First-principles studies of water adsorption on graphene: The role of the substrate

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We investigate the electronic properties of graphene upon water adsorption and study the influence of the SiO_2 substrate in this context using density functional calculations. Perfect suspended graphene is rather insensitive to H_2O adsorbates, as doping requires highly oriented H_2O clusters. For graphene on a defective SiO_2 substrate, we find a strongly different behavior: H_2O adsorbates can shift the substrate's impurity bands and change their hybridization with the graphene bands. In this way, H_2O can lead to doping of graphene for much lower adsorbate concentrations than for free hanged graphene. The effect depends strongly on the microscopic substrate properties. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3033202]

Graphene, i.e., a monolayer of graphite, is the first truly two dimensional material[1,2] and a promising candidate for silicon replacement in semiconductor industry[3] or gas sensing applications.[4,5] Since graphene's discovery the water adsorbates have been discussed as impurities leading to doping,[1,4] while changing the electron mobility in graphene only surprisingly little. Up to now, the microscopic mechanism of this doping without significant changes in electron mobility has remained unclear. Density functional theory (DFT) calculations on single water molecule adsorbates on perfect free standing graphene[6] were in line with previous studies on carbon nanotubes (CNTs) (Ref. 7) and found H_2O physisorption but no H_2O induced impurity states close to the Fermi level. Therefore, the doping effects found experimentally[1,4] are very likely due to more complicated mechanisms than interactions of graphene with single water molecules. The experiments dealing with the effect of water on graphene were carried out using graphene on top of SiO_2 substrates. In addition, for finite concentrations of H_2O on graphene H_2O clusters might form. However, a microscopic theory on the role of the substrate and H_2O clusters in the H_2O graphene interplay has been lacking so far. Apart from the topic of doping water is considered important for various other properties of graphene. Water might contribute to bonding of graphene to its substrate[8] and its hydrolysis products could be used to functionalize graphene and create graphene field effect transistors.[9,10]

In this letter we study the substrate and cluster formation effects in the water graphene system by means of DFT. We show that both highly oriented water clusters as well as water adsorbates in combination with a defective SiO_2 substrate can lead to doping of graphene. To this end, we consider model systems (see Fig. 1) for water and ice in different concentrations on free standing graphene as well as for water interacting with defective SiO_2 substrates. By analyzing the involved dipole moments and comparison to electrostatic force microscopy,[11] we show that the SiO_2 substrate is crucial for obtaining doping by H_2O adsorbates on graphene.

In our DFT calculations, the electronic and structural properties of the graphene-substrate-adsorbate systems are obtained using generalized gradient approximation (GGA) (Refs. 12 and 13) to the exchange correlation potential. For solving the resulting Kohn–Sham equation we used the Vienna Ab Initio Simulation Package (VASP) (Ref. 14) with the projector augmented wave[15,16] basis sets and 875 eV as plane wave cutoff. The graphene-substrate-adsorbate systems are modeled using supercells containing up to 83 substrate atoms (Si, O, and H), 12 adsorbate atoms, and 32 C atoms. In the total energy calculations and during the structural relaxations the k-meshes for sampling of the supercell Brillouin zone were chosen to be as dense as 24×24 and 12×12 k-mesh, respectively, when folded up to the simple graphene unit cell.

First, water adsorption on free standing graphene with different water concentrations is considered. To model a single H_2O molecule on graphene, 3×3 graphene supercells were used. Full relaxation of H_2O with oxygen [depicted in

