Adsorption of titanium and titanium dioxide on graphene: n and p-type doping

J. Sivek,1,‡ O. Leenaerts,1,§ B. Partoens,1,† and F. M. Peeters1,∗

1Departement Fysica, Universiteit Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium
(Dated: December 11, 2013)

Ab initio calculations within the density-functional theory formalism are performed to investigate the ground state, electric charge doping, and electronic properties of titanium and titanium dioxide monolayers adsorbed on a graphene surface. A new ground state structure of Ti monolayer adsorbed on graphene is reported which is shown to be stable up to T = 500 K. Effects due to lower and higher Ti adatoms coverage are studied. We find that the adsorbed Ti provides a strong n-type doping which supports recent experimental observations. On the other hand, TiO2 can induce both p- and n-type doping in the carbon monolayer depending on whether oxygen or titanium atoms are closest to the substrate. We identify the structures which are responsible for the experimentally observed auto-compensation mechanism that leads to the reversion of adsorbate effects after oxidation of the adsorbed Ti.

PACS numbers: 81.05.ue, 61.48.Gh, 68.43.-h, 68.43.Bc, 68.43.Fg

I. INTRODUCTION

The interaction of graphene with metal adsorbates is one of the important research topics since the first successful experimental exploration of graphene.1 Virtually any device assembly incorporating graphene will necessarily include graphene-metal contacts.

Titanium has been widely used for metal contacts on graphene with good adsorption properties.2 Moreover, the interaction between titanium and graphitic surfaces and nanotubes has attracted a lot of attention.3 Ti atoms are able to act as adsorption centers for molecular binding.4 Furthermore, Ti coated nanotubes and graphene have also been proposed for high-capacity hydrogen storage solution.5,6

However, a recent DFT study,7 as well as a very recent experimental observation,8 showed strong structural changes of the adsorbed Ti layer on graphene due to the interaction with oxygen. Experimentally, it was shown that the adsorbed titanium on graphene leads to substantial n-type doping and a reduction of graphene’s mobility. The subsequent exposure of the samples to oxygen has restored graphene’s gate dependent conductivity to almost intrinsic values, effectively cancelling any previous metal–graphene interaction.8

Motivated by these experimental observations we perform ab initio calculations to investigate titanium and titanium dioxide monolayers adsorbed on graphene. For the identified ground state structures, the electronic band structure is calculated and a charge population analysis is performed to investigate the character of the charge carrier doping in graphene. We find a strong n-type doping of graphene induced by adsorbed Ti and identify the highest possible monolayer coverage with stoichiometry Ti3C8. When TiO2 monolayer crystals are aligned on top of the graphene surface we observe p- or n-type doping of graphene, depending on the nature of the atoms that are exposed closest to graphene with oxygen acting as an acceptor and titanium as a donor.

This paper is organized as follows. First, we describe the computational details of our ab initio calculations, followed by an investigation of the ground state structure of a titanium monolayer on graphene. Next the character of the charge transfer between adsorbed Ti and the graphene substrate is examined. Further model titanium dioxide monolayer structures are investigated. To conclude, we report titanium dioxide structure dependent doping of graphene and link this observation with the experimentally observed recovery of the graphene gate dependent conductivity after the oxidation of the adsorbed Ti atoms.

II. CALCULATIONS

All our calculations were performed within the density functional theory (DFT) formalism as implemented in the VASP package with usage of the local spin density approximation (LSDA) for the exchange-correlation functional. We made use of the projector augmented wave method9 and a plane-wave basis set with an energy cutoff of 500 eV. The complete relaxation of atomic positions and supercell size was performed up to the level that the forces are smaller than 0.01 eV Å−1.

For all the used supercells, a sampling of the Brillouin zone was done with the equivalent of a 28 × 28 × 1 Monkhorst–Pack10 k-point grid for the graphene unit cell (containing two carbon atoms). Spin polarization was included in the calculations.

Because periodic boundary conditions were applied in all three dimensions, the height of the supercell was set to 20 Å, to include enough vacuum to minimize the interaction between adjacent layers, and dipole correc-
tions were used. All reported quantitative results of the charge transfer were calculated with the iterative Hirshfeld charge population analysis.

III. RESULTS AND DISCUSSION

The binding energies are calculated with respect to intrinsic monolayer graphene and the isolated atom/molecule of which the binding energy is reported. The formation energy for titanium covered graphene is calculated in relation to intrinsic monolayer graphene and the energy the of Ti atoms in a free standing monolayer titanium crystal with hexagonal symmetry.

