

Electronic structure and band-gap modulation of graphene via substrate surface chemistry

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We have studied the electronic structure of graphene deposited on a SiO₂ surface using density functional methods. The band structure of the graphene monolayer strongly depends on surface characteristics of the underlying SiO₂ surface; for an oxygen-terminated surface, the monolayer exhibits a finite energy band gap while the band gap is closed when the oxygen atoms on the substrate are passivated with hydrogen atoms. We find that at least a graphene bilayer is required for a near zero energy gap when deposited on a substrate without H-passivation. Our results are discussed in the light of recent experiments. © 2009 American Institute of Physics.

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Graphene, which is a single sheet of carbon atoms from bulk graphite, has recently been discovered in a quasifree state.^{1,2} The potential applications are numerous, mainly due to the semimetallic electronic structure of graphene³ coupled with the metallic or semiconductor distinction depending on edge geometry.^{4–7} Recently, monolayers of epitaxially grown graphene on a substrate, such as SiC, were experimentally shown to exhibit reduced conduction properties compared to graphene bilayers and polylayers.^{3,8–12} This effect was explained with density functional theory (DFT) calculations, which showed the graphene monolayer system had an induced gap due to chemical interactions with the top atomic layer of the silicon carbide substrate, terminated with either silicon or carbon.^{13,14} In addition to the electronic structure, the substrate was shown to have an effect on the spectroscopic properties of two-dimensional graphene¹⁵ and may contribute to surface roughness.^{16–18}

Insulating substrates made from silicon dioxide (SiO₂) are widely used as a dielectric medium in integrated circuits. Various experiments have recently studied the deposition of graphene sheets and nanoribbons, which were isolated with mechanical exfoliation.^{11,16–22} To date, no first principle study has focused on addressing how the electronic properties of graphene are modified on a silicon dioxide substrate.

In this report we have studied the role of the underlying silicon dioxide substrate on the electronic properties of graphene using density functional calculations. We find that a single graphene layer, when deposited on oxygen-terminated silicon dioxide, loses its semimetallic characteristics and exhibits band opening due to strong chemical interaction with the underlying substrate. When a second graphene layer is added,^{23,24} the bilayer system shows a reduced gap—although still nonzero. From our calculations, we have shown that the intrinsic metallic band structure of graphene is only recovered when the terminal oxygen atoms of the SiO₂ substrate are passivated with atomic hydrogen. These results may provide valuable insight into substrate induced band modulation of graphenes.

Calculations were based on DFT^{25,26} with the local density approximation exchange-correlation functional and plane wave basis sets. Ultrasoft pseudopotentials were used

to represent ionic cores,^{27,28} and the electronic kinetic energy cutoff for electrons was 650 eV. Geometry relaxations were performed with the criterion that ionic forces are less than 0.02 eV. All calculations were done using VASP code.^{29–35}

A triclinic supercell was used with the following parameters: lattice constants of $a=b=9.832$ Å, $c=22.000$ Å; $\alpha=\beta=90.0^\circ$, and $\gamma=120.0^\circ$. The height of the supercell (c) was tested and found to include enough vacuum buffer between the graphene and the substrate in the adjacent periodic box. The two-dimensional substrate slab was comprised of a $2 \times 2 \times 2$ α -quartz supercell cut in the [100] direction, and this slab was orientated so that the bottom surface was silicon terminated. The oxygen atoms on the top surface of the substrate were at the interface with the graphene monolayer, and the effect of H-passivation on these oxygen atoms was studied. The substrate effect on graphitic materials was previously studied with simulations; for example, carbon nanotube encapsulation in SiO₂,³⁶ the interaction between silicon termination with a silicon carbide substrate,¹³ and nanoribbons on a bulk silicon substrate.³⁷ For this reason we have focused on the surface terminated with oxygen atoms. The unit cell contains 24 silicon atoms and 48 oxygen atoms. Eight hydrogen atoms are used to passivate the bottom silicon atoms, and an additional eight are used for systems where the top oxygen atoms are also passivated.

The hexagonal graphene unit cell was replicated 16 times (32 total graphene atoms) in order to coincide with the SiO₂ substrate supercell. Less than 0.01% lattice mismatch was observed and no effect on the isolated graphene band structure was found.

Considered in this study are a graphene monolayer above the oxygen terminated substrate [Fig. 1(a)], a graphene bilayer above the oxygen terminated substrate [Fig. 1(b)], and a graphene monolayer above the hydroxyl (OH) terminated substrate [Fig. 1(c)]. Electronic charge density plots are used to show if charge transfer occurred between substrate and graphene (see Fig. 2). Band structures were calculated based on k -points along the lines of high symmetry Γ KM Γ and are shown in Fig. 3.

