Origin of Doping in Quasi-Free-Standing Graphene on Silicon Carbide

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(Received 30 September 2011; published 15 June 2012)

We explain the robust $p$-type doping observed for quasi-free-standing graphene on hexagonal silicon carbide by the spontaneous polarization of the substrate. This mechanism is based on a bulk property of SiC, unavoidable for any hexagonal polytype of the material and independent of any details of the interface formation. We show that sign and magnitude of the polarization are in perfect agreement with the doping level observed in the graphene layer. With this mechanism, models based on hypothetical acceptor-type defects as they are discussed so far are obsolete. The $n$-type doping of epitaxial graphene is explained conventionally by donorlike states associated with the buffer layer and its interface to the substrate that overcompensate the polarization doping.

DOI: 10.1103/PhysRevLett.108.246104

PACS numbers: 68.65.Pq, 61.48.Gh, 63.22.Rc, 73.22.Pr

The basis for the unique electronic and optical properties of graphene is the linear dispersion relation of the $\pi$ electrons, which is responsible for Dirac-type quasiparticles with many unusual properties. The band structure in the relevant energy range is made up by double cones in the corners of the two-dimensional hexagonal Brillouin zone; their opening angle is determined by the slope $v_F = \frac{\hbar}{2}\frac{\partial \omega}{\partial k}$ of the dispersion relation called the Fermi velocity, which is an intrinsic material parameter. The origin of these so-called Dirac cones defines the Fermi energy in an isolated and intrinsic graphene layer. At finite temperatures, the reservoir of mobile charge carriers is due to thermal excitation of equal concentrations $n_0$ and $p_0$ of electrons and holes. Evaluation of the Fermi statistics yields a value of $n_0 = \frac{\kappa_B T}{\hbar v_F}$ for this intrinsic charge carrier concentration at temperature $T$ where $k_B$ and $\hbar$ are the Boltzmann and Planck constants, respectively [1]. For room temperature, this amounts to $n_0 = 6.1 \times 10^{10} \text{ cm}^{-2}$ when $v_F = 1.1 \times 10^6 \text{ m s}^{-1}$ is taken for the Fermi velocity [2,3].

Epitaxial graphene on hexagonal silicon carbide is never found to follow this expectation [4]. Graphene on SiC(0001) usually reveals a pronounced $n$-type conductivity with a Fermi level position about 0.45 eV above the Dirac energy and corresponding electron concentrations of $1.2 \times 10^{13} \text{ cm}^{-2}$, i.e., a value more than 2 orders of magnitude larger than $n_0$. For 6H-SiC (001) the band alignment between this substrate material and the graphene layer is asymmetric with the Dirac energy 0.75 eV below the SiC conduction band minimum (CBM) and 2.25 eV above the valence band maximum (VBM).

The $n$-type character of the graphene can be explained by donorlike states at the SiC/graphene interface. This interface is sketched in Fig. 1(a) along with a band diagram which will be discussed below. The graphene layer is sitting on top of a buffer layer that intimately resembles the surface layer of the so-called $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstruction of SiC(0001) that is almost commensurate with the graphene lattice [5]. The buffer layer is partially bound to the silicon atoms of the substrate and is considerably distorted as compared to graphene. Photoelectron spectroscopy shows surface states that can be associated with carbon or silicon dangling bonds superimposed on a broad density of states for the buffer layer that extends up to the surface and the graphene layer anchored at the Dirac energy in (b) stand for hydrogen. The polarization vector inside and outside of the SiC is indicated at the bottom of the figure. Note that the negative polarization charge associated with the discontinuity of the polarization across the interface is not a real charge but a pseudo charge. In order to discern pseudo charge from real charge, it is marked by circles. It is not linked to electrons in real quantum-mechanical states (e.g., band states or defects). $D$ sketches the electrostatic potential between the SiC surface and the graphene layer anchored at the Dirac energy in the graphene layer. For the band bending, information from photoelectron spectroscopy [24] has been taken into account.

