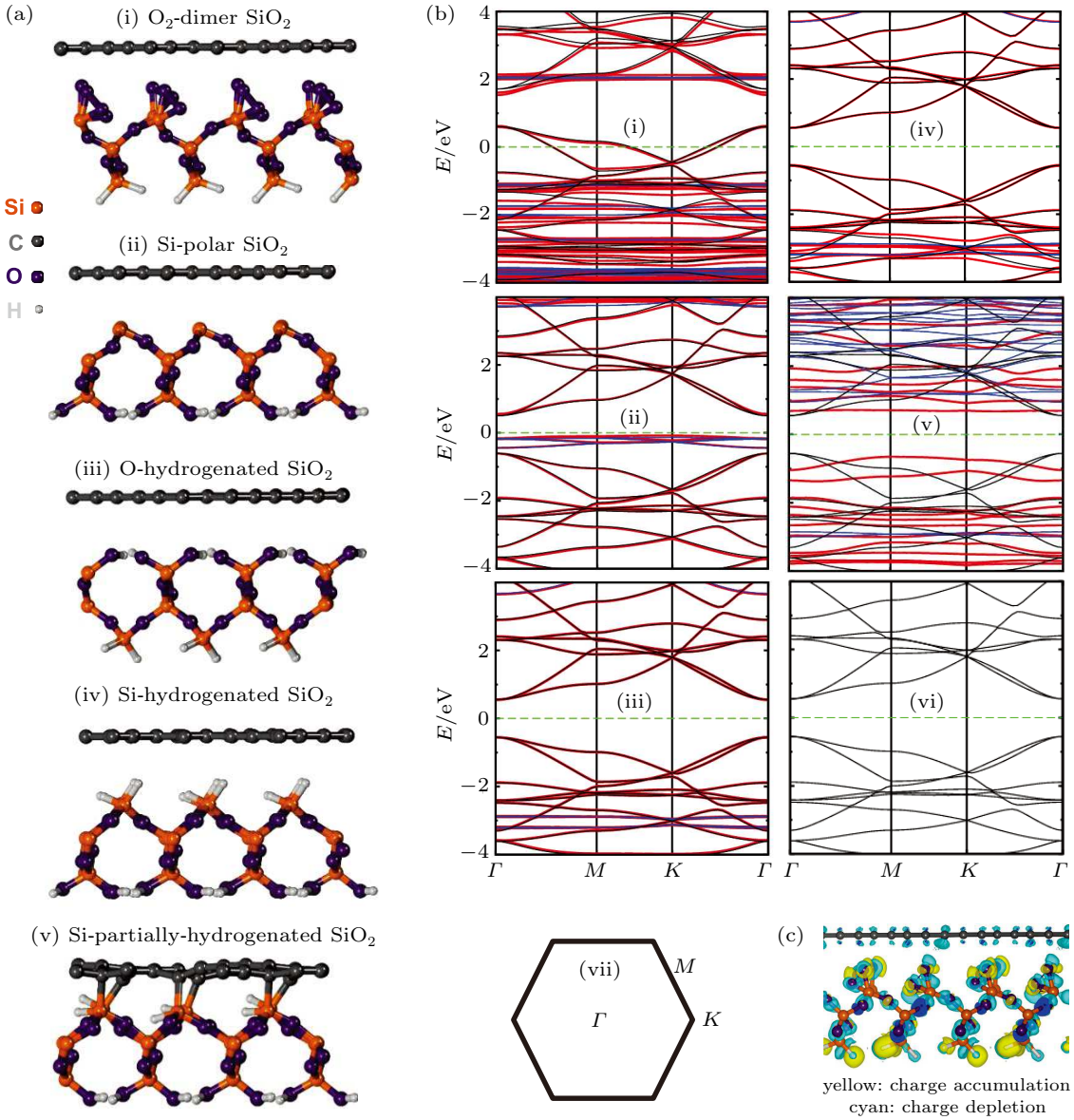


Fig. 1. (color online) (a) Heterostructures of graphdiyne on top of SiO_2 substrates. SiO_2 substrates have five different types of surfaces, including oxygen surfaces (i) without and (iii) with hydrogen termination, silicon surfaces (ii) without and (iv) with full hydrogen termination, and (v) silicon surface with partially hydrogenated termination. (b) Electronic band structures of (i)–(v) the five different heterostructures and (vi) free-standing graphdiyne; (vii) the Brillouin zone of the hexagonal lattice. The band structures of free-standing graphdiyne, SiO_2 surface, and graphdiyne absorbed on SiO_2 are shown in red, blue, and black, respectively. The Fermi energy level in green is shifted to zero. (c) Charge density difference $\Delta\rho$ ($= \rho_{AB} - \rho_A - \rho_B$), where A, B, and AB respectively represent free-standing graphdiyne, SiO_2 surface, and graphdiyne absorbed on SiO_2. The charge accumulated and depleted regions are shown in yellow and cyan, respectively. The isosurface value represents 2.1×10^{-2} e/Å^3.

