Spontaneous polarization induced doping in quasi-free standing epitaxial graphene on silicon carbide from density functional theory

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(Dated: January 27, 2015)

By means of density functional theory (DFT) calculations we have quantitatively estimated the impact of the spontaneous polarization (SP) of the SiC(0001) substrate on the electronic properties of quasi-freestanding graphene (QFG) decoupled from the SiC by H intercalation. To correctly include within standard DFT slab calculations the influence of the SP, which is a bulk property, on a surface confined property such as the graphene’s doping, we attach a double gold layer at the C-terminated bottom of the slab which introduces a metal induced gap state that pins the chemical potential within the gap. Furthermore, expanding the interlayer distances at the bottom of the slab creates a local dipole moment which counters that arising from the slab’s polar character and allows to align the location of the graphene’s Dirac point (DP) for cubic SiC(111) with the chemical potential. Thus, the DP shifts obtained for other polytypes under the same slab model become an almost direct measurement of the SP-induced doping. Our results confirm the recent proposal that the SP induces the experimentally observed p-type doping in the graphene layer which can achieve DP shifts of up to several hundreds of meV (or equivalently, $\sim 10^{12} e/cm^2$) for specific polytypes. The doping is found to increase with the hexagonality of the polytype and its thickness. For the slab thicknesses considered (6-12 SiC bilayers) an ample, almost continuous, range of doping values can be achieved by tuning the number of stacking defects and their location with respect to the surface. The slab model is next generalized by performing large scale DFT calculations where self-doping is included in the QFG via point defects (vacancy plus a H atom) thus allowing to estimate the interplay between both sources of p-doping (SP- versus defect-induced) which turns out to be essentially additive.

PACS numbers: 73.22.Pr, 81.05.ue, 77.22.Ej

**Introduction**—Epitaxial graphene (EG) on silicon carbide (SiC) has been demonstrated to be an excellent material for high-performance technological applications.  [1–5] On the other hand, quasi-freestanding graphene (QFG) on SiC obtained from EG by hydrogen intercalation holds an even greater promise for the realization of graphene-based electronic devices because of its facile large-scale production together with excellent transport characteristics [6–10]. The latter mainly arise from the efficient reduction of the interaction between graphene (G) and SiC, otherwise strongly coupled, by the intercalated H layer. Although this weak interaction fully preserves the Dirac cones [9–12], a p-type doping is routinely detected in experiments [6, 7, 13, 14] which can be as large as $\sim 5.5 \times 10^{12} \text{ cm}^{-2}$ as observed by Speck et al [6] for QFG samples on 6H-SiC(0001) or even $\sim 2.0 \times 10^{13} \text{ cm}^{-2}$ as recently reported on 4H-SiC(0001) by Urban et al [17], while for cubic 3C-SiC(111) Coletti et al found a slight n-type doping [10, 18].

Based on these results, among several others [6, 8, 19–21], Ristein et al [22] pointed to a relationship between the G doping and the hexagonality of the SiC polytype employed as substrate, and proposed a macroscopic spontaneous polarization (SP) doping model whereby the substrate’s SP creates a pseudo-charge at the surface equivalent to a real acceptor layer. The model explains the sign of the doping (since the Si-terminated surface exhibits a negative SP for all polytypes) as well as its dependence on the hexagonality of the polytype, and has found further support in several works [11, 18, 19, 23]. Mamadov et al [24] have very recently corroborated such model by means of a systematic angle-resolved photoemission electron spectroscopy (ARPES) study for 3C-, 4H- and 6H-SiC QFG-systems. Two sources of doping are identified in this study: a surface band bending arising from the bulk dopants and the SP. The former would be responsible for the mild n-type doping encountered in 3C-SiC(111) samples [10, 12, 24] while the latter would account for the $\sim 1.5$ factor between hole dopings in 4H- and 6H-SiC samples [23]. Although not addressed in that work, a third main source is the self-doping induced by the presence of intrinsic defects in the QFG (vacancies and/or adatoms), thoroughly studied within theory [12, 25] but not so well experimentally [6, 26, 27].

