Ab initio study of the relationship between spontaneous polarization and $p$-type doping in quasi-freestanding graphene on H-passivated SiC surfaces

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Quasi-free standing graphene (QFG) obtained from the intercalation of a hydrogen layer between a SiC surface and the graphene is recognized as an excellent candidate for the development of graphene based technology. In addition, the recent proposal of a direct equivalence between the $p$-type doping typically found for these systems and the spontaneous polarization (SP) associated to the particular SiC polytype, opens the possibility of tuning the number of carriers in the Dirac cones without the need of external gate voltages. However, first principles calculations which could confirm at the atomic scale the effect of the SP are lacking mainly due to the difficulty of combining a bulk property such as the SP with the surface confined graphene doping. Here we develop an approach based on standard density functional theory (DFT) slab calculations in order to quantify the effect of the SP on the QFG doping level. First, we present a novel and accurate scheme to estimate the SPs by exploiting the dependence of the slab’s dipole moment with its thickness. Next, and in order to circumvent the DFT shortcomings associated to polar slab geometries, a double gold layer is attached at the C-terminated bottom of the slab which introduces a metal induced gap state that pins the chemical potential inside the gap thus allowing a meaningful comparison of the QFG dopings among different polytypes. Furthermore, the slab dipole can be removed after adjusting the Au–Au interlayer distances. Our results confirm that the SP does indeed induce a substantial $p$-doping of the Dirac cones which can be as large as a few hundreds of meV depending on the hexagonality of the polytype. The evolution of the doping with the slab thickness or, equivalently, with the number of stacking defects, reveals that at least ten SiC bilayers are required to fully develop the SP and recover the macroscopic regime.

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I. INTRODUCTION

Obtaining quasi-freestanding graphene (QFG) from epitaxial graphene (EG) on the Si(111)-face of silicon carbide (SiC) via intercalation of a H layer has recently become a promising route to fabricate large area graphene of high-quality. Due to the reduced graphene-substrate interaction, QFG presents improved carrier mobilities as compared to graphene on the buffer layer (2000–3000 vs 700–900 cm$^2$/Vs) together with a weak dependence on temperature. Excellent performance of QFG-based transistors has been already reported, for instance, by Robinson et al. Furthermore, as observed in scanning tunneling microscope (STM) experiments, QFG is hardly corrugated and almost defect-free, which makes it an interesting system in the context of many-body theories in ”2+1” dimensions. The electronic structure of QFG has been intensively studied during the last few years under different experimental techniques and a general consensus has been reached regarding the preservation of the linear Dirac cones. The most intriguing property, however, is the $p$-type doping consistently found in QFG, which is at striking contrast with the large $n$-type doping values ($\sim e \times 10^{13}$ cm$^{-2}$) generally measured for EG. In Table 1 we present a summary of the doping charges, $\delta \sigma$, or alternatively the Dirac point (DP) shifts with respect to the chemical potential, $\Delta$DP, reported in some representative works. Indeed, an ample range of doping levels has been measured for similarly prepared QFG samples, attaining values larger than 300 meV or even small $n$-type dopings. Furthermore, the values presented in the table hint certain correlation between the doping level and the hexagonality of the underlying SiC polytype; while cubic 3C-SiC(111) samples show relatively small $n$-type doping, all 6H- and 4H-SiC(0001) samples are $p$-doped. This correlation has been recently addressed by Coletti et al to find that hole doping (90 meV) still survives in multilayer graphene obtained on a H-passivated 6H-SiC(0001) surface, while on 3C-SiC(111) it exhibits a small $n$-type doping (~40 meV).

Although the possibility of tuning the doping of the graphene layer across such a wide energy range (equivalent to hole concentrations of up to $2 \times 10^{13}$ cm$^{-2}$) is a key issue for the fabrication of QFG-based elements, the origin of the $p$-type doping has not yet been convincingly addressed and still remains controversial. The two main sources of doping are recognized to be: (i) self-doping induced by intrinsic defects and, (ii) the spontaneous polarization (SP) associated to the particular SiC polytype employed as substrate. The former arises from charge accumulation in the vicinity of defects (vacancies or adsorbates) and their electronic and magnetic properties have been characterized in detail from the theoretical side for both free-standing graphene (FG) and QFG. The latter effect, on the other hand, was recently proposed by Ristein, Mamadow and...
Seyller (RMS) based on macroscopic dielectric theory (Ref. 24). RMS noted that the SP creates a pseudo-charge at the surface equivalent to an acceptor layer which should induce considerable doping charges of the order of $6-9 \times 10^{12}/\text{cm}^2$ for 6H-SiC(0001) substrates. Furthermore, since the SP along the (0001) direction remains negative for all hexagonal SiC polytypes, only p-doping should be induced, in accordance with the experimental observations listed in Table I.

Generally, the SP occurs in crystals with a distribution of dipoles along the surface normal such as those created at planar stacking defects (SDs); that is, when a stacking sequence is altered with respect to that in an ideal cubic crystal (Ref. 24, 26, 27). In the bulk phase periodic boundary conditions impose an internal electric field which compensates that generated by the dipoles. However, at surfaces translation symmetry is broken and the dipoles may add up generating an uncompensated polarization field which leaves a finite electric field at the surface. As a consequence, the electrostatic (Hartree) potential, $V_H$, will raise or lower leading to p-type or n-type doping, respectively, of the graphene’s Dirac cones. The SP is an intrinsic property of the dielectric characterized by its density of dipoles and their sign and magnitude, but the final value of the band bending (BB) at the surface will be also determined by the density of states (DOS) of the 2D surface bands –ideally linear in energy– as well as by the screening capabilities of the free carriers present in the dielectric which, in turn, depend on the temperature and the nature and concentration of impurities (bulk dopants).