FIG. 1 (color online). Sketch and schematic band diagram for the epitaxial (a) and the quasi-free-standing (b) graphene interface with 6H-SiC(0001). Large and small circles represent silicon and carbon atoms, respectively, and the very small circles in (b) stand for hydrogen. The polarization vector inside and outside of the SiC is indicated at the bottom of the figure. Note that the negative polarization charge associated with the discontinuity of the polarization across the interface is not a real charge but a pseudo charge. In order to discern pseudo charge from real charge, it is marked by circles. It is not linked to electrons in real quantum-mechanical states (e.g., band states or defects). $D$ sketches the electrostatic potential between the SiC surface and the graphene layer anchored at the Dirac energy in the graphene layer. For the band bending, information from photoelectron spectroscopy [24] has been taken into account.
Fermi level [5]. The complete ensemble of electronic states associated with the buffer layer and the SiC surface can be combined in an interface density of states with a charge neutrality level $E_0$ as shown schematically in the band diagram of Fig. 1(a). The n-type character of epitaxial graphene on SiC(0001) is most plausibly explained by electron transfer from these interface density of states to the graphene layer.

We should mention at this point that Kopylov et al. [6] have recently discussed this type of doping for monolayer and bilayer graphene. In addition, they discuss an alternative mechanism based on classical donors in the SiC substrate. However, in order to explain electron densities native mechanism based on classical donors in the SiC have recently discussed this type of doping for monolayer graphene on SiC(0001) is most plausibly explained by electron transfer from the interface density of states to the graphene layer.

The situation becomes even more mysterious when a quasi-free-standing monolayer graphene (QFMLG) on hexagonal SiC(0001) is prepared. This hetero system forms when the carbon-rich (6√3 × 6√3)R30° reconstructed top layer of the SiC(0001) surface is delaminated by hydrogen intercalation [7]. With this technique, the carbon–silicon bonds to the substrate are released and the resulting silicon dangling bonds are saturated by hydrogen with remarkable perfection [8]. The Si–H bonds are electronically inactive, and in principle a defect-free interface between SiC and graphene is expected. Consequently, charge transfer to the graphene layer is now restricted to the depletion of the bulk doping of SiC, which is insufficient for any substantial doping as has been argued above. Hence, for the n-type and semi-insulating substrate material usually adopted for quasi-free-standing graphene on SiC(0001), very little n-type doping of the graphene layer by the substrate and a Fermi level in close vicinity of the Dirac energy is expected. The experimental observation, however, is the exact opposite: instead of mild n-type doping QFMLG on 6H-SiC(0001) exhibits a strong p-type conductivity with the Fermi level 0.30 eV below the Dirac energy and hole densities of about $5.5 \times 10^{12}$ cm$^{-2}$, i.e., comparable to the electron densities observed for the epitaxial graphene. A mechanism along the classical lines would require a reservoir of acceptorlike defects now of a comparable capacity, although the interface is passivated by the hydrogen termination of the substrate. All classical models, e.g., involving the antibonding orbitals of Si–H bonds or acceptorlike hypothetical defects of this interface as doping reservoir, are implausible. The question, where the robust p-type doping of hydrogen-intercalated graphene on hexagonal SiC comes from, is therefore a mystery so far and the unraveling of this mystery is the main subject of this Letter.

We suggest that the intrinsic spontaneous polarization of hexagonal SiC is responsible for the p-type doping of the quasi-free-standing graphene layer on top of it. To elucidate this mechanism somewhat, let us briefly reconsider (i) Coulomb’s fundamental law of electrodynamics $\vec{\nabla} \cdot \vec{D} = \rho$ linking the dielectric displacement $\vec{D}$ to the space charge density $\rho$ and (ii) the macroscopic linear relation between electric field $\vec{E}$ and dielectric displacement in matter:

$$\vec{D} = e_0 \vec{E} + \vec{P} = e_0 \vec{E} + \vec{P}_0 + \chi e_0 \vec{E} = e_0(1 + \chi) \vec{E} + \vec{P}_0.$$  (1)

