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Highly *p*-doped epitaxial graphene obtained by fluorine intercalation

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We present a method for decoupling epitaxial graphene grown on SiC(0001) by intercalation of a layer of fluorine at the interface. The fluorine atoms do not enter into a covalent bond with graphene but rather saturate the substrate Si bonds. This configuration of the fluorine atoms induces a remarkably large hole density of $p \approx 4.5 \times 10^{13} \text{ cm}^{-2}$, equivalent to the location of the Fermi level at 0.79 eV above the Dirac point E_D . © 2011 American Institute of Physics.

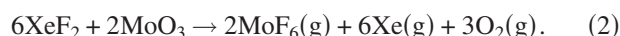
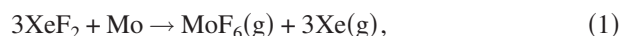
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Many applications of graphene, the single layer of hexagonally coordinated carbon atoms have been proposed since the discovery of its unusual electronic properties.¹ For these applications to be realized, the ability to achieve *n*- and *p*-type doping is required. While *n*-type doping is observed in graphene grown epitaxially on SiC,^{2,3} only marginal *p*-type doping has been achieved by hydrogen⁴⁻⁷ and Au (Ref. 8) intercalation or the adsorption of fluorine-containing molecules such as F4-TCNQ.⁹ Here we present a technique for producing highly *p*-doped graphene on SiC via fluorine intercalation. In contrast to the previous work on fluorinated graphene, (theoretical¹⁰ and experimental¹¹⁻¹⁴), where the fluorine is bound to the graphene transforming it into an insulator, here the graphene retains the linear Dirac dispersion that leads to many of its unusual properties.

Previously, hydrogen,⁴⁻⁷ and gold⁸ have been shown to intercalate between layers of graphene and SiC(0001) produced by thermal decomposition. In both cases a slight *p*-doping of the graphene is observed, $p \approx 6 \times 10^{12} \text{ cm}^{-2}$ and $p \approx 7 \times 10^{11} \text{ cm}^{-2}$, respectively. Surface treatment with strongly oxidizing molecules such as NO₂ has yielded a large net *p*-doping change around $2 \times 10^{13} \text{ cm}^{-2}$,¹⁵ but these molecules are not thermally stable, and it is not clear how to protect the molecules from exposure to ambient conditions. In the present study we have used core level x-ray photoemission spectroscopy (XPS) and angle resolved photoelectron spectroscopy (ARPES) to investigate the interaction of fluorine atoms with the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ/\text{SiC}$ structure and to quantify the amount of *p* doping. Properly treated, graphene becomes doped to an extremely high level ($p \approx 4.5 \times 10^{13} \text{ cm}^{-2}$) and is stable in air and at high temperatures.

Experiments were performed on $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ carbon “buffer layer” on a silicon terminated SiC(0001) surface, prepared by the method of Ostler *et al.*¹⁶ The carbon buffer layer is a covalently bond, electrically inactive graphene

layer¹⁷ in which about one third of the C atoms bind to the Si atoms on the SiC(0001) substrate. This bonding breaks up the π band network so that the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ layer (henceforth *buffer layer*) has no Dirac cone. Hydrogen and gold have been shown to intercalate underneath the buffer layer, breaking the carbon bonds to the substrate and thus decoupling it from the SiC and transforming it into graphene.⁴⁻⁷ Samples were fluorinated following a similar method to McFeely *et al.*¹⁸ whereby buffer layer samples are placed in a reaction chamber with a XeF₂ crystal and heated to 200 °C for 2 h, leading to the dissociation of the XeF₂ and the liberation of reactive fluorine atoms. This method has previously been used to study the interaction between fluorine and silicon surfaces¹⁸ as well as fluorine and graphene¹¹⁻¹⁴ and normally leads to the formation of C–F bonds with the graphene layer. If a sacrificial piece of molybdenum is included in the reaction chamber, an entirely different reaction is promoted, whereby the F atoms bond not to the buffer layer C atoms, but instead to the interfacial Si atoms, as discussed below. At high pressure, XeF₂ reacts with the molybdenum to produce MoF₆ through the well-known reactions (depending on whether the Mo is clean or oxidized),^{19,20}



