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Semiconducting Electronic Property of Graphene Adsorbed on (0001) Surfaces of SiO$_2$

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First-principles total energy calculations are performed to investigate the energetics and electronic structures of graphene adsorbed on both an oxygen-terminated SiO$_2$ (0001) surface and a fully hydroxylated SiO$_2$ (0001) surface. We find that there are several stable adsorption sites for graphene on both O-terminated and hydroxylated SiO$_2$ surfaces. The binding energy in the most stable geometry is found to be 15 meV per C atom, indicating a weak interaction between graphene and SiO$_2$ (0001) surfaces. We also find that the graphene adsorbed on SiO$_2$ is a semiconductor irrespective of the adsorption arrangement due to the variation of on-site energy induced by the SiO$_2$ substrate.

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Exfoliation of graphite [1,2] and thermal annealing of SiC [3,4] have now achieved the single-layered graphite, graphene, which provides us a perfect two-dimensional electronic system. Much effort has been devoted not only to the elucidation of fundamental physics on this new and famous carbon allotrope but also to the exploration of the possibility of application in the next generation of electronic devices [1,5–9]. Graphene possesses a pair of linear dispersion bands at the Fermi level resulting in remarkable electron mobility of a few hundred thousand cm$^2$/Vs, and leading to application of graphene in high-speed switching devices [1,5–10]. On the other hand, these remarkable electronic properties of graphene have been shown to be vulnerable to external conditions such as structural corrugations, atom or molecule adsorptions, and interactions with other graphene or substrate surfaces [8–13]. Although this issue may be fatal to the application of graphene as a switching device in semiconductors, graphene is still applicable as a constituent of sensing devices. From both the fundamental precise two-dimensional physics and applied semiconductor engineering points of view, it is important to elucidate the effects of other materials on the electronic and structural properties of graphene.

Hybrid structures of graphene with insulating substrates are important for both fundamental studies and applications of graphene. Silicon dioxide (SiO$_2$) is widely used as an insulating substrate for device fabrication and physical property measurement. Many experiments reported the modulation of the electronic properties of graphene on a SiO$_2$ substrate, such as band gap opening and decrease of carrier mobility [8–10]. The interaction between the graphene and substrate is considered to play a crucial role in the modulation. Although many theoretical calculations [14–16] have been performed to elucidate the fundamental properties of graphene adsorbed on SiO$_2$ surfaces, there is still no clear physical insight into the fundamental properties of this hybrid system. Therefore, in the present work, we aim to investigate theoretically the energetics and electronic structures of graphene adsorbed on (0001) surfaces of $\alpha$ quartz using realistic and physical surface atomic structures based on first-principles total energy calculations in the framework of density functional theory. Our calculations clearly show that graphene keeps its plane structure, and is weakly bound to the substrate without forming covalent bond with O/Si atoms. The calculated binding energy calculated is about 10 meV per C atom. We also found that the graphene has semiconducting properties with a direct band gap of a few tens of meV. Detailed analysis of the local electrostatic potential reveals that the semiconducting properties are ascribed to the modulation of on-site energy of C atoms induced by the substrate.

All calculations have been performed based on density functional theory [17,18]. We use the local density approximation (LDA) to express the exchange-correlation energy of interacting electrons [19,20]. Ultrasoft pseudopotentials are adopted to describe the electron-ion interaction [21]. The valence wave functions and charge density are expanded in terms of a plane-wave basis set with cutoff energies of 25 and 225 Ry, respectively. The Brillouin-zone integration is performed with a $6 \times 6 \times 1$ $k$ mesh for geometry optimization and with a $12 \times 12 \times 1$ $k$ mesh for self-consistent electronic structure calculations for band dispersion. Geometry optimization has been performed for all atoms in the slab, until the remaining force acting on atoms is less than 0.005 Ry/Å. The conjugated-gradient minimization scheme is used for both the electronic structure calculation and for the geometry optimization.

The surfaces are simulated using a repeated-slab model in which 9 Si atomic layers of $\alpha$ quartz, graphene, and a 10 Å-vacuum region are included. We chose (0001)
surfaces of α quartz as a model surface of SiO₂ on which to adsorb the graphene. To avoid periodic image errors arising from the slab model, we adopt the effective-screening medium method \[22,23\]. We do not consider simple cleaved surfaces (as used for previous calculations) \[14–16\] but fully optimized oxygen-terminated (0001) surfaces to simulate experimentally relevant situations. Previous experimental and theoretical studies \[24,25\] have shown that the upper or lower two subsurfaces of cleaved SiO₂ undergo surface reconstruction at around 300 K to give O-terminated surfaces with six-membered rings as shown in Fig. 1(a). Besides these O-terminated surfaces, cleaved surfaces will also be rapidly hydroxylated under ambient conditions, yielding silanol groups (Si-OH) \[25–27\]. Thus, in this Letter, we also consider the fully hydroxylated SiO₂ surface possessing a zigzag hydrogen bonded network [Fig. 1(b)]. On these surfaces, we put graphene with \[2\]/C₂ lateral periodicity to keep the commensurability condition with the lateral cell of SiO₂ (less than 0.08% lattice mismatch). To investigate how the energetics and electronic structure of graphene depend on the local configuration on SiO₂, we considered three representative arrangements of graphene on SiO₂: top (T) configuration, bridge (B) configuration, and hollow (H) configuration.