In this Letter we investigate the relationship between the SP and the graphene’s p-type doping in perfect as well as defected QFG for several H-passivated hexagonal SiC polytypes via density functional theory (DFT) based calculations. The importance of employing a first principles approach to this end is manifold: it represents a powerful predictive tool when tuning the surface density of e/hole carriers in G-based devices [1, 4, 21], provides a unique way to quantify on equal footing the competition between self-doping and SP and, not the least, allows to
explore the validity of the macroscopic dielectric theory when the system size is shrunk to the nanoscale, as it is not obvious if a direct relationship between the SP and the doping charge in the QFG will still hold. Nevertheless, first principles slab calculations – aiming to model a semi-infinite surface – have not yet been attempted due to at least three non-trivial issues which need to be resolved: (i) combining a bulk and a surface confined property (SP and G’s doping, respectively) typically requires rather thick slabs to achieve convergence (this is specially true for dielectrics with long screening lengths), (ii) an appropriate boundary condition at the bottom of the slab which pins the chemical potential, \( \mu \), within the gap regardless of the selected polytype is a prerequisite to make any differences in the doping among them meaningful and, (iii) the polar character of SiC(111)/(0001) oriented slabs introduces an additional electric field across the di-electric which may considerably alter the final doping level. Additionally, the large dispersion of the \( \pi \) bands forming the Dirac cones requires a hyperfine sampling of the Brillouin Zone (BZ) for an accurate estimation of the doping charge (see below), thus increasing considerably the computational time. Paradoxically, the associated low G-projected density of states (PDOS) around the DP makes the DP shift with respect to \( \mu \), \( \Delta \text{DP} \), a highly precise gauge for the G doping, specially from the experimental side.

The first goal of this work is therefore to set up a calculation strategy that overcomes the above fundamental drawbacks. After considering different slab models we have found that a G/H/(SiC)\(_n\)/Au\(_2\) slab with a double gold layer attached to the lower C-dangling bonds meets satisfactorily the above requirements. The model is then employed to calculate the QFG dopings of different polytypes as a function of the number of SiC bilayers (BLs) in the slab, \( n \). Apart from the cubic 3C-SiC(111), we have considered those with largest hexagonality, namely, 2H-, 4H- and 6H-SiC(0001), having a stacking defect (SD) every two, three and four BLs, respectively. The combined effect of SP and defect-induced self-doping will be addressed at the end of this letter.

**Methods**—All presented calculations have been performed with the GREEN code [30] and its interface to the DFT based SIESTA package [31]. We employed the generalized gradient approximation [32] and included semi-empirical van der Waals interactions [33] to account for the weak G/H/SiC interaction. Dipole-dipole interactions between spurious slab replicas were removed via the usual dipole-dipole corrections [34] (DDC) thus leading to vanishing electric fields in the vacuum. The rest of the calculation parameters are described in detail in Ref. [35]. The G/H/(SiC)\(_n\)/Au\(_2\) model slabs comprised a \((2 \times 2)\) graphene layer placed on top of \( n \) \((\sqrt{3} \times \sqrt{3})R30^\circ\) SiC(111)/(0001) bilayers (BLs) with each Si dangling bond at the upper surface saturated by a hydrogen atom, while the bottom C dangling bonds were saturated by placing a gold plane in registry with the carbon atoms and a second one following an \( fcc \) stacking sequence (see inset in Figure 1(b)). The systems were relaxed freezing the inner SiC BLs to bulk-like positions optimized independently for each polytype. In order to obtain accurate doping charges, large \((100 \times 100)\) \( k \)-supercells were employed to sample the Brillouin zone [35].

