Charge spill-out and work function of few-layer graphene on SiC(0 0 0 1)

O Renault¹, A M Pascon², H Rotella¹,4, K Kaja¹,5, C Mathieu³, J E Rault³,6, P Blaise¹, T Poiroux¹, N Barrett³ and L R C Fonseca²

¹ CEA, LETI, MINATEC Campus, 17 rue des Martyrs, 38054 Grenoble Cedex 09, France
² Center for Semiconductor Components, University of Campinas, 13083–870 Campinas, SP, Brazil
³ CEA, DSM, IRAMIS, SPEC, 91191 Gif-sur-Yvette Cedex, France

Received 15 March 2014, revised 11 May 2014
Accepted for publication 21 May 2014
Published 26 June 2014

Abstract
We report on the charge spill-out and work function of epitaxial few-layer graphene on 6 H-SiC(0 0 0 1). Experiments from high-resolution, energy-filtered x-ray photoelectron emission microscopy (XPEEM) are combined with ab initio density functional theory calculations using a relaxed interface model. The work function values obtained from theory and experiments are in qualitative agreement, reproducing the previously observed trend of increasing work function with each additional graphene plane. Electron transfer at the SiC/graphene interface through a buffer layer (BL) causes an interface dipole moment which is at the origin of the graphene work function modulation. The total charge transfer is independent of the number of graphene layers, and is consistent with the constant binding energy of the SiC component of the C 1s core-level, measured by XPEEM. Charge leakage into a vacuum depends on the number of graphene layers, explaining why the experimental, layer-dependent C 1s graphene core-level binding energy shift does not rigidly follow that of the work function. Thus, a combination of charge transfer at the SiC/graphene interface and charge spill-out into the vacuum resolves the apparent discrepancy between the experimental work function and C 1s binding energy.

Keywords: graphene, silicon carbide, work function, XPEEM, ab initio simulation

(Some figures may appear in colour only in the online journal)

1. Introduction

The outstanding transport properties of graphene (high carrier mobility, ballistic transport observed up to room temperature, ability to sustain large current densities, exceptional optical and mechanical characteristics) make it an attractive material for the study of two-dimensional physics, as well as for application in many devices either as passive (e.g. as electrode material) or active (e.g. as channel material in a transistor) components [1]. However, to employ graphene in a device requires a suitable substrate, conserving the electrical and physical properties of free-standing graphene. If we exclude the exfoliation route for device applications, graphene can be formed from high-temperature annealing of SiC(0 0 0 1) or SiC(0 0 0 -1) [2–5], or directly synthesized on the surface of bulk [6] or thin [7] metallic substrates by chemical vapour deposition. Few-layer graphene (FLG) obtained on SiC(0 0 0 −1) may display all the transport properties of free standing graphene [8], however, the interface between FLG and the silicon face, SiC(0001), is more fully understood both theoretically [9] and experimentally [10]. The growth of graphene on SiC(0001) proceeds on an insulating buffer layer (BL) of a unique $\{6\sqrt{3} \times 6\sqrt{3}\} R30^\circ$ symmetry which de-couples the subsequent graphene layers from the substrate.

For successful interface engineering and device optimization using graphene either as electrode material or as an active layer, control of the work function (WF) is essential as it generally governs the energy level alignments through the heterostructure [11]. This is a considerable theoretical
and experimental challenge due to (i) the intrinsic low-dimensionality of FLG and the peculiar band structure of the graphene π-bands sensitive to substrate interactions, and (ii) the intrinsic non-uniformity of graphene thickness in macroscopic samples [12]. The FLG WF has a layer-thickness dependency due to (i) charge transfer from electronic states at the substrate interface, and (ii) charge redistribution within the FLG by intrinsic screening. Recent work highlights how the charge transfer and charge redistribution mechanisms are sensitive to interactions of the FLG with the substrate [13, 14] and between the graphene layers [15–17].

The WF of FLG heterostructures was studied in the case of insulating [16, 17], semiconducting SiC(0 0 0 1) [12] and SiC(000 1) [14, 15, 18, 19], and various metallic substrates [13, 20, 21]. Ziegler et al. studied exfoliated FLG on SiO2 and found a screening length of four to five graphene layers, and WF differences of 68 meV between single layer and bilayer graphene, and of 54 meV between bilayer and trilayer graphene [16]. Datta et al. [17] showed a similar increase of the surface potential as a function of FLG thickness of up to five layers on SiO2, and interpreted the result in terms of intrinsic screening by the FLG of the charge transferred from a thin interfacial layer of traps at the silica surface. In the case of graphene on metals [13], a layer dependency of the WF was also observed due to spatial variations in the charge transfer at the metal-FLG interface for domains with different in-plane orientations; moreover, contributions to the WF from metal-graphene chemical interactions are also mentioned [13].

Using XPEEM, Hibino et al. [14] measured a 0.3 eV increase in the WF on SiC(0 0 0 1) as the FLG thickness varies between one and six layers. A concomitant shift of 0.4 eV toward lower energies of the C 1s binding energy was observed, suggesting that all the electronic levels of graphene undergo a near rigid shift due to charge transfer between graphene and the SiC substrate. However, the WF and core-level shifts are not perfectly anti-correlated and comparison with theoretical calculations suggest more complex electronic interactions due to chemical bonds between the BL and the substrate. Thus, it is not clear whether all of the energy levels undergo a simple, band bending-like rigid shift as the number of graphene layers increases, or if there are more subtle changes in the band structure.

