Doping of graphene adsorbed on the a-SiO$_2$ surface

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We have performed an ab initio theoretical investigation of graphene sheet adsorbed on amorphous SiO$_2$ surface (G/a-SiO$_2$). We find that graphene adsorbs on the a-SiO$_2$ surface through van der Waals interactions. The inhomogeneous topology of the a-SiO$_2$ clean surface promotes a total charge density displacement on the adsorbed graphene sheet, giving rise to electron-rich as well as hole-rich regions on the graphene. Such anisotropic distribution of the charge density may contribute to the reduction of the electronic mobility in G/a-SiO$_2$ systems. Furthermore, the adsorbed graphene sheet exhibits a net total charge density gain. In this case, the graphene sheet becomes n-type doped, however, with no formation of chemical bonds at the graphene–SiO$_2$ interface. The electronic charge transfer from a-SiO$_2$ to the graphene sheet occurs upon the formation of a partially occupied level lying above the Dirac point. We find that such partially occupied level comes from the three-fold coordinated oxygen atoms in the a-SiO$_2$ substrate.

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Considerable progress has been made in addressing the electronic and structural properties of graphene, however, the development of nanodevices based on graphene is still in its infancy. Graphene is a semiconductor material with zero energy bandgap. The valence and the conduction bands are connected through a linear energy-momentum relation at the K points lying at the corners of the hexagonal Brillouin zone (Dirac points) [1]. The very high electronic mobility, up to 200,000 cm$^2$/Vs, makes graphene a quite suitable material to the development of new electronic (nano)devices. Indeed, there are experimental realizations of field effect transistors (FETs) based on graphene sheets [2–6]. In those systems, SiO$_2$ has been used as the gate dielectric material. Lemme et al. [2] verified a reduction of the electron mobility upon the graphene interaction with the SiO$_2$ gate, while Romero et al. [6] obtained a n-type doping for graphene in contact with a SiO$_2$ gate. In this case, the authors attributed the presence of surface states to the electronic charge transfer from SiO$_2$ to the graphene sheet. In contrast, there are experimental results indicating a p-type doping for graphene on SiO$_2$ gate [7,8]. Very recently n- and p-type doping of graphene, lying on SiO$_2$ substrate, has been tuned through a suitable graphene–SiO$_2$ “interface engineering” [2], where foreign molecules have been placed between the graphene sheet and the SiO$_2$ surface. Indeed, there are experimental and theoretical studies addressing “interface engineering” applied to modify the electronic and structural properties of carbon nanotubes adsorbed on SiO$_2$ [10] as well as on the other semiconductor surfaces like Si(001) [11] and InAs(111) [12].

The most of the experimental results indicate that there are no covalent bonds between the graphene sheet and the amorphous SiO$_2$ substrate (a-SiO$_2$). It has been suggested a physisorption process [13–15] where van der Waals (vdW) interactions play an important role. Graphene sheet feels the corrugations of the a-SiO$_2$ surface, giving rise to electron-rich as well as hole-rich regions on graphene, so called “electron-hole puddles” [10]. Based upon the aforementioned findings, the understanding of the electronic and the energetic properties, within an atomic scale, of graphene on a-SiO$_2$ surface is an important issue to the examined by using ab initio total energy calculations.

In this letter we present ab initio calculations of graphene adsorbed on the a-SiO$_2$ surface, G/a-SiO$_2$. The calculations were performed within the density functional theory (DFT) including the long-range vdW interactions. Our total energy results reveal that vdW interactions rule the graphene adsorption on the a-SiO$_2$ surface. The inhomogeneous topology of a-SiO$_2$ gives rise to electron-rich and hole-rich regions on the adsorbed graphene sheet, in accordance with the experimentally observed “electron-hole puddles” for graphene lying on a-SiO$_2$. However, there is a net charge density gain on the graphene sheet. The electronic charge transfer from a-SiO$_2$ to graphene occurs due to the formation of a partially occupied state above the Dirac point. We find that such partially occupied state is attributed to the formation of three-fold coordinated O atoms within a-SiO$_2$.