**SP induced doping**—Let us first address the problems outlined above related to the use of a slab geometry when trying to estimate the G doping. For the most common practice of capping the lower C-terminated surface with another hydrogen layer these shortcomings become patent. In Figure 1(a) we plot the 2D averaged Hartree potential profiles, \( V_H(z) \), and the layer resolved PDOS for a G/H/(SiC)\(_6\)/H slab assuming a 3C- (black lines) or 2H-SiC (blue) stacking. Since considerable dipole moments were found in both cases (\( \Delta V = 0.8 \) and 1.5 eV for the 3C and 2H slabs, respectively) we elongated the C-H bonds with respect to their optimized values (see Fig. 1(a)) thus reducing the potential drops by as much as 0.7 eV. Unfortunately, and regardless of this expansion, the DP remains pinned at the chemical potential for both slabs. The reason is the absence of any gap states at the bottom of the slab, so that charge neutrality at the graphene layer locks \( \mu \) at the DP. A natural way to overcome this drawback is to introduce states within the gap and localized at the bottom part of the slab. If their associated DOS is much larger than that of the G, then they should pin the slab’s chemical potential just as bulk dopants/defects fix \( \mu \) in a real surface, leaving the G’s Dirac cones free to trap or release electrons in order to screen any internal fields. Attaching a double gold layer at the C-ended lower layer does indeed yield the...
desired boundary condition. In Fig. 1(b) we present the potential profiles and PDOS of such a G/H/(SiC)$_n$/Au$_2$ slab for 3C- and 2H-SiC. The potential drops ($\Delta V = 0.3$ and 0.5 eV) were reduced by 0.2 eV after expanding the Au-C and Au-Au interlayer distances by large amounts (>0.5 Å). We stress that although the expanded bottom geometry is not realistic, its purpose is to modify the local dipole at the bottom of the slab in order to reduce the total slab’s dipole moment. Inspection of the PDOS show that metal induced gap states (MIGSs) appear in both cases as a large broad peak mainly localized at the interface between the last SiC BL and the gold plane, penetrating around three BLs into the substrate. The MIGSs now determine the slab’s chemical potential and, notably, the doping in the QFG layer has almost vanished for the 3C case (black line), while the 2H slab (blue) displays a clear p-doping with a considerable DP shift of around 250 meV. We have also considered attaching single and triple gold layers at the bottom of the slab to find that the former (latter) yields a slight n (p)-type doping in the G [33]. Such slabs may therefore be employed as model systems where bulk dopants already induce certain level of doping [24].

The above analysis provides clear evidence that our slab model allows to address the impact that the SDs present in the film have on the graphene layer. Figure 2(a) shows a precise picture of the Dirac cones in the form of PDOS($k$, $E$) for a 3C, 6H, 4H, and 2H substrate. They have been calculated for a semi-infinite geometry after replacing the Hamiltonian of the lower half of the G/H/(SiC)$_{12}$/Au$_2$ slab by that of the corresponding bulk polytype [38, 39]. Apart from the negligible value of 14 meV for cubic 3C-SiC(111), the graphs clearly reveal how the DP shifts increase with the level of hexagonality attaining several hundreds of meV.

We now turn our attention on how these dopings evolve with the film thickness. Figure 2(b) illustrates the dependence of the graphene doping charge $\delta \sigma$ (left axis) and $\Delta DP$ (right axis) as a function of the slab thickness and the polytype considered. For the 6H and 4H cases we have defined different subsets of data depending on the location of the SD closest to the surface, which may be either between the first and second BLs (4H$_1$ and 6H$_1$) or the second and third (4H$_2$ and 6H$_2$) or the third and fourth (6H$_3$). Except for the 3C case, which remains with a negligible doping for all thicknesses, the rest of plots reveal an overall increase of $\delta \sigma$ with $n$ approaching their respective bulk SP values (indicated by thick horizontal lines at the right of the plot). The 6H and 4H polytypes show a stair-like behavior which can be understood by noting that as $n$ is increased by one, the added BL may or may not introduce an additional SD in the slab. In the former case, the slab’s SP increases and $\delta \sigma$ shows an abrupt raise, whereas in the latter case, the crystalline region increases and hence, the depolarization is more efficient leading to a slight decrease of the doping. For the 2H case, on the other hand, $\delta \sigma$ shows a smooth behaviour with no jumps due to the absence of crystalline regions. However, the SP for this polytype is so large that we find an early saturation of $\delta \sigma$ due to the crossing of the valence band maximum (VBM) by the chemical potential at $n = 12$ (see Fig. 2(a)), so that for larger thicknesses the SiC VBs will also contribute to the screening of the SP.

