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Origin of the high p -doping in F intercalated graphene on SiC

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The atomic and electronic structures of F intercalated epitaxial graphene on a SiC(0001) substrate are studied by first-principles calculations. A three-step fluorination process is proposed. First, F atoms are intercalated between the graphene and the SiC, which restores the Dirac point in the band structure. Second, saturation of the topmost Si dangling bonds introduces p -doping up to 0.37 eV. Third, F atoms bond covalently to the graphene to enhance the p -doping. Our model explains the highly p -doped state of graphene on SiC after fluorination [A. L. Walter *et al.*, Appl. Phys. Lett. **98**, 184102 (2011)]. © 2011 American Institute of Physics. [doi:10.1063/1.3623484]

Graphene is a two dimensional layer of C atoms with hexagonal crystal symmetry.¹ Great interests in this system arises from potential coherent nanoscale electronics applications. Epitaxial graphene on a SiC(0001) substrate is a leading contender in the race to graphene mass production, particularly for electronics.^{2,3} However, for applications, the ability to have both n - and p -doping is required. While n -doping is observed in graphene on Si-terminated SiC (−0.42 eV), only marginal p -doping has been achieved by H (0.10 eV) and Au intercalation (0.2 eV).^{4,5} Recently, a new technique has been introduced for producing highly p -doped graphene on SiC by F intercalation, with a shift of the Fermi level below the Dirac point by ~ 0.79 eV.⁶ The origin of the high p -doping, however, has not been clarified so far.

In this work, the atomic and electronic structures of F intercalated graphene on a SiC(0001) substrate are extensively studied by first-principles calculations. The saturation of the topmost dangling bonds of the Si atoms by the F atoms can only introduce p -doping with a shift of the Fermi level below the Dirac point by 0.37 eV. We observe that the additional p -doping is due to additional F atoms which are chemically absorbed on the graphene. However, such an absorption will split the Dirac point due to lattice distortion and symmetry breaking.

Our calculations employ density functional theory and the generalized gradient approximation of the exchange correlation functional with ultrasoft pseudopotentials⁷ as implemented in the Quantum-ESPRESSO package.⁸ This code already has been used successfully for describing graphene and related systems.^{9,10} A high cut-off energy of 800 eV as well as a precise k -point sampling with an $8 \times 8 \times 1$ mesh are employed to achieve high accuracy in the calculations. Structural optimization is carried out for all systems until the residual forces are converged to 0.003 eV/Å. The SiC(0001) substrate is described by a slab of four SiC bilayers with H-saturated bonds on the second slab surface. In order to avoid any drawback of the periodic boundary conditions, a vacuum layer of more than 10 Å thickness is included. This layer is sufficient to avoid an artificial dipole.¹¹

A $\sqrt{3} \times \sqrt{3} R30^\circ$ SiC substrate cell is used to accommodate a 2×2 supercell of epitaxial graphene, as shown in Fig. 1(a). This is a very good approximation of the experimental $6\sqrt{3} \times 6\sqrt{3} R30^\circ$ reconstruction. The 2×2 supercell experiences $\sim 8\%$ tensile strain to match the $\sqrt{3} \times \sqrt{3} R30^\circ$ SiC substrate cell. It has been demonstrated that this mismatch will change the Dirac point by less than 0.02 eV and, therefore, can be ignored.¹² The accuracy of the approximation for the electronic properties has been shown in Refs. 11–13. Note that also a $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction has been found in experiments.¹⁴ In the following, the amount of F intercalation is measured by the number of F atoms relative to the eight C atoms in a 2×2 graphene supercell. Thus, one F atom within a $\sqrt{3} \times \sqrt{3} R30^\circ$ SiC cell equals a F coverage of 1/8. Since there are three topmost Si atoms (each with one dangling bond) within the $\sqrt{3} \times \sqrt{3} R30^\circ$ SiC cell, a F coverage of 3/8 saturates all dangling bonds.

Graphene is commonly grown on SiC(0001) substrates by thermal graphitization in ultrahigh vacuum with an annealing temperature of about 1000 °C. Growing the first graphene monolayer takes some 5 min.^{5,15} Figure 1(a) gives a top view of the optimized structure of graphene on SiC.

FIG. 1. (Color online) (a) Top and (b) side views of the optimized atomic structure of graphene on a SiC(0001) substrate, showing only the graphene sheet and the topmost Si atoms. Dashed lines indicate the $\sqrt{3} \times \sqrt{3} R30^\circ$ SiC cell. Side views of the atomic structure for (c) a F atom bonded to a topmost Si atom and (d) a F atom on top of the graphene. Subfigures (e) and (f) refer to intercalation of two and three F atoms, while in (g) and (h) an additional F atom is bonded to the graphene.

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FIG. 2. Electronic band structures of graphene on SiC: (a) without F intercalation and with F coverages of (b) 1/8, (c) 1/4, and (d) 3/8.

Only the graphene sheet and the topmost Si atoms are shown. The dashed lines indicate the $\sqrt{3} \times \sqrt{3} R30^\circ$ SiC cell. Two C atoms are located next to two Si atoms and move toward them to form a covalent bond of about 2.01 Å length. The six other C atoms are centered around the third Si atom. Hence, there is a buckling in the graphene sheet. This is demonstrated in Fig. 1(b), which shows a side view of the supercell. In Fig. 2(a), we address the electronic band structures obtained for graphene on SiC without F intercalation. The band structure shows a large energy gap between -1.8 eV and -0.3 eV. The Fermi level is pinned by a state with small dispersion, which is related to the dangling bonds of the topmost Si atoms. Thus, the first graphene layer on SiC should be viewed as a buffer layer.