The amorphous structure was generated through ab initio molecular dynamics (MD) simulations based on the
Ref. [20] we present details on the generation procedure of
2
 described a-SiO

The generalized gradient approximation due to Perdew,
Burke and Ernzerhof (PBE) [22] was used, and the van
der Waals interaction was described within a semiempiri-
cal approach, following the Grimme formula [23]. The
electron-ion interactions were calculated by using norm-
conserving pseudopotentials [24]. All the atomic posi-
tions of the G/a-SiO\textsubscript{2} system were relaxed by using the
conjugated gradient scheme, within a force convergence
criterion of 20 meV/Å.

Figure 1(a) presents the structural model for the ph-
ysisorbed G/a-SiO\textsubscript{2} system, where we have considered
nine G/a-SiO\textsubscript{2} configurations on two different a-SiO\textsubscript{2}
surface structures. At the equilibrium geometry we find a
graphene – a-SiO\textsubscript{2} equilibrium vertical distance
(d\textsubscript{G–SiO\textsubscript{2}}) of 3.64 (3.30) Å for an a-SiO\textsubscript{2} surface cor-
rugation of 1.7 (1.5) Å [23]. Although the relatively short
distance between the graphene sheet and the top-
most O atoms, we do not find the formation of C–O
chemical bonds. The strength of graphene adsorption
on a-SiO\textsubscript{2} can be measured by comparing the total en-
ergies of the isolated systems, viz.: graphene sheet and
a-SiO\textsubscript{2} surface, with the total energy of the graphene
adsorbed system, G/a-SiO\textsubscript{2}. We find that the forma-
tion of G/a-SiO\textsubscript{2} is an exothermic process with an ad-
sorption energy (E\textsubscript{ads}) of 6.3±0.4 meV/Å\textsuperscript{2} Our adsorp-
tion energy and equilibrium geometry results are in good
agreement with the experimental estimative of Ishigami
et al., E\textsubscript{ads} = 6 meV/Å\textsuperscript{2}, and d\textsubscript{G–SiO\textsubscript{2}} = 4.2 Å [14]. Re-
cent theoretical calculations, within the DFT-LDA ap-
proach with no inclusion of vdW interations, obtained
E\textsubscript{ads} = 1 meV/Å\textsuperscript{2} and d\textsubscript{G–SiO\textsubscript{2}} = 3.6 Å for graphene
on a-SiO\textsubscript{2} [6]. In contrast, other experimental measure-
ments obtained d\textsubscript{G–SiO\textsubscript{2}} of 5.8 Å for G/a-SiO\textsubscript{2}, which
may indicate the presence of foreign elements at the G–
SiO\textsubscript{2} interface [3]. We next calculate E\textsubscript{ads} by turning off
the vdW contribution from our total energy results. In
this case, the formation of G/a-SiO\textsubscript{2} becomes no longer
exothermic, E\textsubscript{ads} = −0.4 meV/Å\textsuperscript{2}. Thus, showing that
graphene sheet adsorbs on a-SiO\textsubscript{2} is mediated by vdW
interactions.

Recent experimental findings indicate a corrugation of
≈5 Å on the a-SiO\textsubscript{2} surface, for a lateral scale of
≈100 Å [13]. Meanwhile in Ref. [14] the authors sug-

FIG. 1: Atomic structure of graphene adsorbed a-SiO\textsubscript{2}
surface, G/a-SiO\textsubscript{2} (a) side-view, (b) top-view, details of the equi-
librium geometry of O\textsubscript{three-fold} (c). In (a) the bottommost O
dangling bond was saturated by a H atom and the dashed re-