Here, we have studied the WF of FLG epitaxially grown on 6 H-SiC(0 0 0 1), using high-resolution XPEEM and ab initio density functional theory (DFT) calculations of a relaxed interface. The WF values obtained from theory and experiment are in qualitative agreement: the WF increase is reproduced for each additional graphene plane on the surface. Compared to free-standing graphene, the WF of the stack is modulated by the charge transferred from the interface states to graphene, creating an interface dipole moment. The charge transfer is independent of the number of graphene planes, but a thickness-dependent partial charge spill-out is predicted, explaining the experimental C 1s core-level additional shift in graphene. The results provide a coherent explanation of why the layer-dependent core-level shift does not rigidly follow that of the WF.

2. Experimental and theoretical methods

2.1. WF and C 1s core-level measurements

The sample of epitaxial FLG grown on a Si-terminated 6H-SiC(0 0 0 1) surface was obtained by sublimation of the SiC substrate at 1400 °C for 5 h under ultra-high vacuum (10−6 Pa). This procedure resulted in micron size domains of one, two and three layer graphene (LG). The vibrational fingerprint of graphene was clearly observed with Raman spectroscopy. Note that the SiC substrate was n-doped with a concentration of 1017 cm−3.

Local WF measurements were performed by spectroscopic XPEEM using a NanoESCA instrument (Omicron NanoScience, Oxford Instruments) which has already been described elsewhere [22]. Spectroscopic XPEEM yields absolute local WF values, provided the WF of the electron analyser is known [14, 23], with a typical lateral resolution between 50–150 nm and an uncertainty in the measured WF of 20 meV [24]. Here, we employed soft x-ray synchrotron radiation, provided by the TEMPO beamline at the SOLEIL synchrotron storage ring (Saint-Aubin, FRANCE), and 21.2 eV photons from a conventional He-discharge lamp. The combination of two excitation sources with energies well above the photoemission threshold increases the reliability of the measurements. Possible carbonaceous contamination of the graphene surface during XPEEM imaging using synchrotron radiation has been reported [14]. Therefore, the use of a lower brilliance photon source, which is less likely to modify the surface, provides an important, independent check of the WF values.

Before XPEEM imaging, the sample was heated at 550 °C in vacuum to remove adsorbates, confirmed by micro-spectroscopy of the C 1s core-level. The C 1s spectrum of the clean surface showed the typical graphene component at 284.4 eV and the graphene–SiC interface components at a higher binding energy (285.0–285.5 eV) [25]. The photoemission threshold image series were recorded within two fields of views (FoVs): 34 µm (He I) and 115 µm (synchrotron radiation), with a lateral resolution of 150 nm. The thickness of the FLG domains was determined by low-energy electron emission microscopy (LEEM), and the C 1s core-level XPEEM was excited using synchrotron radiation (hv = 400 eV). The C 1s XPEEM data were recorded with an overall energy resolution of 250 meV, enabling an accurate fit of spectra from individual FLG domains, using distinct core-level components.

2.2. Theoretical model and method

We employed DFT [26] with the local density approximation (LDA) and a plane wave basis set, as implemented in the ABINIT code [27, 28]. Norm-conserving pseudo-potentials were used with a plane wave cutoff of 700 eV [29]. Integration over the Brillouin zone (BZ) was performed on a 6 × 6 × 1 grid for the supercell, mapped according to the scheme of Monkhorst and Pack [30], which was carefully chosen to include the high-symmetry points characteristic of graphene. After fully relaxing a single graphene plane in vacuum
(calculated lattice parameters $a = b = 2.458 \text{ Å}$, lattice angles $\alpha = \beta = 90^\circ$ and $\gamma = 60^\circ$, C–C distance = $1.426 \text{ Å}$), a new hexagonal eight-atom unit cell was created following Varchon et al [9]. By simplifying the geometry to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface [9], this interface model reduces the strain between the graphene layers and the SiC surface while maintaining the number of atoms at a practical level (53–85 atoms, depending on the number of graphene planes considered). In our interface model, the SiC slab was fully relaxed while the graphene was stressed (tensile) in the plane to match the SiC lattice parameters. The resulting interface lattice parameters are $a = b = 5.487 \text{ Å}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, giving an 8.6% lattice mismatch along $a$ and $b$ directions. The $c$ vector was chosen to be long enough so that the vacuum layer avoids any interaction between the system’s periodic images. Moreover, the presence of the vacuum layer allowed the multilayer graphene heterostructures to relax their atomic positions along $c$, relieving some of the elastic energy. Convergence was achieved when the forces on the atoms were less than $0.01 \text{ eV Å}^{-1}$. The impact of stress on the graphene WF will be discussed below.