Here, $e_0$ is the vacuum permeability, $\chi = 1 - \varepsilon$ the electric susceptibility, and $\vec{P}$ the dipole density or polarization in the material under consideration which may have a spontaneous $\vec{P}_0$ and a field-induced component $\chi e_0 \vec{E}$. If we apply both equations to a layer stack system of two materials with dielectric constants $\varepsilon_1$ and $\varepsilon_2$, the change $\Delta(\varepsilon E) = \varepsilon_2 E_2 - \varepsilon_1 E_1$ of the weighted (normal) electric field components across the interface can be calculated, yielding

$$\Delta(\varepsilon e_0 E) = \sigma - \Delta P_0.$$  (2)

For nonpyroelectric materials, $P_0$ is zero and Eq. (2) reduces to the familiar relation between the field change and the integrated space charge density $\sigma$ (in units of charge per area) which holds for any arbitrarily selected range of the layer stack system. When pyroelectrics such as the hexagonal polytypes of SiC are involved, however, Eq. (2) shows that a difference in spontaneous polarization across an interface has the same effect as a negative sheet charge at the interface. Thus, $-\Delta P_0$ can be associated with a pseudo charge that we may call polarization charge in the following.

Although becoming important at interfaces only, the spontaneous polarization is a bulk property of the materials involved, and its change across a specific interface is independent of any structural or geometric details of that interface. Specifically, when a slab of pyroelectric material is embedded between nonpyroelectric layers—vacuum may also serve as the latter—the two surfaces inevitably carry a polarization charge with identical magnitude and opposite sign on the two interfaces that is an intrinsic bulk property of the pyroelectric material. For any electronic material brought into contact with the pyroelectric, this polarization charge is fully equivalent to a sheet of charged dopants on the pyroelectric side of the interface, however, without the necessity of any real quantum-mechanical states associated with those charges. We will show in the following that sign and magnitude of the spontaneous...
polarization of 6H-SiC(0001) is perfectly consistent with
the acceptor concentration needed to explain the p-type
conductivity of H-intercalated graphene on that surface.

As already indicated above, spontaneous polarization
is an intrinsic feature of all polytypes of SiC except for cubic
3C SiC. For the classical semiconductors Si, Ge, GaAs, or
diamond, this feature is missing due to the cubic symmetry
of the material, and therefore it is not considered at hetero
interfaces of these semiconductors. It plays an important
role, however, in the device physics of GaN and its deriv-
atives, which are of wurtzite, i.e., hexagonal crystal struc-
ture [9]. Amazingly, it is very difficult to address it by
experiment. It essentially leads to the polarization charges
discussed above on the polar surfaces of the semiconductor
compounds, which are usually uncompensated completely or
in part by internal charge formation due to depletion or
accumulation of charge carriers or by external buildup of
ionic charge on the surfaces. Only the modulation of the
polarization charge at a surface upon an external perturba-
tion such as strain, temperature variation, or the presence
of optical phonons can be measured [10–12] but not its
base value. As a consequence, no experimental data are
available for the polarization of any hexagonal semicon-
ductor crystal. In order to discuss the polarization of SiC
polytypes, we are therefore restricted to theoretical results.

However, for theory also, spontaneous polarization is
conceptually difficult to address. The reason is that for any
model with periodic boundary conditions, the dipole dens-
ity $\vec{P} = \frac{1}{V} \int \vec{r} \cdot \rho(\vec{r}) dV$ of a system is ill-defined since it
depends on the arbitrary choice of the unit-cell boundaries
over which it is evaluated. Although the charge density
$\rho(\vec{r})$ alone can be quite reliably and accurately determined
by modern density functional techniques, the direct evalu-
ation of the polarization is impossible. A breakthrough
on this route was achieved by Posternak et al. in 1990 for BeO
[13,14]. They constructed a periodic arrangement with a
supercell containing a certain number of double layers of
the wurtzite form together with a number of double layers
of the zinc blende form. The latter one has zero polarization
by symmetry. When calculating the potential along
this periodic superstructure by density functional theory
(DFT), the Born–von Kármán boundary conditions auto-
matically eliminate the average electric field. However, the
discontinuity of this field at the boundaries between the
wurtzite and the zinc blende slab is independent of this
artifact. This field discontinuity can directly be translated
by (2) to the change in polarization. Because $P_y$ is known
to be zero in the zinc blende slabs, $P_y$ can be evaluated by
this trick for the wurtzite parts of the heterostructure. This
quite ingenious approach was later taken by Qteish, Heine,
and Needs [15,16] to calculate the spontaneous polariza-
tion of various SiC polytypes by density functional theory.
They presented results for 2H (wurtzite), 6H , and 8H SiC.

