Diamond as an inert substrate of graphene

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Interaction between graphene and semiconducting diamond substrate has been examined with large-scale density functional theory calculations. Clean and hydrogenated diamond (100) and (111) surfaces have been studied. It turns out that weak van der Waals interactions dominate for graphene on all these surfaces. High carrier mobility of graphene is almost not affected, except for a negligible energy gap opening at the Dirac point. No charge transfer between graphene and diamond (100) surfaces is detected, while different charge-transfer complexes are formed between graphene and diamond (111) surfaces, inducing either p-type or n-type doping on graphene. Therefore, diamond can be used as an excellent substrate of graphene, which almost keeps its electronic structures at the same time providing the flexibility of charge doping. © *2013 American Institute of Physics.*
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Graphene has received considerable interest recently due to its unique electronic properties.[1–8] It has high carrier mobility with a great potential for applications in electronic devices, especially, field effect transistors. However, its intrinsic electronic properties are sensitive to external perturbations, such as nano-ribbon fabrications,[9–11] external electric field,[12–14] epitaxial strain,[15,16] molecular adsorption,[17–19] atom doping,[20–23] and coupling with other two-dimensional sheets[24–26] or substrate surfaces.[27–37] Big research efforts have been devoted to investigate the interactions between graphene and SiO_2,[27–29] SiC,[30–32] and metal surfaces.[33–36] Most of these substrates affect the electronic structure of graphene significantly.

Recently, diamond-like carbon films[38] and diamond surfaces[39,40] have been used as a new ideal substrate for graphene due to its high surface phonon energy and lower surface trap density compared with many other graphene substrates. However, the detailed information about the effect of diamond substrate on the electronic structure of graphene is still unavailable. Most recently, Ma *et al.*[41] have investigated electronic and magnetic properties of graphene adsorbed on diamond (111) surface using first-principles calculations, while the well-known Pandey-chain reconstruction[42,43] of this surface was not considered. On the other hand, the diamond (100) surface is technologically more important, which is the slowest growing surface in chemical-vapor deposition growth.[44,45] Therefore, a systematic theoretical study on the graphene/diamond interfaces is very desirable.

In the present work, we investigate adsorption behaviors and electronic structures of graphene on diamond (100) and (111) surfaces. Our calculations indicate that diamond surfaces overall interact weakly with graphene. Tiny gaps open at the Dirac point of graphene on diamond surfaces.

Charge-transfer complexes form between graphene and diamond (111) surfaces.

The lattice parameters of graphene and bulk diamond used to setup unit cell are 2.46 and 3.57 Å,[7,41,46,47] respectively. In order to simulate the hybrid graphene and diamond nanocomposites, the $2\sqrt{13} \times \sqrt{21}$ $R14.08°$ and 2×2 supercells of graphene are used to match the diamond (100) and (111) surfaces with the lattice mismatch less than 2%, respectively. Both clean and hydrogenated diamond (100) and (111) surfaces, denoted as C_D(100), H_D(100), C_D(111), and H_D(111), are considered in this work, and their atomic structures are plotted in Figs. 1(a)–1(d). Graphene adsorption on clean diamond (100) and (111) surfaces (G/C_D(100) and G/C_D(111)) are shown in Figs. 1(e) and 1(f). The G/C_D(100) supercell contains 10 layers of carbon (280 atoms) and a graphene sheet (68 atoms). The G/C_D(111) supercell contains 12 layers of carbon (72 atoms) and a graphene sheet (8 atoms). The vacuum space in the Z direction is about 20 Å to separate the interactions between neighboring slabs.