The resulting heterostructure containing the interface has a vacuum layer 50 Å thick to insure no sizeable cross-talk occurs between the slab’s periodic images, a 14.87 Å-thick SiC slab made of eighteen silicon atoms and eighteen carbon atoms, and nine hydrogen atoms saturating the C-terminated bottom surface. Following Varchon et al [9], the SiC/graphene interface has one C atom, belonging to the BL, immediately on top of each Si atom at the SiC surface, except for one unpaired Si atom below the middle of the C hexagon. Other C atoms in the BL are located in intermediate positions between the Si atoms below. The unpaired Si atom is important since its dangling bond plays a major role in the electronic structure of the SiC/BL system as discussed below. Mono-, bi-, tri-, and four-layer graphene (1LG, 2LG, 3LG, and 4LG) on the SiC/BL were calculated (figure 1). For each system the thickness of the vacuum layer was kept constant at 50 Å.

The WF is the minimum energy required to extract an electron to a potential far from the surface [31]. The WF is obtained from the following expression:

$$WF = eV_{\text{vacuum}} - E_F$$  \hspace{1cm} (1)$$

where $eV_{\text{vacuum}}$ is the vacuum potential and $E_F$ is the Fermi energy. Figure 2 illustrates the process for obtaining the WF theoretically, where the vacuum potential is the planar average of the total Kohn–Sham potential taken sufficiently far from the SiC/graphene slab along the direction perpendicular to the graphene surface. The SiC valence band edge and conduction band edge (VBE and CBE) are also indicated: we obtained an indirect SiC band gap of 2.00 eV, smaller than the experimental value of 3.03 eV [32], typical of a well-known limitation of DFT/LDA [33]. Due to the presence of surface states associated with the surface Si dangling bond, the Fermi level is pinned slightly below the SiC CBE as will be detailed later (see appendix). Other shifts of the Fermi level/band gap, such as induced by the SiC polytype, are not considered here [34].
obtained employing the (0, 0) specular, back-scattered electron beam. Figure 3(a) shows a typical bright-field image with a field of view of 10 µm and a lateral resolution of 30 nm. A full image series was acquired by varying E, the bias difference between the sample and the electron gun, from 2 to 10 eV. Reflectivity curves of the characteristic regions are shown in figure 3(b). There are intensity oscillations between 1.5 and about 7.5 eV which confirm the presence of FLG domains with one, two and three graphene layers. Following Hibino et al [35], n layers of graphene give \( n - 1 \) intensity minima, however, recent work by Feenstra et al [36] has shown that this depends on the graphene–substrate distance. If the BL is sufficiently far from the substrate it acts as an additional layer, thus \( n \) graphene layers will give \( n \) intensity minima in the electron reflectivity. The XPEEM data were generated pixel-by-pixel from the corresponding C 1s image series recorded within a 17 µm field of view, in a region located in the vicinity of the one chosen for the LEEM measurements. Figure 3(c) presents a map of the intensity of the graphene component of the spectra-at-pixels, obtained after peak fitting.

The C 1s core-level spectra of the one, two and three LG domains marked in figure 3(c) are presented in figure 4. The energy resolution allows analysis of the chemical shifts of the individual core-level components. After Shirley background subtraction, the spectra were fitted using four components, related to the SiC substrate (at low binding energy), the main graphene component, and two components assigned to the BL as described previously [25]. These are related to the out-of-plane C–Si covalent (S1) and the in-plane sp² C–C (S2) bonding states. The main graphene component in the C 1s spectra shifts by 100 meV to a lower binding energy with each additional layer. This will be discussed further in section 4. The SiC component due to the SiC substrate has a constant binding energy of 283.7 eV. The graphene thickness is determined from the attenuation of the SiC photoemission signal of the FLG. Assuming a 0.47 nm inelastic mean-free path of C 1s photoelectrons in graphite [37] with a typical 20% uncertainty, and C atom surface densities of \( 3.8 \times 10^{15} \text{ cm}^{-2} \) and \( 1.22 \times 10^{15} \text{ cm}^{-2} \) for graphene and SiC, respectively, we obtain FLG thicknesses of \( 0.51 \pm 0.05 \text{ nm} \), \( 0.69 \pm 0.07 \text{ nm} \), and \( 0.91 \pm 0.09 \text{ nm} \) for the three domains. These values translate quite reasonably into the one to three graphene layers, assuming a graphene interlayer spacing of 0.34 nm.

Figure 3. (a) Typical 10 µm bright-field LEEM image; (b) electron reflectivity curves extracted from the areas marked in (a); (c) XPEEM C 1s map (FoV: 17 µm, \( h\nu = 400 \text{ eV} \)) of the graphene component intensity.

Figure 4. High-resolution local C 1s core-level of the FLG domains marked in figure 3(c). The main graphene peak is dark grey, the interface components S1, S2, are in lighter grey and the SiC component is black. The vertical line indicates the unchanging position of the SiC component.