Although macroscopic theory predicts a direct relationship between the SP and the doping charge in the QFG layer (Ref. 24), it is not obvious if it still holds at the nanoscale. From the theoretical side, this represents a challenging task; despite several groups have reported ab initio SP estimates for the most common 2H-, 4H- and 6H-SiC(0001) polytypes following different approaches (Ref. 26, 27, 29, 30), no equivalent calculation has been attempted to date addressing its impact on the QFG doping. The difficulties associated to the slab geometries typically employed in ab initio studies of surfaces are various. First, one needs to reconcile a surface property such as the graphene doping with a bulk property such as the SP. Second, the polar character of the Si(0001) slab leads to large surface dipole moments creating artificial electric fields which are hard to remove but which could severely affect the calculated doping levels. Last, a reference chemical potential in the slab independent of the selected polytype is required to render any differences in the graphene doping meaningful. The aim of this study is to precisely develop a framework which circumvents these drawbacks allowing a precise determination of the QFG doping induced by the SP and, ultimately, establish their relationship.

In the spirit of Shi and Ramprasad (SR) our scheme involves two dimensional slabs which can be solved by standard approaches such as density functional theory (DFT). We first generalize the SR slab formalism in order to estimate the bulk SP of the different SiC polytypes including as well the appropriate corrections required by the polar character of the SiC(0001). Next, we address the problem of an adequate boundary condition at the bottom of the slab which could pin the chemical potential within the SiC gap regardless of the specific polytype. To this end we test various bottom terminations, including a H capping layer with and without an additional graphene layer as well as an ultrathin gold film of different thicknesses, to find that the latter solves satisfactorily the chemical potential problem. Semi-infinite QFG surfaces are next constructed and solved via Green’s function methods in order to attain an accurate description of the Dirac cones and allow a precise estimation of their doping for each SiC polytype. Our scheme also provides a detailed picture of the development of the SP as a function of the slab thickness which should be relevant in the context of QFG on thin SiC films. We will assume throughout a perfect defect-free graphene layer thus restricting the study to SP induced dopings. The combined effect of SP and self-doping, on the other hand, is even more challenging and will be presented in a separate work.

The paper is organized as follows: in Sec II the theoretical details of the DFT calculations are summarized. In Section III we present our results for the bulk SiC dielectric properties including various factors that could alter the value of the SP. The central findings of the paper are

| $N$ SiC Polytype | $\Delta$DP | $\delta\sigma$ | Technique | Reference |
|------------------|------------|---------------|-----------|-----------|
| 1 4H, 6H         | 100        | 2.3           | ARPES     | 2 and 3   |
| 1 4H, 6H         | $\sim$150  | 2.3           | ARPES     | 9         |
| 1 3C             | $\sim$100  | $\sim$1.0    | ARPES     | 1         |
| 1 6H             | 13         |               | STS       | 8         |
| 1 6H             | 5.0-6.5    |               | Hall      | 5         |
| 1 4H             | 15.0-20.0  |               | Hall      | 10        |
| 1 4H             | 20.0       |               | Hall      | 28        |
| 1 5.0            |            |               | ARPES     | 11        |
| 1 6H             | 320        |               | STS       | 13        |
| 1 6H             | 320        | 5.0           | STS       | 15        |
| 2 4H, 6H         | 35         |               | ARPES     | 2 and 3   |
| 2 6H             | >0         |               | ARPES     | 4         |
| 2 6H             | 200        |               | STS       | 13        |
| 3 6H             | $\sim$90   | $\sim$0.7    | ARPES     | 14        |
| 3 3C             | $\sim$40   | $\sim$0.7    | ARPES     | 14        |
given in Section IV, where (i) different boundary conditions at the bottom are addressed, (ii) the QFG’s doping due to the substrate’s SP is calculated as a function of the slab thickness and, (iii) the simple macroscopic model of RMS is retrieved after suitable macroscopic averages of our DFT results.

II. THEORETICAL DETAILS

All DFT calculations have been performed with the pseudopotential SIESTA formalism (as implemented within the GREEN package)33 and under the generalized gradient approximation (GGA).34 We generated the atomic orbital basis set according to the double-$\zeta$ polarized (DZP) scheme employing confinement energies of 200 meV for all elements. Real space meshes with a resolution of $\sim0.06$ Å$^3$ (mesh cut-off set to 700 Ryd) were defined for performing the 3-center integrals. Unless otherwise stated, the temperature used in the Fermi-Dirac distribution was $k_B T=10$ meV while dipole-dipole interactions among neighbor supercells were suppressed via the usual dipole corrections.35 Figure 1 shows the geometries of all considered polytypes, cubic 3C-SiC(111) as well as hexagonal 2H-, 4H- and 6H-SiC(0001) in a slab geometry. The density of SDs increases with the hexagonality of the polytype, presenting a SD every four, three and two bilayers (BLs) in the 6H, 4H and 2H structures, respectively. The corresponding lattice constant along the surface normal, $c$, contains two SDs and therefore, is six, four and two times longer that that of the cubic 3C (vertical solid lines in the figure). In all calculations the in-plane lattice constant was always fixed to the experimental value of $a^{\text{exp}}=3.08$ Å (our GGA optimized value is 3.10 Å), while $c$ was optimized for each polytype leading to the values given in Table II. The SDs only cause marginal expansions (below 0.5 %) of the inter-BL spacings.