DFT approach as implemented in the VASP code[17–19].
Initially we obtained the a-SiO\textsubscript{2} bulk phase. We have
used a supercell with 96 atoms and we made a suitable
choice of the lattice constants of the supercell, 12.47 and
12.96 Å along the x and y directions, respectively, in or-
der to match with the calculated equilibrium lattice con-
stant of an isolated graphene sheet (Fig. 1). While the su-
percell volume was minimized along the z direction, thus,
avoiding any artificial strain in the a-SiO\textsubscript{2} bulk. We next
include a vacuum region of ≈12 Å parallel to the z direc-
tion, within the slab method, and then we repeat the MD
simulations in order to get an a-SiO\textsubscript{2} clean surface. In
Ref. [21] we present details on the generation procedure of
amorphous SiO\textsubscript{2} bulk structure. Once we obtained a well
described a-SiO\textsubscript{2} surface, we start to investigate the equi-
librium geometry, energetic stability, and the electronic
properties of a graphene sheet adsorbed onto a-SiO\textsubscript{2}
surface. Here the calculations were performed by using the
DFT approach as implemented in the SIESTA code [21].

The generalized gradient approximation due to Perdew,
Burke and Ernzerhof (PBE) [22] was used, and the van
der Waals interaction was described within a semiempiri-
cal approach, following the Grimme formula [23]. The
electron-ion interactions were calculated by using norm-
O-terminated surface \[20\]. In addition, it has been suggested a p-type doping of the adsorbed graphene sheet. Whereas in a-SiO\(_2\), which also exhibits an O-rich surface \[Fig. 1(a)\], we do not find the formation C–O chemical bonds. In our simulated annealing process all the surface O atoms become twofold coordinated, suppressing the (energetically unfavorable) O dangling bonds. Very recent DFT-LDA calculations indicate that the graphene interaction with the (001) surface of \(\alpha\)-quartz is weak, with no C–O chemical bonds \[27\].

Figure 2(d) depicts the net charge density displacement (\(\Delta \rho\)) on the adsorbed graphene sheet. \(\Delta \rho\) can be written as,

\[
\Delta \rho = \rho[G(\text{SiO}_2)] - \rho[G].
\]

Where \(\rho[G(\text{SiO}_2)]\) and \(\rho[G]\) represent the planar averaged total charge density of the adsorbed \(\text{G}/\text{SiO}_2\) and isolated graphene sheets, respectively. The planar average was performed by considering a region of 0.5 \(\text{Å}\) above and below the graphene sheet. The last term, \(\rho[G]\), was calculated keeping the same equilibrium geometry as that of \(G/\text{SiO}_2\). We find graphene regions with \(\Delta \rho > 0\) as well as \(\Delta \rho < 0\), electron- and hole-rich regions, respectively. Thus, Fig. 2(d) indicates that there is a total charge density fluctuation on the graphene sheet, being in accordance with the recent experimental verification of “electron–hole puddles” in \(\text{G}/\text{SiO}_2\) systems \[16, 28\]. Here we can infer that the inhomogeneous \(\text{a-SiO}_2\) surface topology rules the total charge density fluctuation of the adsorbed graphene sheet. Such fluctuation on the electronic charge density distribution on the graphene sheet should play an important role on the experimentally verified reduction of the electronic mobility for graphene lying on a-SiO\(_2\) surface \[2\].