3.1.2. Local WF and band shifts

The photoemission threshold image series were recorded with synchrotron and laboratory He I radiation with FoV 115 µm and 34 µm, respectively. Prior to the fitting procedure, the images were corrected for two effects: first, the Schottky effect, due to the high electrical field at the surface, induced by the first extractor lens of the objective, which typically shifts the WF value by −98 meV at 12 kV extraction voltage; and the
second correction accounts for the non-isochromaticity of the imaging spectrometer in the dispersive direction (vertical axis on the images) [22]. Figures 5(a) and (b) show the WF maps obtained from the photoemission threshold image series. The maps were generated by a pixel-to-pixel fit of the threshold spectra to a complementary error function [23]. This technique is much more reliable for obtaining the WF, rather than simply extrapolating a straight line down to zero intensity in the threshold region [14], since the theoretical shape of the onset and the energy broadening of the spectrometer are both included in the curve fitting. With this method, the uncertainty in the position of the onset obtained from the fit is ±20 meV. The histograms of the WF values extracted over the FoVs are shown in figures 5(c) and (d). There are clearly three distinct WF values, 4.28 ± 0.03 eV, 4.34 ± 0.03 eV, and 4.39 ± 0.03 eV, corresponding to one, two and three LG, as measured using the C 1s core-level intensity. The WF therefore increases by 50–60 meV per graphene layer.

Hibino et al [35] found that the WF increases by 300 meV when the FLG thickness increases from one to six LG, an average of 50 meV per layer. However the increase was not linear, for one to three LG they report a 200 meV shift. Taking into account the error bars, our values are close to but slightly smaller than Hibino’s. This is also the case when comparing the one to two LG WF shift with Kelvin force microscope (KFM) results reported by Filleter et al [19], who found that 2LG increases the WF by 135 meV when compared to 1LG. For 2LG, our value agrees particularly well with the ab initio calculations of Mattausch and Pankratov [38].

The C 1s graphene binding energies are given in table 1. The binding energy decreases by 90 meV between 1LG and 2LG, and by 80 meV between 2LG and 3LG, whereas the SiC component is constant at 283.7 eV. In both cases the core-level shift is significantly greater than that of the WF. Thus the C 1s binding energy and the WF value do not undergo a rigid shift; therefore, charge transfer between the graphene and the substrate alone is not sufficient to explain the results. The theoretical calculations discussed in section 5 address precisely this question.

3.2. Theory

3.2.1. Graphene/SiC interface The interlayer distances after relaxation of the heterostructure are plotted in figure 6. The SiC/FLG heterostructure is also shown, allowing location of the inter-planar distances. The substrate-induced corrugation of the BL is characterized by a standard deviation of 0.20 Å in the z-coordinate of the C atoms in the BL with respect to the average planar position. This gives a distribution of the distances between the BL and the SiC surface. The z-coordinate distributions for successive graphene layers become narrower. The spread in the calculated inter-planar distances is indicated by the error bars in figure 6. The mean BL to SiC distance is 2.27 Å with respect to the last Si layer, and 2.80 Å with respect to the last C layer, yielding an average of 2.53 Å. The SiC/BL separation of ∼3.2 Å measured by Weng et al [39] seems exceedingly large for the formation of atomic bonds, and may reflect a detachment of the BL from the SiC surface during...
the processing required for optical imaging of the interface. The C–Si distance for the BL C atom immediately above the Si surface atom is 1.98 Å, in excellent agreement with previous calculations [9]. The mean BL/1LG distance is 3.18 Å and the subsequent 1LG/2LG, 2LG/3LG, 3LG/4LG inter-planar distances are 3.20 Å, 3.20 Å, and 3.32 Å, respectively. These values are slightly lower than the measured graphite inter-planar distances (3.35 Å). The inclusion of Van der Waals interactions in the LDA exchange-correlation functional does not seem essential for the calculation of the inter-planar distance in graphene as shown by Mapasha et al [40]. The inter-planar distance in SiC calculated between two successive Si planes is 2.50 Å, in agreement with recent experimental results [39]. The band structure resulting from the relaxed interface presented in the appendix shows the characteristic Dirac cones associated with FLG graphene.

3.2.2. Work function

Table 1 shows the FLG WF of calculated using equation (1) for different values of n, the number of graphene planes on SiC (n = 0 stands for the BL). For the bare Si-terminated SiC slab we found WF of 3.60 eV. For SiC/BL this value is almost unchanged (WF = 3.65 eV). As the number of graphene planes increases above the BL so does the calculated WF, until 4LG, above which WF saturates at 4.76 eV. This high WF value reflects the stress imposed on graphene in our model. Indeed, the calculated WF of bulk graphite, here modelled as a thick graphene slab, is 4.5 eV (very close to its experimental value of 4.6–4.7 eV [41–43]), while for single-layer relaxed graphite it is 4.4 eV. On the other hand, the calculated WF of free-standing graphene under the 8% stress of our model is 5.1 eV. Therefore the impact of tensile stress on the WF of FLG is to increase it by ~16%. While stress tends to increase the WF of several graphene planes, the deformation of the BL tends to lower its WF value: for a planar BL with only the distance to the surface Si atoms optimized, we found a larger WFplanar, = 4.13 eV. On the other hand, we also found that for the same planar graphene model, the WF of the first graphene layer decreases slightly from its value obtained from the fully relaxed model, to WF1planar = 4.17 eV. The reason for this is that the first graphene layer interacts more strongly with the artificially deformed BL, moving closer and raising the value of WF1. For subsequent graphene layers (n = 2–4), the BL is screened by the first graphene plane and does not have such a strong impact on WFn.