Two types of 2D slabs have been considered. First, and in order to address the SiC dielectric properties, we defined (1×1) slabs, H/(SiC)$_n$/H, oriented along the (111) (or (001) for polytypes) direction of different thicknesses $n$, with both the top (Si) and bottom (C) layers fully hydrogenated. A $k$-sampling of (30×30) for all these (1×1) slabs was found enough to achieve well converged values of the SP.

For the second set of slab calculations we added a graphene layer on top of the upper H capping layer, G/H/(SiC)$_n$/X, and assumed a simplified $(2 \times 2)/{\sqrt{3} \times \sqrt{3}} R 30^\circ$ commensurability between the G/SiC(111) lattices with the lattice constant of the slab set to that of the SiC, thus forcing an 8% expansion of the C-C bonds in the graphene with respect to that in the $(13 \times 13)/{6\sqrt{3} \times 6\sqrt{3}} R 30^\circ$ Moiré pattern experimentally observed (this should, nevertheless, have a minor impact on the calculated doping values). As detailed in section IV.A, different terminations X at the bottom of the slab were considered. We included van der Waals dispersion forces for a proper description of the graphene-substrate interactions following the semiempirical scheme of Ortmann and Bechstedt.23,35 In the total energy optimizations we relaxed the first upper and lower surface layers in the slabs until forces were smaller than 0.02 eV/Å while the geometry of the most internal SiC BLs was set to that optimized for the corresponding bulk polytype.

We highlight the fact that, in order to obtain well converged results for the $(2 \times 2)$ slabs, specially regarding the QFG doping charges, we required unusually fine reciprocal space $k$-meshes as large as (100×100) in the self-consistent Hamiltonian’s calculations thus increasing considerably the computational effort. In Figure 2(a) and (b) we plot the graphene projected density of states (PDOS) and its associated charge, respectively. For a broadening of 5 meV the PDOS presents a spiky structure but, fortunately, the $e$ and hole charges are well converged and can be accurately fitted by a quadratic energy dependence with a Fermi velocity of $v_F=0.7$ m/s (for an isolated graphene layer we obtain $v_F=0.9$ m/s, which is about 20% smaller than the experimental value).

Once self-consistent Hamiltonians were obtained for the QFG slabs, we constructed true semi-infinite surfaces after replacing the bottom layers of the slabs by a semi-infinite bulk following the Green’s functions based prescription detailed elsewhere.35 Band structures in the form of $k$-resolved density of states, PDOS($k$, $E$), projected on the QFG, H and uppermost SiC BLs were evaluated employing a broadening (imaginary part of energy) of 5 meV.

![Figure 1. Geometries of the 9 BLs thick G/H/(SiC)$_9$/Au slabs employed to model the QFG for different SiC polytypes. The two planes at the bottom correspond to the capping Au layer (see section IV.A). The out of plane lattice parameter $c$, is indicated by vertical solid lines while dashed horizontal lines are drawn at the location of the SDs. The subindexes in 6H$_1$ and 4H$_1$ indicate that the first SD is the closest possible to the surface.](image-url)
with $\chi_e = \epsilon_r - 1$. $P_b$ corresponds to the bulk polarization induced by the external field, while $P_0$ stands for any source of spontaneous polarization which may arise either from any internal dipoles associated to SDs, $P_{id}$, and/or from the surface dipole, $P_{sd}$, inherent in polar slabs\textsuperscript{31}:

$$P_0 = P_{sd} + P_{id}$$

(3)

A. Relative Permittivities

In the absence of any SP, $P_0 = 0$, and after applying a finite external field across the slab, $E_{ext} \neq 0$, eqs. (12) allow to estimate the relative permittivity, $\epsilon_r$, from the $\partial m/\partial t = P_b/\epsilon_r$, slope via:

$$\epsilon_r = \frac{\epsilon_0 E_{ext}}{\epsilon_0 E_{ext} - \frac{\partial m}{\partial t}}$$

(4)

If the atoms are relaxed under the presence of the electric field eq. (4) provides the static permittivity $\epsilon_r(0)$, while if they are fixed to their zero field equilibrium positions it gives the high-frequency permittivity, $\epsilon_r(\infty)$.

For the more general case where due to both internal and surface dipoles $P_0 \neq 0$, one may still employ eqs. (12) although a second set of slab calculations is needed for an external field of opposite sign, $-E_{ext}$, in order to filter out the $P_0$ contribution. It then suffices to set $\partial m/\partial t = 1/2 (\partial m^+ / \partial t - \partial m^- / \partial t)$ in eq. (4), where $m^\pm$ corresponds to the dipole moment under $\pm E_{ext}$.

In Fig. 3(a) we show the $m(t)$ dependence for (1×1) H/(SiC)$_n$/H slabs with $n=6$, 9, 12 and 15 for all polytypes after applying an external electric field of $E_{ext}=\pm 0.1$ V/Å either keeping fixed the geometry (open circles in the figure) or allowing the atoms to further relax (full circles). The resulting permittivities, high frequency in the former case and static in the latter, are given in Table I. The correct performance of the approach can be judged by the almost perfect linear fits in the plot and the agreement between the theoretical $\epsilon_r$ values and the reported experimental ones for SiC at room temperature: $\epsilon_r(\infty)=6.5$ and $\epsilon_r(0)=9.7$\textsuperscript{43}.

The intercept of $m(t)$ with the ordinate axis provides the total spontaneous polarization in the slab, $P_0$. For the 3C case, where no internal dipoles exist, it directly provides the surface dipole contribution, $P_{sd}/\epsilon_r$, due to the polar character of the slab (which is substantially reduced, but not fully removed, by the capping H layers). For the rest of polytypes we find the expected trend that as the hexagonality of the dielectric increases, the asymmetry between the $\partial m^+/\partial t$ slopes also increases due to the larger $P_0$ (see next subsection).