A. Properties of titanium monolayer on graphene

Properties of single Ti atom adsorption on a graphene surface were already investigated and the most preferable adsorption site for a Ti atom was found to be the hollow site with a binding energy of -1.58 eV per Ti atom. The top and bridge adsorption site were found to be energetically less favorable by 0.62 eV and result in metastable states.

Also high density coverage of graphene with titanium has been previously investigated and some ground state structures were proposed which have stoichiometry TiC\(_8\) and TiC\(_4\) with Ti atoms placed on hollow sites creating monolayer metallic coverage.\[13,14\] However, we report here a different ground state structure. As written above, a single Ti atom placed on top of a free standing graphene surface is strongly bonded at the hollow site with a diffusion barrier high enough to prevent its motion on the surface even at room temperature. This fact suggests that the most preferable high coverage structure for titanium on graphene will be the one in which above every single hollow site there is one Ti atom (i.e., one Ti atom per two C atoms). Even the lattice constants compare favorably for this structure with a mismatch of only 5 % (see Table I).

We have calculated binding energies for a variety of structures with stoichiometry TiC\(_2\) and we also investigated the structure g2x2-3Ti (displayed in Fig. 1) with a lower amount of Ti atoms per C atom (three Ti atoms per eight C atoms) and a larger lattice mismatch of -9 % (Ti atoms are spaced further apart from each other in comparison to the titanium monolayer crystal). The calculated formation energy of -0.93 eV per Ti for g2x2-3Ti system was found to be lowest among all the investigated structures. The lowest formation energy for the TiC\(_2\) system was found to be -0.76 eV per Ti, for the structure consisting of adatoms placed above hollow sites with every fourth Ti atom displaced further from the graphene substrate (see Fig. 2(d) initial state). Substantial formation energy advantage makes the g2x2-3Ti system virtually the only plausible structure for titanium atoms on graphene at large coverage densities.

We have been surprised by this finding that the structure g2x2-3Ti has the lowest binding energy among studied cases. This has motivated us to perform DFT based molecular dynamics simulations of systems with different Ti coverage densities to identify the ground state configurations that may have been overlooked and/or to support the aforementioned findings.

The simulated systems consist of a 4x4 graphene supercell with 2, 4, 8, and 16 Ti adatoms, as displayed in Figs. 2(a-d). At the temperature of 500 K the different systems were allowed to evolve to more favourable states within a time window exceeding 1 ps.

The system with the highest concentration coverage (TiC\(_2\)), with Ti atoms initially placed above every hollow site, does not remain a monolayer crystal. However, something interesting happens: the Ti atoms rearrange themselves so that they create one monolayer on the graphene surface with the same structure as g2x2-3Ti while the redundant Ti atoms create a second layer.

The systems with lower concentration of Ti atoms per C atoms (TiC\(_8\) and TiC\(_4\), Figs. 2(b) and 2(c), respectively) have also undergone structural changes. The separation of adsorbed Ti atoms was too small to prevent atoms from mutual interaction. While adatoms remained adsorbed as a monolayer we have observed the creation of clusters and local rearrangements. Those structural changes occurred despite the presence of the diffusion barrier for adatoms adsorbed on the hollow site (clearly visible for TiC\(_8\), Fig. 2(b)). Again the comparison with the structure g2x2-3Ti reveals remarkable similarities in local arrangements of Ti adatoms, which is more pronounced in the structure TiC\(_4\) (Fig. 2(c)) with higher adatom coverage.

The last of the systems investigated using MD calculations is the one with the lowest Ti concentration - TiC\(_{16}\) (Fig. 2(a)). We found that this case is the only one that maintained its structural properties during the MD simulations. As can be seen in Fig. 2(a) the adsorbed atoms are separated by two carbon hexagonal rings. The separation distance of 6.5 A is found to be sufficient to suppress the mutual adatom interaction observed in the previous cases. The Ti atoms were trapped at the hollow sites and do not pass across the diffusion barrier.

The aforementioned results of the MD calculations
FIG. 2: Top and side view of different graphene structures with different amount of titanium coverage before (left) and after (right) 1 ps of relaxation at $T = 500$ K. The systems consist of (a) 2, (b) 4, (c) 8 and (d) 16 Ti adatoms (light symbols) placed on the graphene sheet in an unit cell with 32 C atoms (dark symbols).