4. Discussion

Here we discuss the consistency of our interface model results and the experimental data on the WF and the C 1s core-levels. The experimental WF shifts by 50–60 meV per graphene layer, whereas the C 1s binding energy in graphene shifts by almost 100 meV per layer. Figure 4 shows that the interface chemistry, represented by the S1 and S2 components of the local C 1s core-level spectra, does not change with the number of graphene layers on SiC. Therefore the increase in the SiC/FLG WF with the number of graphene layers should be of an electrostatic origin, related to an increase of the interface dipole. To confirm this hypothesis we have calculated the interface dipoles D, by integrating the net charge density \( \Delta \rho \), defined as the difference between the heterostructure planar averaged (along x and y) charge density and the SiC and graphene bulk averaged charge densities, multiplied by the displacement vector \( d \):

\[
D = \frac{1}{A} \int_{-\infty}^{+\infty} d \rho(z) \Delta \rho(z) dz, \tag{2}
\]

where \( A \) is the interface area and the z direction is perpendicular to the interface. Because the BL is chemically bound to the Si-terminated SiC, the electric dipole formed between them is quite high, contrary to the dipoles formed between SiC/BL and the graphene layers grown on top, which originate from a weak Van der Waals interaction. Therefore it seems that, for the sake of calculation of interface dipoles, it is more realistic to assume that the BL is part of the substrate, with which it forms strong bonds, rather than part of the graphene layers grown on top, with which it forms weak bonds. Indeed, the magnitude of the interface dipoles, calculated under the assumption that the BL is separated from the substrate, are of several electron-volts, a factor of around seven times higher than the WF variation measured and calculated for this system. On the other hand, under the assumption that the BL is part of the substrate, our calculated dipoles are only a factor of ~1.5 higher. Therefore in all the following dipole calculations we have assumed the substrate to be SiC/BL.

To estimate the interface dipole and how it is affected by the number of graphene layers on SiC/BL, the net charge density was obtained using the following three methods. In method I the net charge was obtained by subtracting the charges of SiC/BL and graphene slabs from the heterostructure charge, similar to the work of Bokdam et al [11]. If the impact of the interface on the location of the atoms is short-ranged, quickly decaying into the bulk-like regions, then this procedure is able to remove the bulk charges from both sides of the
interface, leaving only the net interface charge. Formally the net charge density of the interface structure, $\Delta \rho_{\text{SiC/BL+FLG}}$, can be written as

$$\Delta \rho_{\text{SiC/BL+FLG}} = \rho_{\text{SiC/BL+FLG}} - \rho_{\text{SiC/BL}} - \rho_{\text{FLG}}$$

$$= \left( \rho_{\text{SiC/BL}} - \rho_{\text{SiC}} \right) + \left( \rho_{\text{FLG}} - \rho_{\text{FLG}} \right), \quad (3)$$

where $\rho_{\text{SiC/BL+FLG}}$ is the total charge density of the interface structure, $\rho_{\text{SiC/BL}}$ and $\rho_{\text{FLG}}$ are the total charge densities of the SiC/BL and FLG slabs, respectively, and $\rho_{\text{SiC}}$ and $\rho_{\text{FLG}}$ are the total charge densities of the SiC/BL and FLG sides of the interface which include the charge exchanged across the interface. The total charge densities can be further decomposed in their positive and negative components arising from the contributions from the ions and electrons, respectively. Therefore

$$\Delta \rho_{\text{SiC/BL+FLG}} = \left( \rho_{\text{SiC}} - \rho_{\text{SiC}} \right) + \left( \rho_{\text{ion}} - \rho_{\text{ion}} \right) + \left( \rho_{\text{e}} - \rho_{\text{e}} \right)$$

$$= \left[ \left( \rho_{\text{ion}} - \rho_{\text{ion}} \right) + \left( \rho_{\text{e}} - \rho_{\text{e}} \right) \right] + \left( \rho_{\text{ion}} - \rho_{\text{ion}} \right) + \left( \rho_{\text{e}} - \rho_{\text{e}} \right). \quad (4)$$

The alignment between the electronic charge densities of the SiC/BL of the heterostructure and the bare SiC/BL slab was straightforward, as shown in figure 7, since the interface with the graphene planes has little effect on the nearby SiC/BL layers. For this reason, the first term of the left bracket in equation (4), $\rho_{\text{ion}} - \rho_{\text{ion}}$, can be neglected. In the case of the graphene slab, the alignment with the graphene in the SiC/BL/graphene heterostructure is more difficult because the interface has a considerable impact on the graphene layer separation, moving them closer to each other than in the free-standing graphene slab. In other words, the contribution of the ionic charge density in graphene, shown in equation (4), $\rho_{\text{ion}} - \rho_{\text{ion}}$, is considerable and extends several angstroms away from the interface. We assumed the most external graphene layer in the heterostructure to be the reference for alignment between the charge densities of the four-layer graphene slab (4LG) and the SiC/BL/4LG heterostructure, since the fourth graphene layer is the layer least affected by the interface in all our stack models containing different numbers of graphene planes. From that alignment we obtained the $z_0 = 0$ position of the graphene plane in 4LG closest to SiC. For the other alignments (between the nLG slabs and SiC/BL/nLG heterostructures, for $n = 1, 2, 3$) the graphene plane closest to SiC was fixed at the value of $z_0$ determined from the 4LG. The upper panel of figure 7 shows the resulting mismatch between the position of the electronic charge density peaks in the heterostructure and in the graphene slab obtained with method I. Notice that as the number of graphene layers increases, the mismatch decreases for the most external layers, as expected. Despite the intuitive appeal of method I, the difficulty in aligning the graphene slab with the graphene part of the heterostructure raises the question of whether the role played by the graphene ionic contribution masks the effect of the smaller net charge density. Indeed, the interface dipoles, calculated using method I for different numbers of graphene planes on SiC/BL, are of the order of hundreds of electron-volts. For this reason we have employed two other approaches to calculate the net charge density more accurately.