We have additionally calculated local permittivity profiles across a dielectric slab, $\epsilon_r(z)$, following the SR approach described in Ref. [44]:

$$\epsilon_r(z) = \frac{2E_{ext}}{2E_{ext} - p(z)/\epsilon_r}$$

(5)
FIG. 3. DFT derived bulk dielectric properties for SiC. (a) Dependence of the dipole moment per unit area, \(m\), with the H/(SiC)\(_n\)/H slab thickness, \(t\), for 3C-, 6H\(_1\)-, 4H\(_1\)- and 2H-SiC polytypes. The slabs thickness ranges between 6 and 12 BLs. Lower and upper curves calculated under external fields of -0.1 eV/Å and +0.1 eV/Å, respectively. Open (full) circles correspond to calculations where the atomic positions were fixed (relaxed) after applying the external field, while the straight lines are best fits to the data points. (b) 2D-averaged \(\varepsilon_r(z)\) profile across different 15 BL thick SiC slabs after applying ±0.1 eV/Å external fields. Solid and dotted lines correspond to the high frequency and static permittivities, respectively. The profiles have been obtained after a gaussian smearing for \(p(z)\) employing widths of 2.5 Å.

where \(p(z)\) gives the local dipole moment, which is obtained from the induced charge density, \(\rho^{ind}(z)\):

\[
p(z)/\varepsilon_r = -\varepsilon_0 \int_{-\infty}^{z} dz' \rho^{ind}(z')
\]

The induced charge is approximated by \(\rho^{ind}(z) = \rho^+(z) - \rho^-(z)\), where \(\rho^\pm(z)\) is the charge density profile under an \(\pm E_{ext}\) external field after averaging over the 2D unit cell. In practice, large oscillations at the atomic scale in \(\varepsilon_r(z)\) need to be removed either by taking macroscopic averages over the slab thickness or employing other kind of smoothing. In Figure 3(b) we present \(\varepsilon_r(z)\) profiles of the high frequency (solid lines) and static (dashed) permittivities for a H/(SiC)\(_{15}\)/H slab, respectively. The profiles remain fairly constant in the inner region of the slabs attaining values in good correspondence with those deduced above, and listed in Table II. Notice, however, certain asymmetric features particularly in the static profiles probably related to anomalous dynamical contributions. In fact, these features change with the slab thickness or the precise location of the first SD in each polytype.

### B. Spontaneous Polarizations

In order to obtain the bulk SPs of the SiC polytypes we first estimate \(P_0\) from eqs. (1-3) performing another set of slab calculations in the absence of an external field. Hereafter we also pay attention to the location of the first SD relative to the top Si layer and arranged the 6H (4H) slabs into three (two) subsets, 6H\(_{1-3}\) (4H\(_{1-2}\)), where the subindex increases as the first SD is located further away from the uppermost BL. In Fig. 4 we plot the dipole moment per unit area for all H/(SiC)\(_n\)/H systems with \(n=6-12\). For the SD free SiC(111)-3C slab (black line) there are no internal dipoles and, according to eq. (3), the slope provides directly the surface dipole contribution \((P_{id}^s = 8 C/10^{-5} m^2)\). The 4H and 6H cases (red and green lines, respectively) show almost flat slopes with sudden drops whenever an additional SD is incorporated in the slab. The drops always attain a value of \(\sim 0.01 C/m\), regardless of the slab thickness, the location of the first SD or the actual polytype. Hence, they may be identified with the dipole moment associated to a single SD, \(m_{SD}\), while the horizontal sections correspond to the crystalline regions in the slab. In fact, they are not strictly flat, but present a slight positive slope due to the depolarization field; that is, the crystalline regions tend to screen \(m_{SD}\). Notably, within each subset the dipole moments can be very accurately fitted via eqs. (1-3) (see lines in the figure) by setting:

\[
P_{id} = \varepsilon_r m_{SD} N_{SD}/t
\]

where \(N_{SD}\) is the number of SDs in the slab. In all fits the surface dipole term, \(P_{id}\), always attained a value at least one order of magnitude smaller than \(P_{id}\), as already visually clear. The bulk SP for a given polytype, \(P_S\), is then simply given by:

\[
P_S \approx \frac{\partial P_{id}}{\partial t} = 2\varepsilon_r m_{SD}/c
\]

where \(c \) is the length of the bulk repeat vector along the slab’s normal (specific of each polytype and given in Table II) and the factor two accounts for the fact that there are two SDs per repeat unit (see Fig. I). Our method yields SP values of \(P_{S}^{4H_{1/2}} = -1.5 / -1.5 C \times 10^{-2}/m^2\) and \(P_{S}^{6H_{1/2}} = -1.1 / -0.9 / -0.9 C \times 10^{-2}/m^2\), in very close agreement with previous estimates based on bulk calculation\(26,29,30,47\) (see also Appendix).

On the other hand, the dipole moment for the 2H slabs (blue line) presents an almost perfect linear dependence with \(t\) due to the absence of crystalline regions, so that the SP may be directly derived from the slope yielding \(P_{S}^{2H} = -3.3 C \times 10^{-2}/m^2\), which, again, is in reasonable agreement with previous works\(26,29,47\).
ues. More precisely, and since this end, we recalculated the electronic structure of all the valence/conduction bands (we disregard, however, the dependence of the Fermi-Dirac distribution function, we estimate the calculations when computing the occupation of states via the DFT derived values while lines to best fits to the data points using approximation for \( P_{el} \) in eq. 9.