We first considered the graphene monolayer above the SiO₂ substrate without H-passivation of the terminal oxygen atoms of the substrate. Upon geometrical relaxation, the O-terminated system [see Fig. 1(a)] clearly formed covalent

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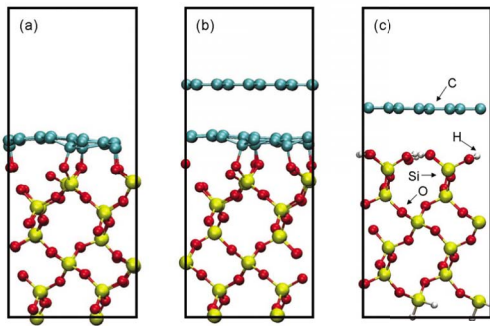


FIG. 1. (Color online) Graphene sheets above the SiO_2 substrate with O-termination and without H-passivation for (a) the monolayer and (b) the bilayer. The H-passivated system (c) is shown and no covalent bonding between graphene and substrate was observed.

bonds with the graphene sheet. Structural analysis revealed that the substrate surface was rough, (the standard deviation is 0.388 \AA from a planar surface), with four of the eight surface oxygen having made covalent contact with the graphene monolayer. The four nearest C–O distances, each representing one terminal oxygen atom lining up with a carbon atom, were $1.43, 1.43, 1.43,$ and 1.46 \AA [see Fig. 1(a)]. The other four oxygen atoms were recessed by an average of 0.71 \AA , which indicates that the structural energy minimum was with four O–C bonds. The short distance between the substrate surface and the graphene sheet (less than 1.5 \AA) was indicative of oxygen-carbon covalent bonding, and therefore the electronic band structure is likely to be affected when compared to isolated graphene or graphene on the H-passivated substrate, described in a later section.

Figure 2(a) shows the electron charge density for the O-terminated system; it is clear that charge density was shared between substrate surface and graphene monolayer, indicating the modification of the electronic structure and the loss of the conducting graphene bands. The band structure for the oxygen terminated substrate with covalently bonded graphene monolayer is shown in Fig. 3(a). The energy gap for the O-terminated system was at least 0.35 eV . The band structure for the O-terminated (no H-passivation) case was not additive and was highly modulated due to the strong covalent interaction between substrate and monolayer. Indeed, it is apparent that the combined band structure shows no resemblance to the semimetallic band structure for an isolated graphene monolayer. In a related context, the effect of the SiC substrate on graphene mono- and bilayers was

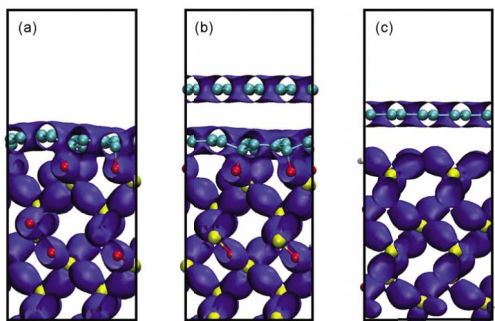


FIG. 2. (Color online) Charge density plots for oxygen terminated substrate without H-passivation for (a) the monolayer, (b) the bilayer graphene systems, and for (c) the H-passivated monolayer system. Charge transfer to the graphene was observed only to the lowest graphene layer that is covalently interacting with the SiO_2 substrate (Ref. 40).

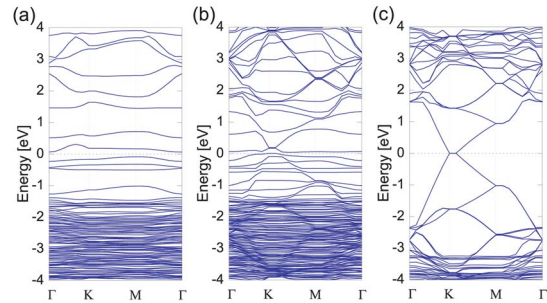


FIG. 3. (Color online) Band structure for (a) the graphene monolayer and for (b) the graphene bilayer above SiO_2 substrate without hydrogen passivation of terminal oxygen atoms, as well as for (c) the graphene monolayer above the H-passivated substrate. The addition of the second graphene layer brings back bands near to the Fermi energy, although still with a finite gap. With a single graphene layer and for a metallic band structure similar to freely suspended graphene, H-passivation is required. The Fermi energy is indicated by the dashed line.

studied computationally and experimentally.^{8,13} Specifically, graphene monolayers grown epitaxially on BN or SiC were not conducting due to strong interactions with the substrate; although bilayers showed a reduced band gap.