In method II we have subtracted the electronic charge densities of a graphene slab with the same distortions and interplanar separations as in the SiC/BL/FLG stack from the electronic charge density of the graphene side of the interface. In practice, the charge density of the distorted graphene slab was obtained by removing the SiC/BL atoms from the model, and recalculating the charge density of the resulting graphene slab without optimizing the positions of the atoms. In this case, $\rho_{\text{ion}}$ and $\rho_{\text{ion}}$ in equation (4) are the ionic and electronic charge densities of a distorted graphene slab. This method accounts for the electronic charge located in the inter-planar regions of graphene in the stack and for the inter-planar graphene separation. Therefore it is supposed to yield a more realistic net charge density. The total charge alignments for SiC/BL/1LG and SiC/BL/4LG obtained with method II are shown in the upper panel of figure 7. As expected, the electronic charge densities are better aligned, implying that in this case both $\rho_{\text{ion}} - \rho_{\text{ion}}$ and $\rho_{\text{ion}} - \rho_{\text{ion}}$ in equation (4) can be neglected. The resulting electronic net charge density is shown in the lower panel of figure 7. The results of method II are summarized in table 1.

To verify method II, we employed one more technique to extract the net charge density transferred across the interface. In method III we have subtracted the electronic densities of the appropriate number of single graphene planes from the electronic density of the graphene side of the interface. In this case, $\rho_{\text{ion}}$ and $\rho_{\text{ion}}$ in equation (4) are the ionic and electronic charge densities of a free-standing single graphene plane, repeated the necessary number of times depending on the number of graphene planes in the SiC/BL/FLG structure. Although this method does not take account of the electronic charge located in the inter-planar regions of graphene in the stack, it intrinsically accounts for the inter-planar graphene separation. The total charge alignments obtained with method III (not shown) are very similar to the alignments obtained with method II, shown in the upper panel of figure 7. The electronic charge densities are better aligned, implying that in this case

| Table 1. Calculated and measured WF's, measured core-level binding energies, calculated interface dipoles, calculated charge transferred from SiC to FLG, and calculated charge spill-out. The calculations used methods II and III (in parenthesis) described in the text. |
|---|---|---|---|---|---|---|
| WF(s) (eV), calculated | 3.60 | 3.65 | 4.31 | 4.55 | 4.75 | 4.76 |
| WF(s) (eV), measured | — | — | 4.28 ± 0.03 | 4.34 ± 0.03 | 4.39 ± 0.03 | — |
| C 1s BE (eV) | 283.7 | 284.57 ± 0.05 | 284.48 ± 0.05 | 284.40 ± 0.05 | 1.64 (48.41) | 1.64 (114.22) |
| Charge transferred (e Å⁻²) | 0.0026 (0.011) | 0.0029 (0.010) | 0.0030 (0.008) | 0.0030 (0.007) |
| Charge spill-out (%) | — | — | 16.1 | 10.3 | 9.7 | 8.4 |

J. Phys. D: Appl. Phys. 47 (2014) 295303
O Renault et al
Figure 7. (a) SiC/BL/1LG; (b) SiC/BL/4LG. Top panel: electronic charge density alignment (black: SiC/BL/graphene; blue dotted: SiC/BL slab) using different methods (see text): red thin: graphene slab (method I); green dotted–dashed: distorted graphene slab (method II). Bottom panel: net electronic charge densities obtained from the subtraction between the SiC/BL/graphene and the SiC/BL slab and the distorted graphene slab densities.

$\rho_{\text{FLG}} - \rho_{\text{FLG}}^{\text{ion}}$ in equation (4) is smaller than in method I, but not as small as in method II, since the deformation of the FLG is not accounted for. The resulting interface dipole, which is considerably higher than that obtained using method II, as well as the transferred charge and spill-out charge, are shown in parentheses in table 1.

The results obtained with methods II and III follow the same trends. Table 1 shows the dipole per unit area, obtained from equation (2) with the lower and upper integration limits replaced by the middle of the SiC slab, and the vacuum region beyond the last graphene plane, respectively. The dipole increases with the number of graphene layers for the cases SiC/BL/1LG up to SiC/BL/4LG. To simplify the following discussion, we only show the results obtained with method II which seems more reliable based on the values obtained for the interface dipole.

The interface dipole variation supports the hypothesis that the WF dependence on the number of graphene planes is due to electrostatics only, i.e. interface charge transfer to an increasing number of graphene layers. However, it does not explain the simultaneous near invariance of the measured C 1s core-level shift in SiC or the amplitude of the C 1s core-level shift in graphene with respect to the WF shift.