There is a net electronic charge density gain of about \(3 \times 10^{13} \text{e}/\text{cm}^2\), Fig. 2(d), thus, indicating a n-type doping on the adsorbed graphene sheet. Our electronic band structure calculation, Fig. 2(a), confirms statement above. The shape of the Dirac cone has been maintained, since the graphene sheet weakly interacts with the a-SiO\(_2\) substrate. Due to the electronic charge transfer from a-SiO\(_2\) to the graphene sheet, the Dirac point lies below the Fermi energy (\(E_F\)). The n-type doping occurs due to the presence of a partially occupied state (c1) below the conduction band minimum (CBM) pinning the Fermi level above the Dirac point, see inset of Fig. 2(a). Figure 2(b) presents the density of states (DOS) of \(G/\text{a-SiO}_2\) (gray region), and separately the contribution from the adsorbed graphene sheet (solid line), and the a-SiO\(_2\) surface (light gray region). We find, in contrast with previous investigations \[6\], that c1 comes from the formation of three-fold coordinated O atoms \(O_{\text{three-fold}}\) in a-SiO\(_2\). Those \(O_{\text{three-fold}}\) sites may occur when we have a slightly higher local concentration of Si atoms or nearby oxygen vacancies in a-SiO\(_2\) \[24, 32\]. The Si–O\(_{\text{three-fold}}\) bond lengths (1.82–1.86 \(\text{Å}\)) are stretched in comparison with the ones of the two fold coordinated O atoms, ~1.66 \(\text{Å}\), Fig. 2(c). Those larger bond lengths reduce the binding energy of the electronic states along Si–O\(_{\text{three-fold}}\), giving rise to the partially occupied state, c1, just below the CBM and pinning the Fermi level. We find that the electronic states of c1 are localized on the Si atoms nearby \(O_{\text{three-fold}}\). In order to verify the adequacy of the proposed origin of c1, we calculate the electronic structure of \(G/\text{a-SiO}_2\) by suppressing the presence of \(O_{\text{three-fold}}\), i.e. we have only two fold coordinated O atoms within the a-SiO\(_2\) slab. In this case, we do not find the formation of c1, and the Dirac point lies on the Fermi level. That is, the adsorbed graphene sheet becomes neutral. Those results support the proposed role of \(O_{\text{three-fold}}\) on the non-covalent n-type doping of graphene on a-SiO\(_2\) substrate. It is worth to note that, for the neutral graphene sheet, we find the same picture for the electron- and hole-rich regions, as depicted in Fig. 2(d), however with different values of \(\Delta \rho\). The total charge density fluctuation on the neutral graphene is about 25% smaller in comparison with the (n-type) doped ones.

Finally, we have considered the presence of oxygen vacancies \(O_V\) in a-SiO\(_2\). We have examined three plausible \(O_V\) configurations, on the topmost surface site, and on the subsurface sites, indicated as V1–V3 in Fig. 1(a), respectively. We verify that those vacancies do not give rise to a donor level on the a-SiO\(_2\) surface. For V1 and V2 we find the formation of Si-dimers on the surface (Si–Si bond length of 2.24 \(\text{Å}\)) inducing the formation of occupied (empty) electronic states near the valence (conduction) band maximum (minimum). Whereas V3 gives rise to a deep occupied state within the a-SiO\(_2\) bandgap.

In conclusion, we find that vdW interactions rules the graphene adsorption on the a-SiO\(_2\) surface. Through a charge density map on the adsorbed graphene sheet we verify that the inhomogeneous \(\text{a-SiO}_2\) surface topology promotes an electronic charge density displacement on
the graphene, giving rise to the experimentally verified “electron-hole puddles” \cite{16,28}. Such electron-rich and hole-rich regions should contribute to the experimentally verified reduction on the electronic mobility of graphene sheets lying on a-SiO$_2$ surfaces. We find a net charge density gain on the adsorbed graphene sheet, thus, characterizing a n-type non-covalent doping on the graphene. The electronic charge transfer from a-SiO$_2$ to the graphene sheet comes from the formation of a partially occupied state above the Dirac point, which is attributed to the formation of three-fold coordinated oxygen atoms in a-SiO$_2$. Those three-fold coordinated oxygen atoms may occur upon slightly high local concentration of Si atoms or nearby oxygen vacancies.