Following the fluorination process, the samples are covered by a layer of Mo (oxidized by air exposure), which is readily removed by sonication in ethanol. The presence of this Mo residue indicates that it is the gaseous MoF₆, not XeF₂, that interacts with the graphene. Samples were transported through air to the electronic structure factory endstation at beamline 7 of the Advanced Light Source, Lawrence Berkeley National Laboratory and annealed to $\sim 600^\circ\text{C}$ in vacuum to clean the surface for ARPES and core level measurements.

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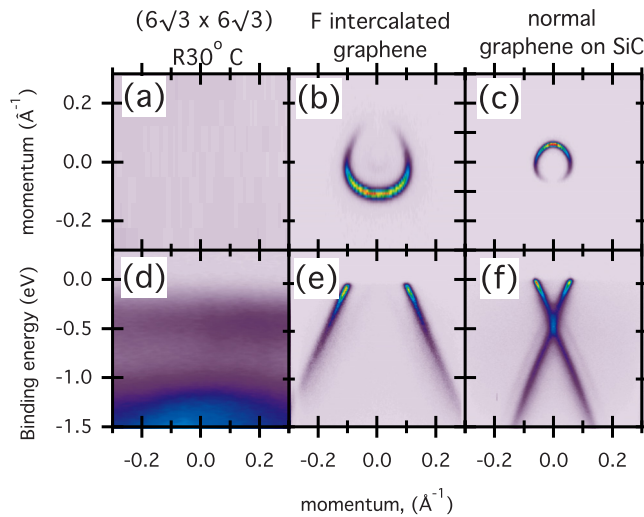


FIG. 1. (Color online) Experimental constant energy cut at the Fermi energy (a, b, and c) and valence band map (d, e, and f) from (a and d) buffer layer, (b and e) graphene prepared by interaction of fluorine with the buffer layer, and (c and f) graphene on buffer layer. The *p*-doped character of the fluorine intercalated sample is evident.

The Fermi surfaces and band structures of three samples are presented in Figs. 1(a) and 1(d), a buffer-layer sample ($6\sqrt{3} \times 6\sqrt{3}$)R30°/SiC without fluorination; Figs. 1(b) and 1(e), the same buffer-layer sample later treated with fluorine; and for comparison, Figs. 1(c) and 1(f), a graphene sample grown conventionally, consisting of an active graphene layer on top of the inactive buffer layer.¹⁷

As reported previously, the buffer layer sample is insulating,¹⁷ having no Fermi surface and having only a flat band appearing around 0.4 eV binding energy [see Figs. 1(a) and 1(d)]. After fluorination, the circular Fermi surface and linear bands of graphene appear. Projection of the linear bands indicate a Dirac crossing well above the Fermi level, as expected for *p*-type doping, and extrapolating the band to the region above the Fermi edge locates it 0.79 eV above E_F . The Fermi surface size can be used²¹ to quantitatively evaluate the hole density at ($p \approx 4.5 \times 10^{13} \text{ cm}^{-2}$), which is an order of magnitude larger than previously observed for H intercalated graphene ($p \approx 6 \times 10^{12} \text{ cm}^{-2}$). For comparison, the conventional Argon grown graphene on buffer layer on SiC samples¹⁶ are *n*-type with a much smaller charge density ($n \approx 1 \times 10^{13} \text{ cm}^{-2}$) and Fermi surface [Figs. 1(c) and 1(f)]. These results suggest that the buffer layer is transformed by fluorination into a *p*-type graphene. The linewidth of the ARPES π bands at the Fermi level ($\sim 0.014 \text{ Å}^{-1}$), which directly gives the electron mean-free path from defect scattering, is comparable to that from the conventional graphene sample ($\sim 0.009 \text{ Å}^{-1}$) indicating a similar clean, defect-free graphene layer on the fluorine samples. We now discuss core-level photoemission measurements of samples (i) and (ii) which demonstrate that the fluorine intercalates under the buffer-layer/SiC interface. This is completely different from fluorographene/fluorographane materials recently discovered, which are wide band gap semiconductors owing to covalent C–F bond formation.^{13,14,22}