The interface dipole is the product of the charge transferred across the interface and the separation of the positive and negative charges. Table 1 shows that the calculated electronic charge transferred from SiC/BL to graphene is almost constant as the number of graphene layers increases. On the other hand, the spread of the charge transferred at the graphene side increases with the number of planes, as shown in the lower panel of figure 7. Therefore, the SiC/BL/graphene dipole only changes with the number of graphene layers because the more graphene planes there are, the larger is the separation between the charge centroids at each side of the interface, with no impact on the electronic states on the SiC/BL side of the interface. This explains why the C 1s level in SiC is unchanged.

However, due to the atomically-thin character of FLG, part of the transferred charge leaks into the vacuum, as shown in table 1. The fraction of the leaked charge originating from the transferred charge (i.e. excluding the leaked charge belonging to the topmost graphene plane) was calculated by subtracting the electronic charge of the graphene slab from that of the interface structure. The latter is obtained by integrating the net electronic charge density starting from the average $z$-coordinate of the topmost graphene plane to some distance a few angstroms away in the vacuum region. The convergence of the integration was checked by changing the endpoint of the integral in vacuum. As the number of graphene layers increases, the amount of leaked charge calculated with this method decreases from 16% of the transferred charge for SiC/BL/1LG to 8% for SiC/BL/4LG. In other words, thicker graphene slabs are able to contain more negative charge, shifting the C 1s core-level in graphene to a lower binding energy, as observed experimentally.

These results should be of interest in the perspective of more complex heterostructures, for example by epitaxial growth of a semiconductor on top of FLG to open and control gaps in the graphene. The layer-dependent charge spillage may therefore be as important a parameter as the WF shift, and the combination of the two may allow more complex band engineering.
5. Conclusion

We have used high-resolution energy-filtered XPEEM and \textit{ab initio} DFT calculations of a relaxed interface model to determine the work function of FLG on SiC(0001). Work function values obtained from theory and experiments are found to be in qualitative agreement with an increase of the work function with each additional graphene layer. Compared to isolated graphene, the work function is modulated by the charge transfer from interface states to graphene, creating an interface dipole moment. In the calculations, the charge transferred is independent of the number of graphene planes, and this is consistent with the constant C 1s-SiC core-level binding energy measured by XPEEM. A layer-dependent partial spill-out of the transferred charge is predicted theoretically, and explains the experimental C 1s-graphene core-level binding energy variations, with a layer-dependent shift not rigidly following the work function evolution.

Acknowledgments

The theoretical work was financially supported by the Nanosciences Foundation of Grenoble (France) in the frame of the Chairs of Excellence awarded to L.R.C.F. and A.M.P. and L.R.C.F. also thanks INCT/Namitec and CNPq (Brazil) for their financial support. The experimental part was performed at the Nanocharacterization Platform of MINATEC and supported by the GRAND project and the French National Research Agency (ANR) through the Recherche Technologique de Base (RTB) program. J.R. was funded by a CEA CFR grant and C.M. was funded by the CEA Nanosciences project k-PEEM. The authors thank the referees for their invaluable suggestions.

Appendix

Band structure of the modelled SiC/FLG heterostructures.

Figure A1 shows the total density of states (DOS) projected on particular Si atoms of the SiC slab, and on C atoms of the BL. The well-defined SiC band gap in the inner part of the SiC slab (2.0 eV) taken on Si atom #4 in the figure is slightly smaller than its calculated bulk value (2.32 eV) due to the small thickness of the SiC slab employed, which allows surface and interface states to reach the central region of the slab. The projected density of states (PDOS) are similar for all C atoms in the BL, which are represented by only one line in the graph. The PDOS are also similar for the bonded Si interface atoms #1a and #1b, both represented by a single line in the graph. The PDOS associated with the lonely Si interface atom #2 differs from the ones taken at atoms #1a and #1b only by its higher DOS near the edges of the band gap. This is expected
since those edge states are associated with the dangling bond localized at the unpaired interface atom #2. The edge state near the SiC CBE is fully occupied and pins the Fermi level near the SiC CBE. Even though these interface states are quite close to the SiC band edges, conferring a metallic character to the interface as previously observed [44], they are rather localized with very little dispersion, indicating that the interface is a poorly conductive metal.

Figure A2 shows the band structure obtained from the DFT calculations for the SiC/BL system, SiC/BL/1LG and SiC/BL/2LG. The most important feature is the absence of cones at the K high symmetry point in the BZ for the BL, whereas the Dirac cones are present for both the 1LG and 2LG systems. The absence of cones shows that the BL does not have the electronic structure of an isolated 1LG, but behaves as a transition region between SiC and graphene [44]. Figure A2(b) also shows that the addition of graphene layers on SiC/BL does not change the characteristics of the interface state associated with the lonely Si atom. For SiC/BL/1LG the cone at K is recovered, with the Fermi level pinned 0.6 eV above the Dirac point, indicating electron transfer from SiC to graphene. The small band gap of 47 meV at K is induced by the interface, with no contribution from any residual distortion or by the stress imposed on graphene by the interface model. For BL+2LG the two π and π* bands typically associated with two graphene planes can be easily identified, showing a small band gap of 0.2 eV. The cones indicate that all of the graphene planes separated from SiC by the BL are structurally intact. A crucial point, however, is that the destruction of the Dirac cones in the BL does not result from its deformation, but instead it is induced by the SiC surface states. The distinction between the impact of geometrical deformation and surface states on the BL was achieved by calculating the band structure of the deformed BL in the absence of the SiC slab. The result is shown in the inset of figure A2(a), where the Dirac cone appears at K, as in the unbackgulated graphene.