Next, we considered the graphene bilayer above the substrate without H-passivation of terminal oxygen atoms [see Fig. 1(b)]. The presence of the second layer of graphene decreased the energy gap but did not fully recover a zero gap. The charge density plot and corresponding band structure are shown in Figs. 2(b) and 3(b), respectively. A direct band gap of 0.10 eV was observed and no charge transfer was found for the top graphene layer. A nonzero but decreased band gap is consistent with experimental results with a SiC substrate with polylayers of graphene.⁸

Finally, we have studied the effect of hydrogen passivation on an oxygen terminated SiO_2 substrate with a graphene monolayer. We considered the hydrogen passivation of the eight terminal oxygen atoms that interface the graphene monolayer [see Fig. 1(c)]. The oxygen atoms on the substrate surface were now hydroxyl groups (OH), and geometrical optimizations indicated that the graphene sheet clearly had no covalent interaction with the substrate. Indeed, the distance between the plane of terminal oxygen and the graphene monolayer was separated by 3.36 \AA , which is a typical van der Waals (vdW) distance between oxygen atoms with two lone-pair of electrons and sp^2 hybridized carbon.³⁸ The hydroxyl (OH) groups were parallel to the plane of the graphene monolayer (the standard deviation for the eight surface oxygen atoms was 0.02 \AA with respect to the average plane, considerably smaller than the case without H-passivation). This effect is explained by the presence of hydrogen bonds; the $\text{OH}\cdots\text{O}$ hydrogen bond distances for surface groups was on average 1.80 \AA , indicating strong structural stabilization via a hydrogen bond network that is planar across the substrate surface.

The electron lone-pair of each oxygen atom was pointed toward the graphene sheet, and the optimized structure was the results of maximum π -bond attraction between oxygen lone pair and graphene p_z orbitals, which extended downward from the monolayer. This physisorption (or vdW attraction) is much weaker than covalent or hydrogen bonding, and similar to the vdW contact between adjacent graphene sheets in the graphite crystal structure. Figure 2(c) shows the electronic charge density of the system with H-passivated terminal oxygen atoms. No charge transfer between graphene

and substrate was observed, consistent with the band structure resembling isolated graphene [see Fig. 3(c)].

The geometrical perturbation of the substrate on the graphene was negligible as compared to the case without H-passivation where surface roughness was observed. In terms of electronic band structure, due to the lack of geometrical modification and the lack of charge transfer at for the OH terminated substrate, the above results suggest the presence of the substrate should have a negligible impact on the band structure of the graphene, and the conduction properties of graphene should continue to be similar to graphite. The band gap was 0.00 eV for the composite SiO₂ + graphene system. Figure 3(c) shows the band structure of the H-passivated system (OH termination), and it is clear that the metallic bands corresponding to the graphene monolayer are present and unaffected. Our calculations indicate that in order to recover the semimetallic band structure of isolated graphene when using a SiO₂ substrate, the O-terminated SiO₂ substrate surface must be H-passivated.

It should be noted that most of the nanoelectronics experiments are carried out using amorphous silicon dioxide as a substrate, while our calculations have considered an α -quartz substrate. Simulations involving an amorphous surface are challenging and are beyond the scope of the present paper. It is possible to design experiments based on crystalline α -quartz as has been done for carbon nanotube-based electronics.³⁹ In addition, to provide more robustness to our calculations, we have considered the following two scenarios. We have first tested a substrate with disorder, specifically with 50% H-passivation, and found that the substrate covalently bonds to the graphene similar to the fully unpassivated case. Because of this, a similar band gap opening was observed (0.52 eV). Second, we have considered the interaction between a graphene monolayer with another silicon dioxide polymorph, namely a $2 \times 2 \times 1$ tridymite substrate surface with terminal oxygen atoms (no H-passivation). We find, similar to that of the quartz system, chemical bonding between graphene and underlying substrate resulting in band gap opening of 0.26 eV.

In summary, we have shown that the hydrogen passivation of the oxygen-terminated SiO₂ substrate is critical for determining the conduction properties of suspended graphene sheets. The electronic band structure of the graphene monolayer and composite system shows metallic behavior for substrate systems that are H-passivated and therefore have no covalent contact with the graphene sheet. SiO₂ substrates are regularly used on chip devices and the realization of graphene based interconnects with this familiar substrate instead of a completely new one such as boron nitride or silicon carbide is important from a fabrication point of view. In addition, SiO₂ substrates should be easier to chemical modify due to the reactivity of terminal oxygen atoms, thus making SiO₂ more suitable of graphene-based devices.

Our results indicate that the electronic properties may be tuned by chemical modification of the substrate surface prior to graphene deposition. One possibility is to use pH. Treatment with a high pH would decrease the concentration of H-passivation on the surface, when the graphene monolayer is deposited, more covalent interactions would take place and more semiconducting behaviors may result. This is important for graphene-based transistor devices. With treatment of a low pH solution, the concentration of surface H-passivation

would increase, and therefore this technique may be promising for graphene-based interconnect devices where metallic conduction is desired.

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