Part of the spontaneous polarization can be ascribed to
the relative elongation of the longitudinal Si–C bonds
along the $c$ axis and the contraction of the bonds transverse
to it. For the wurtzite crystal structure (2H-SiC) with only
two double layers in the unit cell, this distortion is char-
acterized by the longitudinal bond length in units of the
hexagonal lattice parameter $c$, denoted as internal param-
ter $u$. When bond lengths and angles are chosen the same as
in the cubic polytype (zinc blende) and only the stacking
sequence is changed from staggered to eclipsed, the so-
called ideal wurtzite structure with $u = 3/8$ is achieved.
The projection of the transverse bonds on the $c$ axis is then
$1/8c$, and since they are three times as many as the
longitudinal bonds and point backwards relative to them,
a simple geometric evaluation of the dipole density based
on equally polarized bonds results in zero. In real cases, the
internal parameter $u$ for wurtzite alloys is usually between
0.2 and 2% larger than 3/8 [17]. By taking only this purely
geometric effect into account, a negative polarization
(polarization vector opposing the conventional $c$-axis
direction) for hexagonal SiC corresponding to negative
effective polarization charge on the Si-terminated (0001)
surface is expected (see Fig. 1). However, even when this
geometric relaxation is suppressed in DFT calculations by
choosing all Si–C bond lengths identical in the hexagonal
as well as in the cubic slabs of the model system (i.e.,
modeling the ideal wurtzite structure or its analogue), the
loss of the cubic symmetry alone induces a relaxation of
the space charge density with a contribution to the polar-
ization that has the same sign but an even larger magnitude
than the ionic relaxation contribution for 2H-SiC.
$-3.33 \times 10^{-2}$ C/m$^2$ compared to $-0.99 \times 10^{-2}$ C/m$^2$
[16,18]. This is quite in contrast to wurtzite BeO that has
first been studied as a pyroelectric model substance [13].
Here, the geometric contribution to the polarization is the
dominating one.

Unfortunately, and probably due to the computational
demand of an ab initio and self-consistent quantum-
mechanical modeling, only the 2H polytype of SiC with
the smallest unit cell has been treated by the approach
outlined above [16]. For 6H and 8H SiC, the spontaneous
polarization was only calculated for an idealized hexagonal
crystal structure with bond lengths and angles like in cubic
SiC. The contribution of the ionic relaxation of the real
polytypes relative to this structure is thus not included in
the calculations. We may take the ratio $c/a$ of the longi-
dudinal and transverse hexagonal lattice parameters as
relative measure for this ionic relaxation. It deviates from
the corresponding values for the idealized structures by
+0.49% for 2H SiC, +0.15% for 4H SiC, and
+0.16% for 6H SiC [19]. The effect of ionic relaxation
is thus about 3 times larger in 2H SiC than in the other
polytypes, and since it contributes only 23% to the sponta-
neous polarization, even in the former case we may neglect
it within the uncertainties of the calculations for 4H and 6H
polytypes. For 6H SiC adopted usually as a substrate for
quasi-free-standing graphene, the spontaneous polarization
then is $P_0 = -9.49 \times 10^{-3}$ C/m². As outlined above, this value is equivalent to a sheet of negatively charged donors on the Si face of the substrate with density $|P_0|/e = 5.9 \times 10^{12}$ cm⁻². This deviates by less than 10% from the hole density in the quasi-free-standing graphene layer measured on top of it (see above).