References

1. Novoselov K S, Fal’ko V I, Colombo L, Gellert P R, Schwab M G and Kim K 2012 Nature 490 192
2. Luxmi P J, Srivastava N, Feenstra R M and Fisher P J 2010 J. Vac. Sci. Technol. B: Microelectron. Nanometer Struct.—Process., Meas., Phenom. 28 C5C1
3. Seyller T et al 2008 Phys. Status Solidi b 245 1436
4. Emtsev K 2009 Nature Mater. 8 203
5. de Heer W A 2012 Phys. Scr. 2012 014004
6. Wittenberg J and Bocquet M L 2009 Surf. Sci. 603 1841
7. Vo-Van C, Kimouche A, Reserbat-Plantey A, Fruchart O, Bayle-Guillaume P, Bendahb N and Coraux J 2011 Appl. Phys. Lett. 98 181903
8. Sprinkle M et al 2009 Phys. Rev. Lett. 103 226803
9. Varchon F et al 2007 Phys. Rev. Lett. 99 126805
10. Riedl C, Coletti C and Starke U 2010 J. Phys. D: Appl. Phys. 43 374009
11. Bokdam M, Khomyakov P A, Brocks G and Kelly P J 2013 Phys. Rev. B 87 075414
12. Mathieu C, Barrett N, Rault J, Mi Y Y, Zhang B, de Heer W A, Berger C, Conrad E H and Renault O 2011 Phys. Rev. B 83 235436
13. Giovannetti G, Khomyakov P A, Brocks G, Karpan V M, van den Brink J and Kelly P J 2008 Phys. Rev. Lett. 101 026803
14. Hishio H, Kageshima H, Kotsugi M, Maeda F, Guo F Z and Watanabe Y 2009 Phys. Rev. B 79 125437
15. Ohta T, Bostwick A, McChesney J L, Seyller T, Horn K and Rotenberg E 2007 Phys. Rev. Lett. 98 206802
16. Ziegler D et al 2011 Phys. Rev. B 83 235434
17. Datta S S, Strachan R D, Mele E J and Johnson A T C 2008 Nano Lett. 9 7
18. Burnett T, Yakimova R and Kazakov O 2011 Nano Lett. 11 2324
19. Fillerter T, Emtsev K V, Seyller T and Bennewitz R 2008 Appl. Phys. Lett. 93 133117
20. Murata Y, Starodub E, Kappes B B, Ciobanu C V, Bartelt N C, McCarty K F and Kodambaka S 2010 Appl. Phys. Lett. 97 143114
21. Murata Y, Nie S, Ebenonnasir A, Starodub E, Kappes B B, McCarty K F, Ciobanu C V and Kodambaka S 2012 Phys. Rev. B 85 205443
22. Escher M, Winkler K, Renault O and Barrett N 2010 J. Electron Spectrosc. Relat. Phenom. 178–179 303
23. Bailly A et al 2008 Nano Lett. 8 3709
24. Renault O, Brochier R, Roule A, Haunmesser P H, Krömer B and Funnemann D 2006 Surf. Interface Anal. 38 375
25. Emtsev K V, Spec F, Seyller T, Ley L and Riley J D 2008 Phys. Rev. B 77 155303
26. Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
27. Gong Z et al 2009 Comput. Phys. Commun. 180 2582
28. Gonze Z, Rignanese G M and Caracas R 2005 Z. Kristall. 220 458
29. Fuchs M and Scheffler M 1999 Comput. Phys. Commun. 119 67
30. Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
31. Verstraete M J et al 2004 Phys. Rev. B 70 205427
32. Humphreys R G, Bimberg D and Choyke W J 1981 Solid State Commun. 39 163
33. Hybertsen M S and Louie S G 1984 Phys. Rev. B 30 5777
34. Pankratov O, Hensel S, Götzfried P and Bockstedte M 2012 Phys. Rev. B 86 155432
35. Hibino H, Kageshima H, Maeda F, Nagase M, Kobayashi Y and Yamaguchi H 2008 Phys. Rev. B 77 075413
36. Feenstra R M, Srivastava N, Gao Q, Widom M, Diaconescu B, Ohta T, Kellogg G L, Robinson J T and Vlassiouk I V 2013 Phys. Rev. B 87 014406
37. Tanuma S, Powell C J and Penn D R 2011 Surf. Interface Anal. 43 689
38. Mattausch A and Pankratov O 2008 Phys. Status Solidi b 245 1425
39. Weng X, Robinson J A, Trumbull K, Cavalero R, Fanton M A and McCarty K F 2012 Phys. Rev. B 85 205402
40. Willis R F, Feuerbacher B and Fittou B 1971 Phys. Rev. B 4 2441
41. Reihl B, Gimzewski J K, Nicholls J M and Tosatti E 1986 Phys. Rev. B 33 5770
42. Claessen R, Carsten H and Skibowski M 1988 Phys. Rev. B 38 12582
43. Mattausch A and Pankratov O 2007 Phys. Rev. Lett. 99 076802