1. **SP dependence with e/hole concentration**

Last, we explore the robustness of the SP versus the e/hole concentration in the intrinsic dielectric. To this end, we recalculated the electronic structure of all H/(SiC)\(n\)/H slabs self-consistently at different \( k_B T \) values. More precisely, and since \( k_B T \) only enters our calculation for the same figure we present the bilayer resolved DOS for the slab without H atoms at the bottom of the slab in order to reduce the dipole-dipole interactions between slab images (recall the step from the reduction of the potential step between the vacuum regions at both sides of the slab (see text for further explanations). Solid circles correspond to the DFT derived values while lines to best fits to the data points using approximation for \( P_{el} \) in eq. 9.

**FIG. 4.** Dipole moment per unit area (in the absence of an external electric field) as a function of the H/(SiC)\(n\)/H slab thickness \( t \) for all the SiC polytypes. Blue, red and green dark lines correspond to the 2H, 4H\(_{1/2}\), 6H\(_{1/2/3}\) and 3C cases, respectively (see text for further explanations). Solid circles correspond to the DFT derived values while lines to best fits to the data points using approximation for \( P_{el} \) in eq. 9.

**FIG. 5.** (a) Evolution of \( P_S \) for all polytypes as a function of the electronic (or Fermi-Dirac) temperature, \( k_B T \). Same color scheme as in Fig. 4. (b) Electron/hole concentration at each temperature \( k_B T \); results for all slabs and polytypes are superimposed to the SP.

A. **Slab models for QFG**

Let us first address in detail the drawbacks of the slab geometry when modeling polar surfaces. To this end, we consider the QFG system G/H/(SiC-3C)\(_6\)/X already described in section II, and examine different terminations X at the bottom of the slab in order to reduce the surface dipole and obtain a boundary condition at the bottom of the slab which could reasonably mimics that expected from a semi-infinite SiC(111) surface. Essentially, we seek for electronic states within the gap and localized at the bottom of the slab which could lead to a well defined chemical potential, \( \mu \), in a similar manner as dopant impurities determine the chemical potential in a real dielectric. Although the discussion below is restricted to slabs six BLs thick, we have checked in all cases that increasing the slab thickness up to twelve BLs does not alter our conclusions.

We start with the most common practice of saturating the C dangling bonds at the bottom of the slab with H atoms. In Fig. 6(a) we plot the Hartree potential profile, \( V_H(z) \), before (green line) and after (dark) adding the H capping layer. A reversal of sign and a substantial decrease of the surface dipole is immediately obvious from the reduction of the potential step between the vacuum regions at both sides of the slab (recall the step arises from the external electric field applied to remove the dipole-dipole interactions between slab images). In the same figure we present the bilayer resolved DOS for both cases. For the slab without H atoms at the bottom no trace of the graphene bands is seen in the energy window due to the huge doping induced by the unsaturated C atoms. Under the presence of the H-capping layer, on the other hand, the chemical potential (or Fermi level) remains fixed at the DP and within the gap. The surface dipole may be reduced by expanding the C-H bond lengths at the bottom of the slab thus generating a local...
FIG. 6. (a) left: $\delta V_H(z)$ profile along a G/H/(SiC)$_6$/H slab depicted at the center and, right: the corresponding DOS projected, in ascending order, on the bottom H layer, the six SiC BLs, the intercalated H layer and the graphene; green (dark) lines correspond to a slab calculation without (with) the H capping layer at the bottom. (b) Dark lines same as in (a) while blue lines correspond to the same H-saturated slab after elongating the C-H bonds at the bottom by 0.45 Å. (c) Same as (b) but for a G/H/(SiC)$_6$/H/G slab; dark lines correspond to the relaxed geometry and blue after elongating the C-H bonds by 0.4 Å and shifting the bottom graphene layer by another 0.4 Å. (d) Same as (c) but for a G/H/(SiC)$_6$/Au slab; dark lines for the relaxed geometry and blue after expanding the Au-C bonds by 0.5 Å. (e) Same as (d) but for a G/H/(SiC)$_6$/Au$_2$ slab; blue lines correspond to expansion of the Au-C bonds and the Au interlayer distances by 0.5 Å and 0.65 Å, respectively, with respect to the relaxed geometry (dark). (f) Same as (e) but for a G/H/(SiC)$_6$/Au$_3$ slab after applying 0.4 Å elongations to the C-Au and both Au-Au interlayer spacings (blue) with respect to the relaxed geometry (dark).
dipole that may counterbalance the former. The resulting potential after an outwards 0.45 Å displacement of the saturating Hs is shown by the blue lines in Fig. 3(b). Although the potential step is essentially removed, the position of the DP remains pinned at μ. This is a consequence of the absence of gap states at the bottom of the slab, so that charge neutrality forces the bands of graphene to follow any band bending (BB) and pins μ at the DP. Indeed, as long as the BB does not cross into the conduction or valence bands this picture will remain regardless of the presence of any internal dipoles in the slab. Therefore, slab models with a H capping layer at the bottom are not suitable for the estimation of any SP-derived doping.

A natural way of introducing gap states could be to add another graphene layer at the bottom leading to a more symmetric G/H/(SiC)n/H/G geometry. The Hartree potential and DOS for such case are given by the dark lines in Fig. 4(c). We now find an enhanced BB which leads to the pinning of μ at the valence band edge of the lower SiC BL together with large n- and p-type dopings at the bottom and top graphene layers, respectively. Expanding the bond lengths at the bottom of the slab by considerable amounts (blue lines) hardly changes the doping level at the top graphene and hence, this model can also be ruled out for the estimation of any influence of SPs.