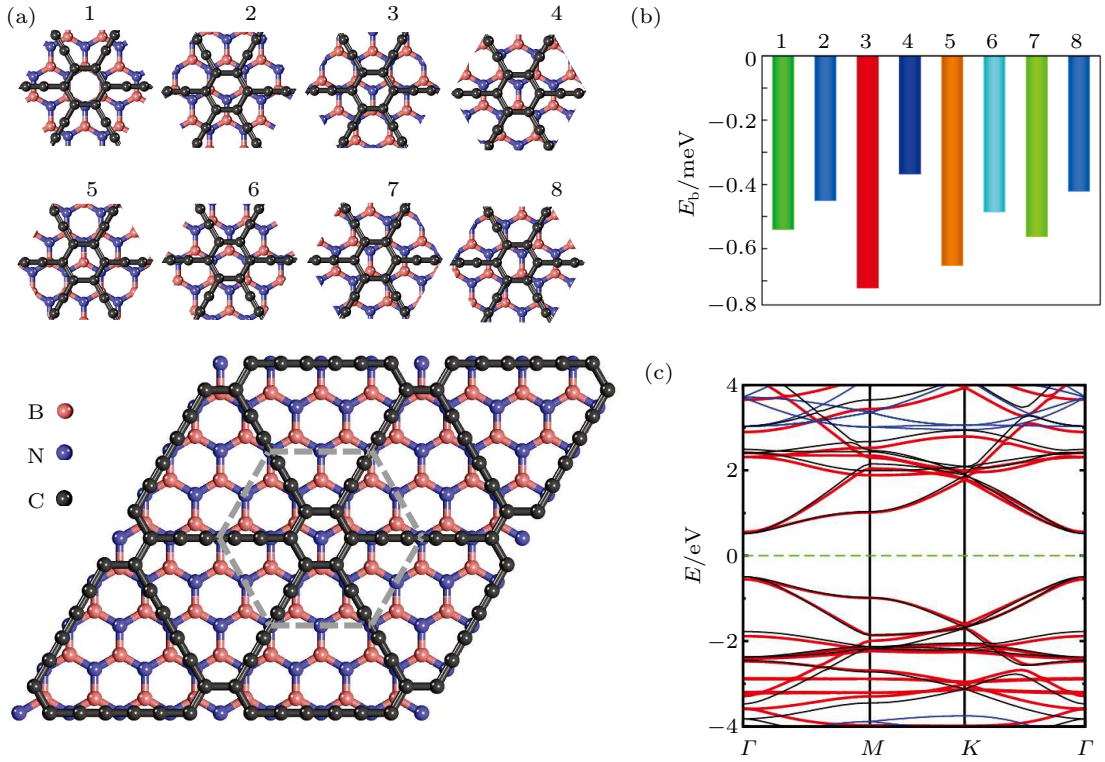


Fig. 2. (color online) (a) Heterostructures of graphdiyne on top of the hexagonal boron–nitride (h-BN) layer. Eight different stacking geometries are presented. The most stable one (♯3) is shown in a 2×2 supercell. (b) The binding energy E_b ($= (E_{AB} - E_A - E_B)/N_{atom}$) as a function of the stacking geometry, where E_A, E_B, and E_{AB} are the total energies of free-standing graphdiyne, the h-BN layer, and graphdiyne on h-BN, respectively, and N_{atom} is the total number of atoms per unit cell. (c) Electronic band structure of the geometry ♯3 (in red). The band structures of free-standing graphdiyne (in black) and mere h-BN layer (in blue) are also shown. The Fermi energy level in green is shifted to zero.

Table 1. The charge transfer ΔQ between graphdiyne and the substrates, and ΔQ is in units of the electron charge. O_2-dimer and Si-polar represent the SiO_2 with reconstructed oxygen termination and Si termination, respectively. H-O and H_2-Si represent fully hydrogenated surfaces. H-Si represents partially hydrogenated surface. The value in the parenthesis refers to the charge transfer on the surface oxygen atoms.

Substrate	ΔQ_{GDY}	ΔQ_{SiO_2}
SiO_2: O_2-dimer	−0.60	+0.60 (+0.43)
SiO_2: Si-polar	+0.06	−0.06
SiO_2: H-O	−0.02	+0.02
SiO_2: H_2-Si	−0.00	+0.00
SiO_2: H-Si	+2.60	−2.60
	ΔQ_{GDY}	ΔQ_{BN}
h-BN	+0.05	−0.05

To compare with the sensitivity of the electronic properties of GDY to the surface morphology of the SiO_2 substrate, we also use h-BN monolayer as an alternative substrate. Eight representative stacking orders numbered from 1 to 8 are considered, as shown in Fig. 2(a). A complete view of the whole ♯3 unit cell is given below, with only the central hexagonal part given (in gray dashed line) for the eight stacking structures. The stacking structure is shifted along the armchair direction of h-BN from ♯1 to ♯6, while along the zigzag direction from ♯7 to ♯8. To evaluate the relative stability of the stacking structures, we calculate the interlayer binding energy per atom as E_b ($= (E_{AB} - E_A - E_B)/N_{atom}$), where