Figures 2(a)–2(c) show the fully optimized geometric structures of graphene adsorbed on O-terminated SiO₂ surfaces. In all cases, graphene keeps its plane and hexagonal atomic network, maintaining the spacing of 2.9 Å for T, B, and H configurations, when bound to the SiO₂ surfaces. Of the three configurations, the hollow one is the most stable. The calculated binding energy per C atom of H configuration is 15 meV, about 3 meV greater than that of the other two configurations (Table I). These results indicate that the energetics of graphene on O-terminated surfaces are not very sensitive to the adsorption site \[28\].

We also find similar optimized structures and energetics for graphene on fully hydroxylated SiO₂ surface. As shown in Figs. 2(d)–2(f), graphene essentially retains its initial structure with separations of about 2.93 Å for all configurations. The binding energies of graphene on hydroxylated surfaces are 8, 10.7, and 13 meV for T, B, and H configurations, respectively. Thus, as for the O-terminated surface, graphene is loosely bound to the surface without any site selectivity.

These energetics of adsorption of graphene on both O-terminated and hydroxylated surfaces correspond well

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>O terminated</th>
<th>Hydroxylated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>2.88</td>
<td>2.96</td>
</tr>
<tr>
<td>Bridge</td>
<td>2.90</td>
<td>2.93</td>
</tr>
<tr>
<td>Hollow</td>
<td>2.89</td>
<td>2.91</td>
</tr>
</tbody>
</table>
with the previous experimental work [29], in which the binding energy was determined to be 16 meV per C atom. However, the spacing between the graphene and the surfaces was about 1.3 Å larger than those spacings obtained in our calculations. This structural discrepancy probably arises from the difference between the model SiO$_2$ structure used in the calculation and the amorphous SiO$_2$ used in the experiment. For instance, the nanometer scale structures on SiO$_2$, such as steps and adsorbates of environmental materials, lead to larger spacing between graphene and substrates. It must be pointed out that our results are inconsistent with previous theoretical results, in which a graphene monolayer is found to bound strongly to O-terminated SiO$_2$ substrates. It must be pointed out that our results are inconsistent with previous theoretical results, in which a graphene monolayer is found to bound strongly to O-terminated SiO$_2$ substrates. 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is spatial inhomogeneity in the electrostatic potential of C atoms of graphene. Indeed, the electrostatic potential on graphene adsorbed on SiO$_2$ strongly depends on the C sites and is shallower by 59–100 meV than that of C atoms belonging in isolated graphene [Tables III and IV]. The variation of the electrostatic potential is 23 and 45 meV for graphene on O-terminated and hydroxylated SiO$_2$ (0001) surfaces with on-top arrangements, respectively. These values are the same order as the gap energy of graphene on SiO$_2$. Indeed, single orbital tight-binding calculations for isolated graphene with on-site energy variation result in the energy gap of 10 meV at K point. Thus, we conclude that the variation in electrostatic potential or on-site energy of C atoms disrupts the degeneracy of the $\pi$ and $\pi^*$ bands at the K point resulting in their semiconducting character. The on-site energy difference can be observed in the wave functions from the top of valence band [$\alpha$ state in Fig. 3(c)] and the bottom of the conduction band [$\beta$ state in Fig. 3(c)] at the K point. The distribution of the wave function of the $\pi$ state in graphene is not equivalent between adjacent C atoms as in the case of hexagonal boron nitride which exhibit $\pi$ bonding character. The inhomogeneous on-site energy of the C atoms is induced not by the charge transfer between the graphene and the surfaces but by the inhomogeneous charge distribution on the SiO$_2$ surfaces. Indeed, our analyses of charge distribution show that there is no charge transfer to or from graphene. The charge redistribution occurs only at the interfacial region, and induces very small dipole moments.

Next, we investigate the electronic properties of bilayer graphene on SiO$_2$ surfaces. We find that the equilibrium interlayer distance with AB stacking arrangement is 3.35 Å. Figures 4(a) and 4(b) show the electronic energy band of bilayer graphene adsorbed on O-terminated and hydroxylated SiO$_2$ surfaces. These systems exhibit the parabolic bands around the Fermi level which resemble those of pristine bilayer graphene. Detailed analyses of the electronic energy bands around the Fermi level revealed that a small band gap of less than 6 meV is still opened [see the inset of Fig. 4(a)]. The band gap values of bilayer graphene with different configurations on both O-terminated and hydroxylated SiO$_2$ surfaces are listed in Table II. However, these band gaps are within the accuracy limitation of the LDA, and therefore we can assume that the band gap value is zero. Thus, the zero gap of the graphene layer is recovered when a second graphene layer is placed.

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[28] It should be noted that LDA well reproduces the interunit spacing of van der Waals materials.