First-principles calculations are based on density functional theory (DFT) implemented in SIESTA.[48] Recently developed van der Waals density functional (vdW-DF)[49] is adopted due to its good description on long-range vdW interactions.[50–54] All geometry structures were fully relaxed with a conjugate gradient algorithm[55] until the energy and force are less than 10^{-4} eV and 0.02 eV/Å, respectively. Double zeta plus polarization orbitals basis set is used to give a reliable description[53] for valence electrons ($1s$ of hydrogen, $2s^2 2p^2$ of carbon) within the framework of linear combination of numerical atomic-orbital basis set.[56] Dipole correction is employed to cancel the errors of electrostatic potential, atomic force and total energy, caused by periodic boundary condition.[57] We have carefully tested k-point sampling in the surface Brillouin zone with 5×3 (for G/D(100)) and 16×16 (for G/D(111)) regular mesh, and by about 10^4 k points for calculating the tiny bandgaps at the Dirac point of graphene.

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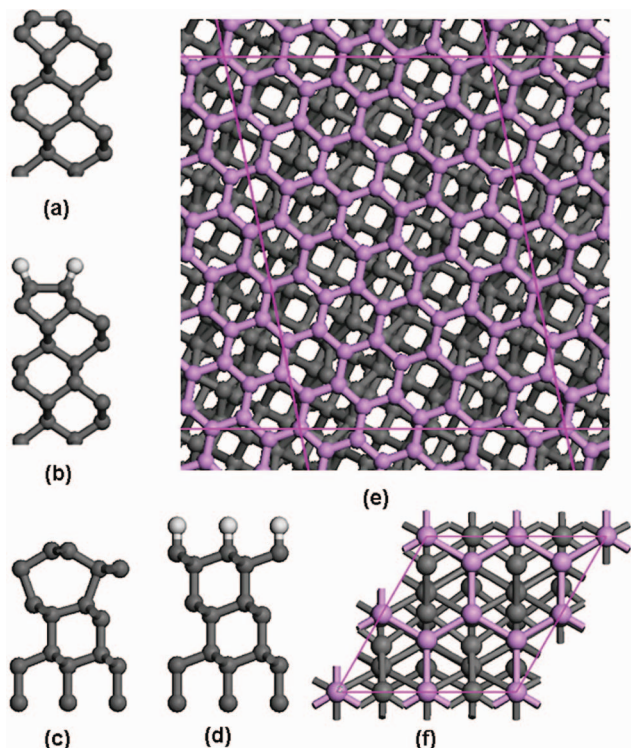
FIG. 1. Atomic geometries of (a) C_D(100), (b) H_D(100), (c) C_D(111) and (d) H_D(111), and supercell geometries for (e) G/C_D(100) and (f) G/C_D(111). The white and gray (purple) balls denote hydrogen and carbon atoms, respectively. Carbon atoms in graphene are highlighted.

In order to characterize the stability of graphene on diamond surfaces, a binding energy is defined as

$$E_b = E(G/D) - E(G) - E(D), \qquad (1)$$

where $E(G/D)$, $E(G)$, and $E(D)$ represent the total energy of graphene adsorbed on diamond surface, unsupported graphene, and diamond surface, respectively. As an benchmark, vdW-DF calculations give a good bilayer distance of 3.34 Å and binding energy of −31 meV per carbon atom for bilayer graphene, which fully agree with previous experimental measurements[58,59] and theoretical calculations.[60]

Electronic band structures of four different diamond surfaces are plotted in Fig. 2, which are in line with previ-

TABLE I. DFT vdW-DF calculated equilibrium distances D_0 (Å) when graphene adsorbs on four different diamond surfaces with corresponding binding energy E_b (meV) per carbon atom of graphene.

vdW-DF	D_0	E_b
G/C_D(100)	3.36	−57
G/H_D(100)	2.86	−50
G/C_D(111)	3.34	−58
G/H_D(111)	2.89	−58

ous theoretical results.[61] On clean diamond (100) surface (C_D(100)), two neighboring carbon atoms come together to form double-bonded dimers, introducing occupied π and unoccupied π^* states into the fundamental bandgap of diamond (Fig. 2(a)). On hydrogenated diamond (100) surface (H_D(100)), surface hydrogen will remove these π and π^* states, which leads to a wide bandgap (Fig. 2(b)). Clean diamond (111) surface (C_D(111)) exhibits a Pandey-chain reconstruction,[42,43] in which the top two rows of C atoms form zigzag chains and the system becomes nonmagnetic and metallic (Fig. 2(c)). Hydrogenated diamond (111) surface (H_D(111)) is also a wide bandgap semiconductor (Fig. 2(d)) similar to hydrogenated diamond (100) surface.