A, B, and AB represent graphdiyne, h-BN, and heterostructure of graphdiyne on h-BN, respectively, and N_{atom} is the total number of atoms per unit cell; the results are shown in Fig. 2(b). Obviously, the binding energy differences are quite small, only 0.4 meV/atom at maximum, suggesting no special preference of stacking order on h-BN. The ♯3 stacking is relatively more stable than the others. Choosing ♯3 heterostructure, we calculate the band structure and Bader charge transfer, which are respectively shown in Fig. 2(c) and Table 1. As expected, we find that the large band gap of h-BN has no obvious effect and the main feature of the top valence and the bottom conduction bands of graphdiyne is maintained. The Bader charge analysis shows that there is nearly no charge transfer between graphdiyne and h-BN.

4. Conclusion

We study the interface effect of SiO_2 and h-BN substrates on the structural and electronic properties of graphdiyne by using the first-principles method. All possible surface terminations of the SiO_2 substrate are considered, including Si termination with dangling bond, Si terminations with full and partial hydrogenation, and oxygen terminations with dimerization and hydrogenation. We find that graphdiyne can maintain a flat geometry when physically absorbed on both h-BN and SiO_2 substrates. A lack of surface corrugation in graphdiyne on

substrates, which may help maintain the electronic band character, is due to the weak Van der Waals interaction between graphdiyne and the substrate. It is worth pointing out that on Si-partially-hydrogenated SiO_2, a covalent type bonding between graphdiyne and SiO_2 forms and varies the band structure of graphdiyne, which is detrimental to electronics applications. Interestingly, the O_2-dimer SiO_2 substrate has spontaneous p-type doping on graphdiyne via interlayer charge transfer even in the absence of extrinsic impurities in the substrate. Our result may provide a stimulus for future experiments to unveil its potential in electronic device applications.

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