Our next trial model consists of replacing the H capping layer by a metallic one with the hope that the creation of a metal-induced gap states (MIGS) could effectively pin μ within the gap. As shown in Fig. 4(d)-(f), this is indeed the case when one, two or three Au layers, respectively, are used to passivate the C dangling bonds. We found energetically more favorable to place the Au layer in contact with the C atoms at top positions while additional Au layers are stacked following an fcc sequence. For the 1 ML case, dark line in (d), the MIGS appears as a large peak in the middle of the gap which penetrates up to three bilayers into the dielectric. The top graphene is now only slightly n-doped and although the dipole is still considerable it may be again suppressed by expanding the Au-C spacings (blue lines). The expansion leads to an enhancement of the MIGS’s DOS and a slightly larger doping. Adding a second Au layer changes the doping to p-type with the MIGS still pinning the chemical potential within the gap although this time slightly closer to the valence band (dark lines in (e)). In order to compensate the surface dipole we now require Au-C and Au-Au expansions as large as 0.50 and 0.65 Å, respectively, but with the fortunate outcome of removing the doping and leaving the DP aligned with μ. For the sake of completeness, we present in (f) the case of three Au layers, where a moderate p-doping is now obtained even after elongating the interlayer spacings.

In summary, we find that μ can be pinned at the bottom of the slab and within the gap after capping the C atoms with an Au layer via the appearance of a MIGS. Furthermore, the surface dipole can be removed by expanding the Au-C and Au-Au interlayer distances by large amounts (≈ 0.5 Å) while the actual doping in the graphene layer can be tuned by choosing the thickness of the metallic layer, obtaining n-doping for one atomic plane, no doping for two and p-doping for three. The pinning of μ occurs due to the much larger DOS of the MIGS compared to that of the QFG, and we stress that it is an essential prerequisite to make meaningful any differences in the graphene doping among different polytypes. Also note that our model slabs may be as well employed to quantify any doping in the graphene arising from defects.33

B. Doping of graphene due to the substrate’s SP

Once we have proven that both the SP and the QFG doping can be evaluated under the same slab-based framework we may explore their interplay as a function of the SiC polytype and the slab thickness. We choose the G/H/(SiC)n/Au2 slab with elongated bonds at the bottom shown in Fig. 6 as our model system for all calculations presented in this section since in the absence of SDs it yields hardly any doping (see Fig. 6(e)). The Au1 and Au2 terminations should anyhow yield similar doping charges if the DP location for the 3C case is used as the reference when comparing against the rest of polytypes.

In order to achieve a more accurate picture of the surface electronic structure we calculated the graphene and SiC projected density of states (PDOS) under a semi-infinite geometry after replacing the Hamiltonian matrix elements involving the lower layers in the 12 BL thick slab by those corresponding to an ideal bulk termination as outlined in section II.32. Figure 7 shows k-resolved PDOS on graphene, the intercalated H layer and the first three SiC BLs for the 3C, 6H1, 4H1 and 2H slabs and for the maximum thickness considered, n=12. For the 6H and 4H stackings we again take care of the the location of the uppermost SD and group the results accordingly (see III.B). The semi-infinite geometry provides a continuum of states for the valence band while the Dirac cones across the gap are clearly visible in all plots. In accordance with the experimental trend, the DP shift with respect to the chemical potential, ∆DP, increases with the hexagonality of the polytype; starting from a marginal value of 14 meV for the SD free surface (a), we obtain a value as large as ∆DP=320 meV for the 2H case (d), that is, equivalent to a p-type doping surface charge density of δσ = 17 e x 10^{12}/cm². The 6H1 and 4H1 surfaces (b)-(c), also show substantial shifts of 183 and 240 meV, respectively, corresponding to charges in the 5-10 e x 10^{12}/cm² range.

It is important to note, however, that despite the model system is semi-infinite, the doping calculated for each polytype depends on the particular slab employed to perform the matching with the bulk. This is because the Fermi level and the Hamiltonian matrix elements employed for the surfacemost layers in the semi-infinite are extracted from the slab calculation and, hence, they im-
FIG. 7. DOS($k, E$) projected on graphene, H and first three SiC BLs of a G/H/(SiC)$_{12}$/Au slab with that of the corresponding bulk (see Sec. II for further details). Four different SiC polytype surfaces are shown: (a) 3C, (b) 6H, (c) 4H and (d) 2H. The DP shift, $\Delta$DP, is indicated in each plot in meV.

FIG. 8. Doping of the graphene layer for all G/(SiC)$_n$/Au$_2$ slabs considered in this work as a function of $n$, the SiC polytype and the location of the SD closest to the surface (same color scheme as in Fig. 4); left axis gives the surface charge density and right axis (quadratic scale) the Dirac point shift, $\Delta$DP=$\Delta$P$-\mu$. Horizontal lines at the right give the bulk SP andered, whereas those employed for the bulk like layers are extracted from a separate bulk calculation in which no band bending can occur due to the periodic boundary conditions (in fact, the $\Delta$DP values differ by less than 5 meV when deduced from equivalent PDOS plots extracted directly from the slab calculation).

Fig. 8 shows the calculated graphene doping for all surface systems as a function of the number of BLs, $n$, included in the slab. Except for the 3C case, where the DP remains close to $\mu$, the surface charge densities, $\delta \sigma$, increase almost linearly with $n$ and approach the SP values given in Table III (indicated in the plot by thick horizontal lines at the right). At the largest thicknesses considered, $n=12$, the dopings for the 4H (red) and 6H (green) surfaces have already reached their respective $P_S$ limits (see next subsection) while the 2H surface shows a poorer convergence presumably requiring thicknesses of around $n=20$ BLs in order to fully develop the SP. The correlation between $\delta \sigma$ and the SP becomes also patent after noting the stairlike behavior of the doping for the 4H and 6H polytypes, highly reminiscent of that appearing in Fig. 4 in fact, the doping mainly depends on the number of SDs in the slab, with positive jumps whenever a new SD is incorporated in the slab while if the added BL follows the cubic stacking the doping decreases only slightly.