In a more recent calculation by Brandino et al. [20], the spontaneous polarization of SiC polytypes is revisited by a full quantum-mechanical treatment based on the work of Resta [21]. The results for 2H and 4H SiC are the same as those obtained by Qteish et al. [15,16] within 15%. For 6H SiC they find a value of $P_0 = -1.5 \times 10^{-2}$ C/m², i.e., about 50% larger than the value cited by Qteish et al. and corresponding to a negative charge density of $|P_0|/e = 9 \times 10^{12}$ cm⁻².

It should be mentioned at this point that Davydov and Troshin [22] have reviewed in 2007 the calculations of spontaneous polarization in SiC polytypes performed by different methods. They find a considerable scatter of the results that ranges for 2H SiC from $-1.11$ to $-4.32 \times 10^{-2}$ C/m². This indicates a substantial uncertainty also for the theoretical value of 6H SiC cited above. The agreement between the graphene hole density and the polarization calculated by Qteish et al. [15,16] is therefore somewhat fortuitous.

We conclude that spontaneous polarization of the hexagonal SiC substrate is directly responsible for the doping of quasi-free-standing graphene on its (0001) surface. The spontaneous polarization creates a pseudo-acceptor layer that is fully equivalent to real acceptors. Being a bulk property of the substrate, it constitutes an invariant pseudo-sheet charge density only characteristic for the respective hexagonal polytype of the substrate material. We have illustrated this doping mechanism of quasi-free-standing graphene on hexagonal SiC(0001) in the band diagram of Fig. 1(b).

The pseudo-polarization charge will be present for epitaxial graphene layers as well, but in this case it is obviously overcompensated by doping due to the interface density of states as explained above. Thus, when the spontaneous polarization of the substrate is properly taken into account, this density of states must account for both $-P_0/e$ and the observed electron density $n$ in the epitaxial graphene layer.

The SiC substrates used in the experiment [8] were semi-insulating, i.e., with doping concentrations smaller than $10^{14}$ cm⁻³. The areal charge density in the depletion layer of the SiC substrate associated with the band bending indicated in the figure is for such material in all cases smaller than $5 \times 10^{10}$ cm⁻². This is less than 1% of the pyroelectric pseudocharge or the areal charge density in graphene, and we have therefore omitted this charge in the band diagrams of Fig. 1 where the total negative and positive charge count of the interface is balanced.

There are a number of obvious tests of the polarization doping model suggested here: (i) preparing quasi-free-standing graphene with a defect-free interface on the carbon-terminated faces of the hexagonal SiC substrates should lead to $n$-type doping; (ii) on cubic SiC it should lead to undoped graphene layers; and (iii) varying the hexagonality of the SiC polytype should increase the doping level proportionally since the spontaneous polarization is mainly induced at the inversion of the stacking sequence of the double layers [16]. For 4H-SiC, for example, the polarization is expected to be 6/4 times larger than that for 6H-SiC. For most of these tests, the preparation of the corresponding defect-free interfaces has not been realized to date. Only for the silicon terminated surface of 3C-SiC, Coletti et al. [23] have recently reported on quasi-free-standing graphene. In fact, the $p$-type doping as observed for the 6H-SiC is absent, and a mild $n$-type doping with an electron density of about $1.3 \times 10^{12}$ cm⁻² is found instead that can easily be explained by residual defects at the interface. We interpret the vanishing of the $p$-type character for QFMLG when going from the hexagonal 6H to the cubic 3C polytype as a very strong argument in support of the polarization doping model suggested in this Letter.

The authors are grateful to Professor Lothar Ley for many fruitful and stimulating discussions. The work was supported by the Deutsche Forschungsgemeinschaft and by the ESF through the EUROCORES program EuroGRAPHENE.

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[18] Following the commonly used sign convention for the $\hat{c}$ axis direction in hexagonal pyroelectrics, the spontaneous polarization $P_0$ of SiC polytypes as calculated by Qteish et al. is opposite to $\hat{c}$. Nevertheless, the authors quantify their results in Refs. [15,16] with positive $P_0$ values. Keep this in mind when comparing their results with other literature.