FIG. 3: Plane-averaged deformation electron density of g2x2-3Ti configuration obtained from the difference between the electron density of the g2x2-3Ti structure and the electron densities of the subsystems consisting of only carbon or titanium atoms.

TABLE I: Lattice constants and workfunctions.

| structure                  | $\Phi$ (eV) | $a$ (Å) |
|----------------------------|-------------|---------|
| graphene                   | 4.49        | 2.447   |
| hexagonal monolayer Ti     | 4.72        | 2.566   |
| rectangular monolayer TiO2 | 8.54        | 3.141   |
| hexagonal monolayer TiO2   | 8.51        | 2.945   |

Since the direct charge transfer calculations proved to be insufficient in determining the type of doping we also...
performed electronic band structure calculations and calculated the workfunction of the pristine and hybrid materials. As can be seen from the electronic band structure of the g2x2-3Ti configuration (see Fig. 4), strong n-type doping occurs to graphene. The Dirac cone, still present in the electronic band dispersion, is shifted by -2.61 eV below the Fermi level. The calculation of the workfunction reveals the same type of doping, albeit in a partially counterintuitive way. As shown in Table I the work function of free-standing graphene is 4.49 eV, while the work function of an isolated hexagonal titanium monolayer is 4.72 eV. From a simple comparison of these values there is no precondition for charge transfer to occur from Ti to the graphene substrate. However, for closely separated metal-graphene structures (2.1 Å for g2x2-3Ti) the chemical interaction prevails and is responsible for n-type doping even when the workfunction of the metal is larger than the graphene work function. In the final system the computed workfunctions on graphene (3.97 eV) and titanium side (4.72 eV) indicate a charge transfer to graphene. The workfunction difference increases as compared to the pristine values (0.81 eV compared to 0.23 eV).

B. Properties of Titanium dioxide monolayer on graphene

Let us now consider the case of TiO$_2$ adsorption on graphene. As a model approach for studying the interaction of titanium dioxide on graphene surfaces we have chosen monolayer TiO$_2$ films derived from anatase, (101) with hexagonal and (001) with rectangular symmetry, which were proven to be stable. From the broad range of possible configurations the structure g2x2-hex-TiO$_2$ with lattice mismatch of about 4 % (displayed in Fig. 5(c)) was found to be the most stable. Ti atoms are arranged in a monolayer triangular lattice, similar to the one found in the previously discussed structure g2x2-3Ti, and oxygen atoms are placed between every three neighbouring Ti atoms. The TiO$_2$ monolayer is buckled due to the alternating displacement of oxygen atoms above or below the plane of Ti atoms. The other displayed model configurations in Figs. 5(a) and 5(b), while being metastable, will be discussed below as examples which lead to different doping properties.

![Graphene]({{ SITE_URL }}/images/Graphene.png)

**FIG. 4:** Band structure of the g2x2-3Ti configuration. The energies are relative to the Fermi level ($E_F = 0$). The Dirac point lies -2.61 eV below the Fermi level showing strong n-type doping. The amount of carbon p$_z$ character is indicated by the blackness of the bands.

![Model Structures]({{ SITE_URL }}/images/ModelStructures.png)

**FIG. 5:** Model structures for a TiO$_2$ monolayer on a graphene sheet. The systems (a) g2x2-aligned hex-TiO$_2$ and (c) g2x2-hex-TiO$_2$ contain 3 TiO$_2$ molecules per 8 C atoms, whereas (b) the g-sq8-TiO$_2$ configuration has 2 TiO$_2$ molecules per 8 C atoms. The carbon atoms are given by gray colour (a mesh in schematic picture on the left), Ti atoms are in light gray and O atoms are shown in red (dark, small circles in schematic picture on the left).

The charge population analysis performed on the TiO$_2$-graphene structures were found to be much more robust than for the titanium covered graphene. The Ti-O bonds exhibit an ionic character with Ti atoms gaining positive charge after loosing two electrons in favour of the O atoms. Besides the charge redistribution in the TiO$_2$ layer the g2x2-hex-TiO$_2$ structure shows also p-type doping of the graphene layer. The amount of charge transferred from graphene, calculated with iterative Hirshfeld charge population analysis, is 0.126 e per TiO$_2$ unit.