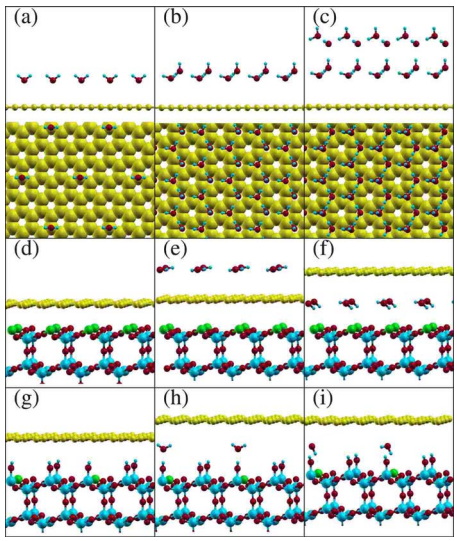

FIG. 1. (Color online) Model systems for water interacting with graphene. [(a)–(c)] Free standing graphene with single water adsorbates (a), a bilayer (b), and a tetralayer (c) of ice Ih. Carbon atoms yellow, oxygen red, and hydrogen small blue balls. [(d)–(i)] Graphene on top of SiO_2 with every second [(d)–(f)] or eighth [(g)–(i)] surface Si atom forming a Q_3^0 defect. Water adsorbates are considered on top of graphene (e) and between the graphene and the substrate (f), (h), and (i). Fully coordinated Si atoms are depicted as big blue balls, Si atoms at Q_3^0 defects in green.

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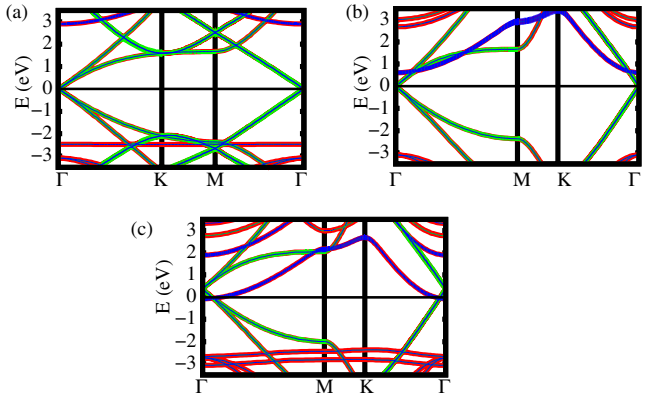

FIG. 2. (Color online) Band structures of supercells with fully relaxed single molecules (a), a bilayer (b), and a tetralayer (c) of water on graphene corresponding to Figs. 1(a)–1(c), respectively, are shown. The graphene π bands are marked in green, the nearly free electron bands in blue. Due to the H_2O dipole moments, graphene's nearly free electron band is shifted with respect to its π bands.

Fig. 1(a)] or hydrogen nearest to the graphene yielded adsorbed configurations with binding energies of 40 and 36 meV and molecule sheet distances of 3.50 and 3.25 Å, respectively. These values are in the same order as those obtained by Leenaerts *et al.*,[6] indicating physisorption of single water molecules on graphene. Analyzing the density of states/band structures for these two adsorption geometries we find qualitative agreement with Refs. 6 and 17: none of these configurations exhibits energy levels due to the adsorbate near the Dirac point, as shown in Fig. 2(a), for the configuration with oxygen closest to graphene. The highest occupied molecular orbital of H_2O is more than 2.4 eV below the Fermi energy and its lowest unoccupied molecular orbital is more than 3 eV above it. The absence of any additional impurity level close to the Dirac point is independent of the H_2O orientation and its lateral position.[18] This shows that single water molecules on perfect free standing graphene sheets do not cause any doping.

The supercell applied here corresponds to an adsorbate concentration of $n=2$ nm^{-2}, which is well inside the range of concentrations (1–10 nm^{-2}) found experimentally in Ref. 11. The lateral dimension $a=4.5$ Å of the hexagonal ice Ih (0001)-surface unit cell corresponds to a concentration of 5.7 H_2O nm^{-2} per layer. Thus, increasing the H_2O concentration significantly above the $n=2$ nm^{-2} from above leads to water clusters or icelike structures, rather than isolated molecules.

To gain insight into doping of graphene by water clusters and ice overlayers we studied fully relaxed[19] bilayers and four layers of ice Ih adsorbed on graphene. These overlayer structures have been proposed as basis of ice growth on various hexagonal metal surfaces[20,21] and can be modeled as $(\sqrt{3}\times\sqrt{3})R30°$ overlayer on the simple graphene unit cell. The lattice mismatch in this configuration is 0.23 Å—on the same order as found for water overlayers on Ni(111) (Ref. 20)—and therefore a reasonable starting point for studying ice on graphene.