Graphene adsorption behaviors based on vdW-DF calculations are summarized in Table I. The adsorption height is 3.36, 2.86, 3.34, and 2.89 Å on C_D(100), H_D(100), C_D(111), and H_D(111) surfaces, respectively. The equilibrium distance on two clean diamond surfaces C_D(100) and C_D(111) is reasonably close to the value about 3.35 Å in graphite[62] and bilayer graphene.[58,59] At the same time, recent theoretical studies[29] have suggested that graphene adsorbs on reconstructed hydroxylated SiO_2 surfaces exhibited weak vdW interactions with an equilibrium spacing of 2.9 Å, which is consistent with our calculated results for graphene on two hydrogenated diamond surfaces H_D(100) and H_D(111). The binding energy is very small, consistent with the weak interaction suggested by large adsorption distances.

As shown in Fig. 3, when graphene is adsorbed on diamond surfaces, its intrinsic electronic structures around the
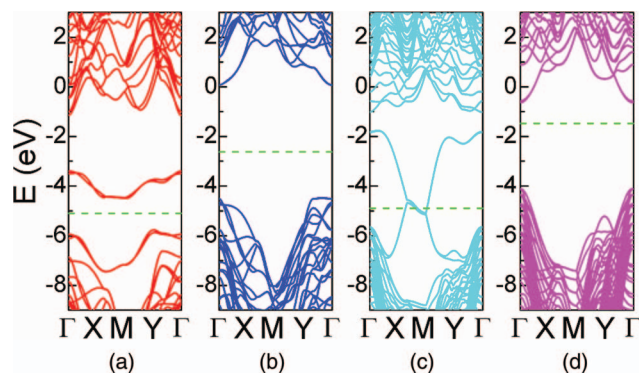

FIG. 2. Electronic band structures of (a) C_D(100), (b) H_D(100), (c) C_D(111) and (d) H_D(111). The vacuum level is set to zero and the Fermi level is marked by green dotted lines.
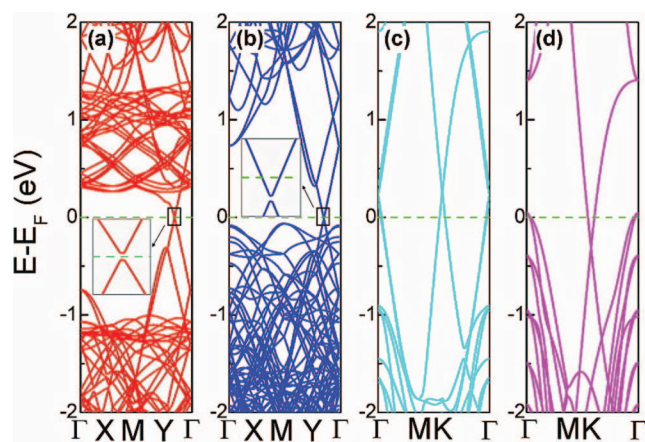

FIG. 3. Electronic band structures of (a) G/C_D(100), (b) G/H_D(100), (c) G/C_D(111) and (d) G/H_D(111) at the equilibrium distances. The Fermi level is set to zero and marked by green dotted lines.