The QFG doping dependence displayed in Fig. 2 constitutes one of the central results of this work as it clearly establishes a relationship between the SP and QFG p-doping also providing an estimate for the slab size required to reach the bulk SP limit: at the largest thickness considered, $n = 12$, the doping amounts to 60-80% of the SP while, from extrapolation, we expect that almost a 100% should be already reached at $n \gtrsim 20$ BLs. Simple electrostatic arguments dictate that the difference between $\delta \sigma$ and the SP can be entirely attributed to the macroscopic electric field within the dielectric, $\boldsymbol{E}$ (generally known as the depolarization field) via [33]:

$$\varepsilon_0 \varepsilon_r \boldsymbol{E} = \delta \sigma + SP.$$

A further remarkable issue in Fig. 2(b) is the fact that an ample range of dopings can be obtained in an almost continuous way by controlling the number of SDs, their density and their proximity to the surface G layer. This is in line with the wide spread of experimental values reported for the graphene’s doping within the same polytype. For instance, for the most commonly used 6H-SiC(0001) substrate, our calculated dopings fall in the $4 - 6 \times 10^{12}/\text{cm}^2$ range, in excellent agreement with a number of experimental results varying from 2.0 to $6.2 \times 10^{12}$ cm$^{-2}$ [6, 13, 21, 24]. Smaller $\delta \sigma$ values
FIG. 3. Top (a) and side (b) view of the geometry corresponding to a vacancy embedded in an (8×8) supercell of G/H/2H-SiC(0001)/Au2. In (a) only graphene atoms and the H atom saturating the dangling bond are shown. DOS(\vec{k}, E) projected on the first layers of the surface for 3C-SiC(111) (c) and 2H-SiC(0001) (d). Doping levels are indicated in meV. For the 3C cubic case, a considerable hole concentration of \(20.2\, e \times 10^{12}/\text{cm}^2\) (\(\Delta D_P=208\, \text{meV}\)) is induced in the \(\pi\) bands in order to compensate the electron charge accumulated in the vicinity of the defect \(\pi\). As expected, the doping is even larger for the 2H slab, \(\Delta D_P=300\, \text{meV}\) or \(31.3\, e \times 10^{12}/\text{cm}^2\), since the SP further contributes to the doping. Most importantly, the difference in \(\delta\sigma\) between both polytypes is \(11\, e \times 10^{12}/\text{cm}^2\), which coincides very nicely with the SP-induced doping of \(10\, e \times 10^{12}/\text{cm}^2\) found for undefected 2H slabs at \(n = 6\) (blue line in Fig. 2(b)) indicating that the SP- and self-doping mechanisms are basically additive. This is not a trivial result as it is not clear \(a\ priori\) if the self-doping mechanism will affect the depolarization field \(\vec{E}\) which, as mentioned above, plays an important role in the final G doping. Our results thus suggest that the self-doping, already very large on its own, hardly alters the incomplete compensation of the SP pseudo-charge by the G’s \(\pi\) bands.

In summary, we have presented a methodology within the framework of standard DFT slab calculations that accounts for the contribution of the SiC substrate’s SP to the QFG doping. The scheme relies on the pinning of the slab’s chemical potential at the bottom of the slab via the creation of MIGSs states after saturating the lower C-dangling bonds with a gold bilayer. One may additionally incorporate self-doping contributions due to defects or adsorbates in the G layer. Application to QFG on 6H-, 4H- and 2H-SiC(0001) substrates indicates that full compensation of the SP by the G doping should occur at thicknesses of \(n \geq 20\) BLs, while thinner slabs yield an ample range of dopings depending on the polytype and the precise termination of the surface. Other sources of doping, such as self-doping in the G layer, or bulk dopants, may also be incorporated into the calculations. Apart from the obvious applicability of the analysis to ultrathin SiC films, the scheme should also work satisfactorily in other dielectrics exhibiting an SP although the nature of the metallic layer and the interlayer expansions required to minimize the surface dipole will in general need to be tuned for the specific system.

J.S. acknowledges Polish Ministry of Science and Higher Education for financing the postdoctoral stay at the ICMM-CSIC in the frame of the fellowship Mobility Plus. H.A. and J.C. acknowledge financial support from the Spanish Ministry of Innovation and Science under contract Nos. MAT2012-38045-C04-04 and MAT2013-47878-C2-R respectively.

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### Notes
- \(\Delta D_P\) is the difference in doping.
- \(\pi\) bands are affected by self-doping.
- QFG experiments have been carried out on 2H surfaces.
- The scheme relies on the pinning of the chemical potential at the bottom of the slab.
- The scheme should work satisfactorily in other dielectrics exhibiting an SP.
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