The supercell band structures [Figs. 2(b) and 2(c)] show that the electric field by proton-ordered ice on top of graphene changes the energy of graphene's nearly free electron bands. In contrast to pristine graphene, where these bands start at 3 eV above the Dirac point or in the case of single H_2O adsorbates on graphene [Fig. 2(a)], their bottom is at 0.6 eV above and 0.1 eV below the Dirac point for a bi- and a tetralayer of ice Ih on top of graphene. This shift is due to electrostatic fields induced by the H_2O dipole moments and results in hole doping for the tetralayer of ice on graphene.

The water adlayers cause a change in contact potential $\delta\phi$, which can be estimated using the H_2O dipole moment $p=6.2\times10^{-30}$ C m and the relaxed structures to be $\delta\phi=1.4$ and 5.4 V for a water bi- and tetralayer, respectively. While only the latter structure causes doping, the corresponding change in contact potential exceeds the experimental value $\delta\phi_{\mathrm{exp}}=1.3$ V in Ref. 11 by more than a factor of 4. However, water strongly diluted in N_2 has been found to cause hole doping in graphene on SiO_2.[4] Given these two experiments, doping due to multiple fully oriented ice overlayers as in Fig. 2 is likely not the most important interaction mechanism for water and graphene.

We now turn to studying the effect of the SiO_2 substrate in the water-graphene interplay. The SiO_2 surfaces used in the experiments[4,11] are amorphous and challenging to model from first principles. To obtain qualitative insight to the most important physical mechanisms, it is, however, a reasonable starting point to consider crystalline SiO_2 in the β-cristobalite form as a substrate.[22]

The (111) surface of this modification can be used to create the most likely defects on SiO_2 amorphous surfaces. These are the so called Q_3^0 and Q_4^1 defects[23] having one under coordinated silicon and oxygen atom, respectively. Furthermore, the unit cell of this surface is nearly commensurate with the graphene lattice. The lattice constant $a_{\mathrm{SiO_2}}=7.13$ Å (Ref. 24) results in a surface unit cell $a_{\mathrm{SiO_2}}/\sqrt{2}=5.04$ Å, which is 4% larger than twice the lattice constant $2a_0=4.93$ Å of graphene. As the SiO_4 tetrahedra in SiO_2 are known to adjust to external strain easily, we model graphene on SiO_2 by 2×2 or 4×4 graphene supercells with lateral dimension $2a_0$ or $4a_0$. As substrate we put 4% laterally strained and hydrogen passivated β-cristobalite with six Si atoms per surface unit cell in vertical direction. We then created the defects by removing H passivation atoms, added the H_2O adsorbates, and relaxed until all forces were less than 0.08 eV Å^{-1}. In this way, we consider passivated and defective SiO_2 surfaces—the latter containing either undercoordinated silicon or oxygen atoms—as substrate for graphene. The effect of water exposure is simulated by putting water molecules on top of graphene as well as between the graphene and the substrate.

Graphene on top of fully passivated SiO_2 means two inert systems are in contact with each other. Consequently, there are no bands in addition to graphene's Dirac bands at the Fermi level and no doping occurs. (The band structure is not shown here for brevity.) This changes strongly for graphene on defective SiO_2. As a model system, we study Q_3^0 defects in β-cristobalite (111) surfaces. Depending on the supercell size, 2×2 and 4×4, in these periodic structures every second and eighth surface Si atom is under coordinated, respectively, and forms a Q_3^0 defect [see Figs. 1(d)–1(i)].

These defects lead to additional states in the vicinity (±1 eV) around the Fermi level [see Figs. 3(a) and 3(d)].