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\[1\] A. C. Neto, F. Guinea, A. H. C. Neto, N. M. R. Peres, K. S. Novoselov, K. Novoselov, A. K. Geim, and A. Geim, Rev. Mod. Phys. 81, 109 (2009).

\[2\] M. C. Lemme, T. J. Echtermeyer, M. Baus, and H. Kurz, IEEE Elect. Dev. Lett. 28, 282 (2007).

\[3\] X. Li, X. Wang, L. Zhang, S. Lee, and H. Dai, Science 319, 1229 (2008).

\[4\] X. Wang, Y. Ouyang, X. Li, H. Wang, J. Guo, and H. Dai, Phys. Rev. Lett. 100, 206803 (2008).

\[5\] J. B. Oostinga, H. B. Heersche, X. Liu, A. F. Morpurgo, and L. M. K. Vandersypen, Nature Materials 7, 151 (2008).

\[6\] H. Romero, N. Shen, P. Joshi, H. R. Gutierrez, S. A. Tadigadapa, J. O. Sofo, and P. C. Eklund, ACS Nano 2, 2037 (2008).

\[7\] S. Berciaud, S. Ryu, L. E. Brus, and T. F. Heiz, Nano Lett. 9, 346 (2009).

\[8\] S. M. Song and B. J. Cho, Nanotechnol. 21, 335706 (2010).

\[9\] R. Wang, S. Wang, D. Zhang, Z. Li, Z. Fang, and X. Qiu, ACS Nano 5, 408 (2011).

\[10\] J. S. Soares, A. P. M. Barboza, P. T. Araujo, N. M. B. Neto, D. Nakabayashi, N. Shadmi, T. S. Yarden, A. Ismach, N. Gebfinger, E. Joselevich, et al., Nano Lett. 10, 5043 (2010).

\[11\] W. Orellana, R. H. Miwa, and A. Fazzio, Phys. Rev. Lett. 91, 166802 (2003).

\[12\] Y. H. Kim, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett. 92, 176192 (2004).

\[13\] E. Stolyarova, K. T. Rim, S. Ryu, J. Maultzsch, P. Kim, L. E. Brus, T. F. Heinz, M. S. Hybertsen, and G. W. Flynn, PNAS 104, 9209 (2007).

\[14\] M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams, Nano Lett. 7, 1643 (2007).

\[15\] A. Sinitskii, D. V. Kosynkin, A. Dimiev, and T. J. M. ACS Nano 4, 3095 (2010).

\[16\] J. Martin, N. Akerman, G. Ulbricht, T. Lohmann, J. H. Smet, and K. Von Klitzing, Nat. Phys. 4, 144 (2008).

\[17\] G. G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).

\[18\] G. G. Kresse and J. Hafner, J. Phys. 6, 8245 (1994).

\[19\] G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).

\[20\] W. L. Scopel, A. J. R. da Silva, and A. Fazzio, Phys. Rev. B 77, 172101 (2008).

\[21\] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002).

\[22\] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

\[23\] S. Grimme, J. Comput. Chem. 27, 1787 (2006).

\[24\] N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).

\[25\] The a-SiO$_2$ surface corrugations was inferred by the calculation of the variance of vertical positions of the top-most O atoms, while for the adsorbed graphene sheet, we considered the variance of vertical positions of the graphene C atoms.

\[26\] Y. J. Kang, J. Kang, and K. J. Chang, Phys. Rev. B 78, 115404 (2008).

\[27\] T. C. Nguyen, M. Otani, and S. Okada, Phys. Rev. Lett. 106, 106801 (2011).

\[28\] C. Stampfer, F. Molitor, D. Graf, K. Ensslin, A. Junger, C. Hierold, and L. Wirtz, Appl. Phys. Lett. 91, 241907 (2007).

\[29\] Z. Y. Lu, C. J. Nicklaw, D. M. Fleetwood, R. D. Schrimpf, and S. T. Pantelides, Phys. Rev. Lett. 89, 285505 (2002).

\[30\] V. O. Sokolov and V. B. Sulimov, J. NosnCryst. Sol. 217, 167 (1997).

\[31\] B. P. Feuston and S. H. Garofalini, J. Chem. Phys. 91, 564 (1989).

\[32\] K. Winer and L. Ley, Phys. Rev. B 37, 8363 (1988).