Dirac point is almost not affected. Possibly through slight orbital hybridization between graphene and diamond surfaces, tiny bandgaps of 3, 1, 5, and 4 meV are opened at the Dirac point of graphene on C_D(100), H_D(100), C_D(111), and H_D(111) surfaces, respectively, which are much smaller than that (11 and 53 meV) for graphene adsorbed on Cu surface and for graphene/boron nitride heterobilayers.[25] Furthermore, these bandgap values are significantly lower than k_BT (25 meV) at room temperature and should not have a notable effect in experiment. Notice that a recent theoretical work,[41] without considering reconstruction on the surfaces,[42,43] has predicted that graphene interacts strongly with non-reconstructed diamond (111) surface, which is mainly contributed by interactions between π states on the graphene layer and carbon dangling bonds localized on the diamond surface. As a result, they got a small adsorption height (2.78 ∼ 2.98 Å) and a relatively large bandgap (0.4 ∼ 0.8 eV) at the Dirac point of graphene.

The Fermi level of graphene on C_D(100) remains in the induced gap, meaning no charge transfer between graphene and this diamond surface. Little charge transfer has been found at the interface between graphene and H_D(100), with an −0.01 eV shift of the Fermi level from Dirac point, a very weak n-type doping. Interestingly, different charge-transfer complexes are formed at the interfaces between graphene and diamond (111) surfaces, which move the Dirac point of graphene 0.26 eV above the Fermi level on C_D(111) and −0.31 eV below the Fermi level on H_D(111), resulting in strong p-type and n-type doping, respectively. This can be easily understood on the basis of the Schottky-Mott model,[63] since the work function of graphene (4.4 eV) is smaller than the work function (4.9 eV) of C_D(111) but larger than the ionization potential (3.5 eV) of H_D(111).[61] Notice that the vdW-DF calculated work function of graphene reported here is in good agreement with previous theoretical results (4.2 ∼ 4.7 eV)[33,34] and experimental measurements (4.6 eV).[64,65]

According to the π-electron tight-binding model in graphene,[26,66] the dispersion relation near the Fermi level of graphene can be approximated as

$$E(k) = \pm\sqrt{\Delta^2 + (\hbar v_F k)^2}, \qquad (2)$$

where k is the wave vector relative to the Dirac point of graphene, v_F is the Fermi velocity, and Δ is the onsite energy difference between the two sublattices ($\Delta = 0$ for free-standing graphene). In our calculated band structures, v_F is 0.8×10^6 m/s for graphene adsorbed on diamond surfaces, the same as pristine graphene. Thus, intrinsic electronic properties of graphene, especially, high carrier mobility, can be preserved on diamond substrates. DFT calculations underestimate the Fermi velocity of graphene by 15% ∼ 20% compared to the experimental value,[67] while our result is reasonably close to the value in previous calculations for graphene/boron nitride heterobilayers.[26]

Based on the linear dispersion relation close the Dirac point of graphene,[7] the charge carrier (hole or electron) concentration of doped graphene can be estimated by the following equation:[68,69]

$$N_{h/e} = \frac{(\triangle E_D)^2}{\pi(\hbar v_F)^2}, \qquad (3)$$

where $\triangle E_D$ is the Dirac point shift relative to the Fermi level. The charge carrier density of graphene adsorbed on different diamond (111) surfaces is 5×10^{12} cm^{-2} and 7×10^{12} cm^{-2} in graphene on clean hand hydrogenated diamond (111) surfaces. These values are more than 2 orders of magnitude larger than intrinsic charge carrier concentration of graphene at room temperature ($n = \pi k_B^2 T^2/6\hbar v_F^2 = 6 \times 10^{10}$cm^{-2}).[70] Thus, charge transfer at the interfaces between graphene and different diamond surfaces with tunable work functions provides new potential for graphene-diamond based Schottky diodes.[71–73]

In summary, we have investigated atomic structures and electronic properties of graphene adsorbed on diamond surfaces using DFT calculations. Diamond can be used as a promising substrate material for graphene since it preserves the unique electronic structure of graphene to a large extent. The main substrate effect is tiny gaps opening at the Dirac point of graphene on diamond (100) surfaces and charge-transfer complexes forming between graphene and diamond (111) surfaces.

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