The avoided crossing in Fig. 3(a) indicates a significant hybridization of the defect and the graphene bands and demonstrates the impurity state's importance for conduction elec-

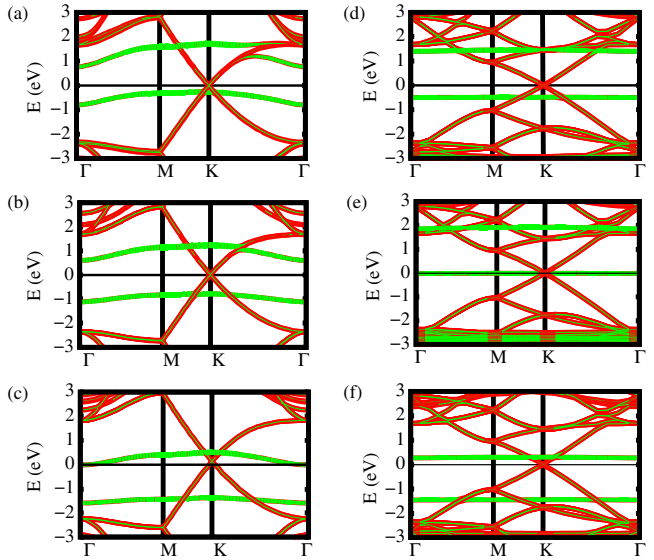

FIG. 3. (Color online) Band structures for graphene on defective SiO_2 substrates. [(a)–(c)] 2×2 and [(d)–(f)] 4×4 graphene supercells with every second [(a)–(c)] or eighth [(d)–(f)] surface Si atom forming a Q_3^0 defect. The corresponding geometries are shown in Figs. 1(d)–1(i), respectively. Spin up and down bands are shown at the same time. Contributions at the defect site are marked as green fat bands. (a) and (d) Without water adsorbates. (b) With water on top of graphene. (c), (e), and (f) With water between the graphene and the substrate. (c) and (f) H_2O dipole moment pointing tilted downward. (e) H_2O dipole moment pointing upward.

tron scattering in graphene. In the pure SiO_2 graphene model systems [Figs. 3(a) and 3(d)], the impurity bands do not cross the Fermi level. This situation can be changed by water adsorbates, which may sit either in between the graphene and the substrate [Figs. 3(c), 3(e), and 3(f)] or on top of graphene [Fig. 3(b)]. In all cases, the electrostatic dipole moment of the water adsorbates comes along with strong local electrostatic fields, which allow to shift the impurity bands significantly with respect to the graphene bands. As Fig. 3 demonstrates, this shift strongly depends on the place of adsorption and the orientation of the water molecules, leading either to hole doping [Figs. 3(c) and 3(f)] or electron doping [Fig. 3(e)].

This strong effect of water is very general and not limited to the examples shown in Fig. 3. Similar effects of water can be found for graphene on the (0001) plane of α-quartz or β-cristobalite with Q_4^1 defects. Although the interaction mechanisms of water, SiO_2, and graphene presented here are not exhaustive, the comparison of water adsorption on perfect free standing graphene to water adsorption on graphene lying on a (defective) SiO_2 substrate allows the following conclusions: perfect free standing graphene may have water adsorbates on top but its electronic transport properties are insensitive against perturbations by the water adsorbates. Single molecules will not create any impurity states close to the Dirac point. For obtaining doping effects, one needs highly ordered H_2O cluster or ice structures.

The substrate changes the situation completely. The dipole moments of H_2O adsorbates cause local electrostatic fields that can shift the substrate's defect states with respect to the graphene electrons and cause doping. The hybridization of substrate defect states with the graphene bands can be reduced by H_2O in between the graphene and the substrate, leading to less scattering of graphene electrons at defects in the substrate. On the other hand, impurity bands can be shifted toward the Fermi level by H_2O adsorbates, leading to increased electron scattering. So, for graphene on a substrate, H_2O much more likely affects the electronic properties than for free standing graphene. The effect of water strongly depends on properties of the substrate such as the amount and type of defects.

This finding might explain experiments on CNTs:[25] CNTs on SiO_2 substrates are much more sensitive to water in their environment than suspended CNTs or CNTs separated from the SiO_2 substrate by poly(methylmethacrylate) (PMMA) coating. In experiments similar to those in Refs. 3 and 26 these effects can be checked for graphene. Some molecules like NO_2 lead to acceptor states even without a substrate[5] while doping effects due to other molecules like H_2O strongly depend on the substrate. This can open the possibility of selective graphene gas sensors.

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