The character of the doping is also visible in the electronic band structure shown in Fig. 6 with a clear hole doping of graphene and a shift of the Dirac cone above the Fermi level by 0.5 eV. The observed doping can be explained from geometrical arguments. The bounded oxygen and titanium atoms can induce p- or n-type doping
FIG. 6: Band structure of g2x2-hex-TiO$_2$ configuration. The energies are relative to the Fermi level ($E_F = 0$). The Dirac point lies 0.5 eV above the Fermi level showing p-type doping. The amount of carbon $p_z$ character is indicated by the blackness of the bands.

when close to the graphene surface. The TiO$_2$ monolayer in the g2x2-hex-TiO$_2$ structure can be seen as consisting of three layers – a titanium layer sandwiched between two oxygen layers, thus exposing oxygen atoms to graphene. Similar charge transfers have been observed at the interface between graphene and rutile TiO$_2$ (110), where hole doping in graphene and an accompanying shift of the Fermi level relative to the Dirac cone was observed.

The aforementioned reasoning proves to be valid also for the other systems we have investigated. The model structures in Figs. 5(a) and 5(b) differ by the amount of oxygen or titanium atoms they expose to the graphene surface. The charge population analysis as well as the electronic band structure provide consistent evidence of p- or n-type doping depending on whether oxygen or titanium atoms are closer to the carbon atoms, respectively. The shift of the Dirac cone with respect to the Fermi level is -1.69 eV for g2x2-aligned hex-TiO$_2$ and 0 eV for g-sq8-TiO$_2$ structure, and the amount of charge, calculated with iterative Hirshfeld method, transferred from graphene is -0.452 e and 0.026 e, respectively.

Recently it was found experimentally that the graphene gate dependent conductivity can be recovered after oxidation of adsorbed Ti atoms. This recovery can be explained with the autocompensation of the titanium dioxide surface exposed to graphene. We showed above that TiO$_2$ structures can induce both p- or n-type doping in graphene thus opening the possibility of mutual compensation of the doping effects. Although the groundstate TiO$_2$ monolayer induces hole doping to graphene, the performed calculations suggest that metastable states of TiO$_2$ monolayers can be responsible for the recovery of the graphene gate dependent conductivity. However, the geometrical nature of the autocompensation does not imply the actual presence of the above considered monolayer TiO$_2$ crystals on the graphene surface in the experiment. Existence of any TiO$_2$ nanostructure with both p- or n-type doping sides exposed to the graphene surface will lead to similar effects.

IV. CONCLUSIONS

We have demonstrated strong n-type doping of Ti covered graphene. While the various charge population analysis methods failed to provide reasonable quantitative results for the shift of the Dirac point with respect to the Fermi level our investigation of the increased difference of the work functions ($\Phi_M - \Phi_G$) provided a consistent picture of the character of the induced doping. Titanium is found to be strongly chemisorbed on graphene and the highest monolayer coverage is found to have stoichiometry Ti$_3$C$_8$. The studied TiO$_2$ monolayer crystals aligned on top of graphene induce charge doping that depends on the nature of the atoms that are closest to graphene with oxygen acting as an acceptor and titanium as a donor. The ground state structure of TiO$_2$ monolayer covered graphene exhibits p-type doping of graphene, nevertheless the calculations suggest these metastable states of TiO$_2$ monolayer can be responsible for the recovery of the graphene gate dependent conductivity after oxidation of adsorbed titanium, as recently found in experiment.

Acknowledgments

This work is supported by the ESF-Eurocores program EuroGRAPHENE (project CONERAN) and the Flemish Science Foundation (FWO-Vl). This work was carried out using the HPC infrastructure of the University of Antwerp (CalcUA) a division of the Flemish Supercomputer Center (VSC), which is funded by the Hercules foundation.

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004), URL http://www.sciencemag.org/content/306/5696/666.abstract.
[2] J. A. Robinson, M. LaBella, M. Zhu, M. Hollander, R. Kasarda, Z. Hughes, K. Trumbull, R. Cavalero, and D. Snyder, Appl. Phys. Lett. 98, 053103 (pages 3) (2011), URL http://link.aip.org/link/?APL/98/053103/1.
[3] S. Dag, E. Durgun, and S. Ciraci, Phys. Rev. B 69, 121407 (2004), URL http://link.aps.org/doi/10.1103/PhysRevB.69.121407.
[4] I. Carrillo, E. Rangel, and L. F. Magaña, Car-