C. Macroscopic model

We end this section by presenting a macroscopic analysis of our results in order to rationalize the $\delta \sigma(t)$ behavior shown in Fig. 8 as well as to establish its connection with the $P_S = -\delta \sigma$ relationship predicted by RMS. To this end, we display in Fig. 9 macroscopic averages of the charge redistribution profile, $\delta \rho(z)$, and its Hartree potential, $\delta V_H(z)$, for a G/H/(SiC)$_{12}$/Au$_2$ slab considering a 3C (a)-(b) and 2H (c)-(d) stacking --the original profiles are also shown (rescaled) as thin lines in each plot. Both slabs present a region at the center of the dielectric where charge neutrality is preserved ($\delta \rho(z)=0$) while the potential ramp $\delta V(z)/\partial z$ remains constant. Thus the entire system may be split into four sections, namely: a central (neutral) dielectric region ($I$), the left and right edges ($L$ and $R$) which will be metallic due to the G at $R$ and the Au layers at $L$, and the vacuum region $V$ where both $\delta \rho(z)$ and the electric field vanish. The widths of each region, $d_{I/L/R}$, may be determined by requiring $\sigma_I=0$ and $\sigma_R = -\sigma_L$, where $\sigma_i$ is the total charge per unit area in region $i$. The model satisfies the Gauss’ law $\sigma_{R/L} = \mp \varepsilon \varepsilon_0 E_I$, with $E_I = (\delta V_H(R) - \delta V_H(L))/d_I$ being the local electric field in the dielectric (see Figs. 9(b) and (d)) generally denoted as the depolarization field in the context of ferroelectricity. Its origin is the incomplete compensation of the SP by the graphene doping charge so that net charges of opposite signs reside at each surface of the slab (in Fig. 9(b) we have a net negative
Finite positive depolarization fields consistently appear for the rest of slabs and polytypes, as shown in Fig. 10(a) where we plot the $E_I$ dependence on the slab thickness $n$. For the 2H case, and discarding the thinnest slab $n=6$ for which region $I$ is not well defined, we obtain an almost linear behavior, indicating that the depolarization field should vanish at large $n$ (linear extrapolation gives a slab thickness of around 50 Å). The 4H and 6H polytypes also show an overall decrease as $n$ increases with upwards jumps when the added BL follows a cubic stacking. After comparison against Fig. 8 a clear anticorrelation is found between the depolarization field $E_I$ and the doping charge $\delta \sigma$. Assuming $\delta \sigma$ corresponds to the free charge surface density and $P_S$ to the bound charge, one would then expect that $P_S = \sigma_R - \delta \sigma$. Although this simple relation may hold, within our uncertainty limits, for the 6H and 4H polytypes, it is not satisfied for the 2H. For instance, at $n=8$ it would yield an underestimated SP value of $P_S \approx 2-13 = -15 \times 10^{12}/\text{cm}^2$. In order to understand the origin of this discrepancy we adopt the approach of Dawber et al., whereby the metallic surfaces are treated as finite dielectrics with permittivities $\epsilon_{L/R}$ and a constant effective electric field across them given by: $E_{L/R} = V_{L/R}/d_{L/R}$. Under this assumption there will be no free charges in the system and the continuity equation for the displacement field across the $I/R$ and $I/L$ interfaces yields:

$$\epsilon_I E_I - P_S = \epsilon_L E_L = -\epsilon_R E_R$$  \hspace{1cm} (9)$$

Since the total potential drop across the slab can be expressed as $\Delta V = p/\epsilon_0 = V_L + V_I + V_R$, with $p$ the slab’s dipole moment, we may obtain an expression for the depolarization field in terms of the SP and $p$:

$$E_I = \frac{p/\epsilon_0 + d_m P_S}{d_l + \epsilon_I d_n}$$  \hspace{1cm} (10)$$

where $d_m = (d_L/\epsilon_L - d_R/\epsilon_R)$ is a distance that solely depends on the metal electrodes. Using (10) with the calculated $P_S$ values given in Table II and taking $d_m$ as a parameter, however, does not lead to good fits for the data points shown in Fig. 10(a). In fact, accurate fits can only be achieved if the SP is allowed to vary with the slab thickness thus treating $P_S(n)$ as further parameters. In Fig. 10(b) we plot the optimized SP values as a function of $n$ while the lines in (a) correspond to the fitted depolarization fields. For the 2H slabs we find a strong increase of $P_S$ with $n$, while the 4H and 6H slabs only show an overall moderate increase. Although the values in the figure should be taken with care since the uncertainties in the fitted parameters are large, we believe it is nevertheless a strong indication that the SP requires a considerable number of BLs to fully develop. In view of these results we may conclude that the fact that the graphene doping charges obtained for thin slabs ($n < 10$) remain below the bulk SP values is a consequence of both the depolarization field and the incomplete build up of the SP.