One conventional route to restore the electronic structure of free graphene is to generate further graphene layers by annealing the sample. However, these layers will be *n*-doped. Two newly developed methods, H (Ref. 4) and Au (Ref. 5) intercalation, restore the original shape of the electronic bands but introduce *p*-doping, which, however, is rather weak: 0.10 eV for H and 0.20 eV for Au intercalation. The restoration of the Dirac point and the *p*-doping are attributed to the fact that the H/Au atoms saturate the topmost dangling bonds of the SiC(0001) substrate and enable charge transfer from the graphene to the intercalated atoms.

To check whether F atoms tend to saturate the dangling Si bonds or chemically absorb on the graphene, we calculate the formation energies of these two cases. The corresponding structures are shown Figs. 1(c) and 1(d). The formation energy of F intercalated into the graphene-SiC system is given by

$$E_f = E_0 + n\mu - E_i, \quad (1)$$

where E_0 and E_i are the total energies without and with intercalation, respectively. In addition, n represents the number

of F atoms in the unit cell and μ is the chemical potential of F. We find that E_f is 0.75 eV higher for the configuration of Fig. 1(c) than for the configuration of Fig. 1(d). Therefore, we confirm previous experimental results that the F atoms do not form covalent bonds with the graphene but rather saturate the dangling Si bonds of the SiC(0001) substrate.⁶

Side views of the structures of F intercalated graphene on SiC at coverages of 1/4 and 3/8 are shown in Figs. 1(e) and 1(f), respectively. For F coverages of 1/8, 1/4, and 3/8, we find a distance of 3.51 Å between the graphene and the F layers. As the graphene sheet hardly buckles, we can conclude that it is weakly bonded by van-der-Waals forces.¹⁶

Electronic band structures for F coverages of 1/8, 1/4, and 3/8 are depicted in Figs. 2(b)–2(d), respectively. The dispersion of free standing graphene is restored. For a F coverage of 1/8, the Dirac point is located at the Fermi level, i.e., the graphene is not doped. However, for F coverages of 1/4

FIG. 3. (Color online) (a) Single F atom bonded to graphene. (b) Brillouin zones of pristine graphene (dashed) and of a 3×3 supercell (full lines). (c) Band structure for a coverage of 5.6%.

FIG. 4. (Color online) Electronic band structure of fluorinated graphene on SiC at a F coverage of 1/2, corresponding to Fig. 1(h). The dashed lines give an estimation of the Dirac point.

and 3/8 ML, p -doping is indicated by a shift of the Fermi level below the Dirac point by 0.32 eV and 0.37 eV, respectively. Therefore, the first step of the F intercalation is the restoration of the Dirac point. The second step is the introduction of p -doping. However, by fully saturating the dangling bonds of the topmost Si atoms of the SiC(0001) substrate, the calculated doping level of 0.37 eV is only about half of the experimentally reported value of 0.79 eV for a 60% fluorinated sample.⁶

Experiments indicate that graphene films can be fluorinated on one or on both sides.^{17–20} Graphene fluorinated by XeF₂ gas with a F coverage of 25% becomes transparent with a band gap of about 2.93 eV.¹⁸ In the presence of Mo, the XeF₂ gas reacts, and MoF₆ gas is produced at high pressure.⁶ However, we cannot exclude the possibility that F bonds to the graphene layer in the presence of MoF₆ gas. We, therefore, have calculated the band structure of graphene fluorinated with a F coverage of 1/18 = 5.6%. Figure 3(a) shows the relaxed atomic structure of a 3 × 3 graphene supercell with one F atom attached. Due to the Brillouin zone folding, as shown in Fig. 3(b), the Dirac point is located at the Γ point, see Fig. 3(c). Moreover, the Fermi level shifts 0.5 eV below the Dirac point, which splits to give rise to a small band gap of 0.1 eV. We, therefore, find that graphene becomes p -doped under fluorination with low F coverage, whereas there is no Dirac point and a large band gap of 2.93 eV for high F coverage (~25%).

Our results indicate that there is a third fluorination step in which F atoms bond to the graphene. We consider two more structures with a fourth F atom included, which is either attached below, Fig. 1(g), or above, Fig. 1(h), the graphene sheet. The F coverage in both cases is 1/2. We find that the formation energy of the second configuration is 0.11 eV higher than that of the first configuration. Consequently, it is energetically favorable if the fourth F atom bonds on top of the graphene. The electronic band structure for this case is shown in Fig. 4. The Dirac point splits and a band gap of

0.31 eV opens. We estimate that this behavior corresponds to a shift of the Fermi level below the Dirac point by 0.58 eV. Therefore, the third step enhances the p -doping. However, the Dirac point is not maintained and a band gap is opened due to the lattice distortion and symmetry breaking. Apparently, the band gap will greatly influence the carrier mobility in the graphene.

In conclusion, we have analyzed the process and consequences of fluorination of an epitaxial graphene buffer layer on a SiC(0001) substrate. We propose a three-step fluorination process. In the first step, F atoms intercalate between the graphene and the SiC and restore the Dirac point in the band structure. In the second step, saturation of the topmost Si dangling bonds introduces p -doping up to 0.37 eV. In the third step, additional F atoms covalently bond to C atoms on the top side of the graphene sheet, which enhances the p -doping. The latter is the origin of the highly p -doped state observed for F intercalated graphene on SiC.

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