V. FINAL DISCUSSION AND CONCLUSIONS

We have quantitatively studied, at the DFT level, the impact of the bulk spontaneous polarization of the SiC substrate on the graphene’s electronic properties. First, we have presented a novel alternative scheme to calculate the SP for polar surfaces based on standard DFT slab calculations. It is shown that once the dipole moment per unit area associated to a single SD, $m_{SD}$, is
obtained, the $P_S$ value for any polytype can be immediately calculated via eq. (8). The derived values are in good correspondence with previous works, while we estimate their accuracy to be around 20–30% which, given the well recognized difficulties associated to such calculations, seems satisfactory enough. A first source of error is the accuracy of the calculated relative permittivities (up to around 10% after comparison with the experimental $\varepsilon_r$ values), while a second more subtle source is related to the slab’s geometry optimization. Here only the two upper and lower BLs of the slab were allowed to relax while test calculations including all atoms in the relaxations lead to $P_S$ values 10–20% smaller. However, it is doubtful that unconstrained relaxations provide more realistic values due to anomalous dynamical contributions. In this sense, the approach of Meyer et al proposing as appropriate boundary condition for atomic relaxations a vanishing internal electric field by applying a finite external field could improve the accuracy although at the expense of longer computation times in the self-consistent process.

Next, we examined different terminations for the G/H/SiC/X slab model which is a crucial prerequisite to correctly account for the influence of the SP. We have chosen a slab terminated with a double Au capping layer which (i) pins the chemical potential at the bottom of the slab (instead of at the DP), hence it reasonably mimics a semi-infinite SiC substrate, (ii) presents a reduced slab dipole after expanding the Au-Au bonds and, (iii) leads to a vanishing doping of the graphene for the SD free 3C-SiC(111) substrate. Based on this slab model we have calculated the DP shifts and graphene doping charges for 2H-, 4H- and 6H-SiC(0001) substrates as a function of the slab thickness. Our results indeed confirm the experimentally observed $p$-doping in the graphene layer and reveal that it increases with the slab thickness and the hexagonality of the polytype, although remaining below or very close to the bulk SP value which, for each polytype, represents the upper limit to the SP-derived doping (as dictated by macroscopic electrostatics). In the case of 6H and 4H substrates this limit is already reached for slabs around 10 BLs thick but for the 2H it is considerably larger (given the hyperfine $k$-sampling employed, it is beyond our computational resources while from extrapolation we estimate it around 20 BLs). After analyzing the macroscopic averages of the charge densities and the electrostatic potentials we ascribe this slow convergence to the presence of a depolarization field arising from incomplete charge compensations as well as to the fact that the SP requires several layers to fully develop. Interestingly, for the most common 4H- and 6H-SiC polytypes, we find certain dependence of the doping on the precise location of the SD closest to the surface; for a given thickness the doping decreases by around $2 \times 10^{-12}/\text{cm}^2$ the deeper it is buried due to the depolarization effect of the crystalline layers at the surface.

In summary, we have studied the relationship between the graphene doping and the SiC substrate’s SP in QFG surfaces from first principles calculations. Our findings suggest the possibility to tune the level of the graphene’s doping almost in a continuous way by manipulating the number and location of the SDs closest to the surface. The results should naturally apply as well to ultrathin SiC films.

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$\delta\rho$ corresponds to the total charge density minus that of the isolated atoms while $\delta V_H$ to its associated electrostatic potential. We show these quantities rather than the total ones, $\rho$ and $V_H$ since the formers provide better resolution.

Appendix A: Spontaneous Polarizations deduced from 3D unit cells

For the sake of completeness we present an alternative estimate of the bulk SPs based on the more traditional formalism proposed by Posternak et al in Ref. [45] and Qteish et al in Ref. [26], which is probably the simplest one since it only requires a bulk-type (3D) calculation. Due to the imposed periodic boundary conditions the electric field generated by the internal dipoles at the SDs is compensated by a (local) depolarization field across the rest of the unit cell, $-E_{SD}$. If the internal dipole is sufficiently localized to leave a substantial region of the unit cell free of dipoles, one may obtain $-E_{SD}$ from the slope $\delta V_H/\delta z$ across this region once the electrostatic potential has been macroscopically averaged. The associated spontaneous polarization is then obtained via:

$$P_S = -\epsilon_r \epsilon_0 \frac{\partial V_H}{\partial z} \quad (A1)$$

As shown in Ref. [43], eq. (A1) may still be used in geometries where the dipoles are too close among them by constructing a larger supercell after adding extra SD free layers. In Fig. 11(c) we plot the macroscopically averaged Hartree potential, $\delta V_H(z)$, and the associated charge densities, $\delta\rho(z)$, for the 6H-, 4H- and 2H-SiC(0001) bulk phases. For the latter case, and since the dipole density is large, we generated several 3D supercells 6 to 9 BLs thick comprising two or four 2H BLs plus four or five 3C crystalline BLs (see notation in the figure). We quote in the plots the slopes of the depolarization potentials obtained after linear fits of $\delta V_H(z)$ in the crystalline regions. For the 2H supercells we obtain a range of values $P_S^{2H}=1.8-2.3 \ C \times 10^{-2}/m^2$ for the spontaneous polarization. However, we recall certain ambiguities on the particular choice of $z$ at which $\partial (V_H)/\partial z$ is obtained. For instance, values obtained using the local value of the partial derivative at the center of the ramp, or including in the fits either the positive or negative sections of the ramp may lead to deviations larger than a
factor of 2 from those given in the figure, which represents a much larger error bar than that estimated using our approach.

FIG. 11. Macroscopically averaged charge density profiles (solid lines and right axis) and their associated Hartree potentials (dashed lines and left axis) for bulk calculations of different SiC polytypes. Green, red and blue lines correspond to 6H, 4H and mixed 2H-3C SiC bulk phases, respectively. For the latter we have considered several different supercells after varying the number of 2H and 3C units included (indicated in each plot). Thick straight lines overimposed on the Hartree potential ramps (depolarization regions) correspond to linear fits which slopes provide the $P_S$ values indicated for each plot in $C \times 10^{-2}/m^2$ units.