Core level photoemission spectra of the buffer layer before and after exposure to fluorine are presented in Fig. 2. After fluorine treatment, a clear F 1s peak is observed at 686.9 eV binding energy (not shown), confirming the pres-

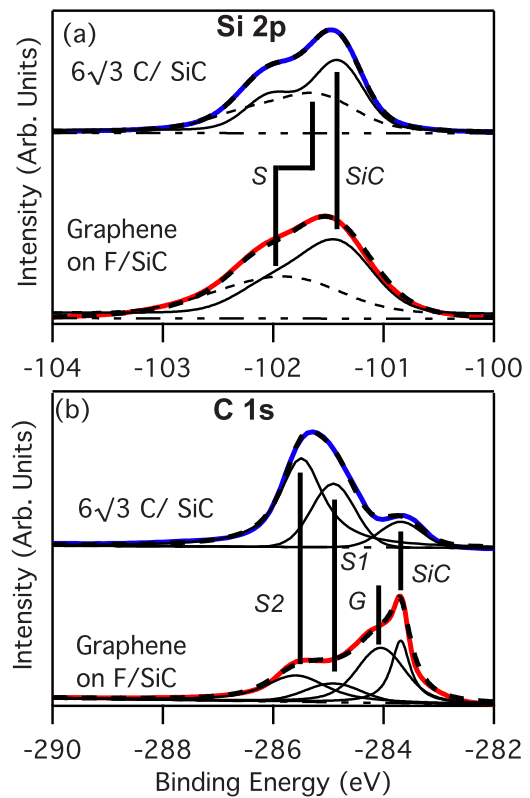


FIG. 2. (Color online) XPS data taken using 350 eV photons of the ($6\sqrt{3} \times 6\sqrt{3}$)R30° buffer layer before (upper panels) and after (lower panels) fluorination. In each case the thick solid (red and blue) lines represent the experimental data while the dashed and thin solid (black) line represent the fit. (a) Si 2*p* core levels are fitted to two spin-orbit-split doublet peaks, representing the bulk (SiC) and surface (S) contributions (Ref. 23). Fluorine bonding to interfacial Si is indicated by a shift in the surface doublet, S, of -0.18 eV after fluorination. (b) C 1*s* core levels before fluorination consist of a bulk (SiC) peak and two surface peaks (S_1, S_2) representing buffer layer C atoms bonded to the substrate (Ref. 17). After fluorination, the latter peaks are weakened, and a new graphene-derived peak (G) is observed. No C–F bonds are observed.

ence of fluorine. Except for a small residual oxygen peak only peaks relating to C, F, and Si are present in XPS scans up to a binding energy of 850 eV. The Si 2*p* peak features [Fig. 2(a)] are comparable to previous data from the buffer layer²⁴ and are fitted to two doublets representing the bulk (SiC) and surface, (S) contributions to the spectrum. The doublets consist of two Lorentzian–Gaussian peaks with identical line widths separated by -0.605 eV and with an amplitude ratio of 2:1. In all cases the Lorentzian width is 0.08 eV while both the bulk (0.5 to 0.7) and surface (0.75 to 1) Gaussian widths increase after fluorination. The increase in the Gaussian width is an indication of inhomogeneity of the sample interface. The position of the bulk doublet is unchanged (-101.42) upon exposure to fluorine, while the surface doublet, S, shifts from -101.6 to -101.78 eV , showing that the fluorine interacts with, or is near to, the substrate silicon atoms. This splitting is similar to, but larger than, the Si 2*p* splitting observed in H-intercalated graphene.⁴ The observed chemical shift is much smaller than observed for SiF species,¹⁸ indicating a relatively weak charge transfer from the Si atoms.

That the fluorine atoms do not covalently bond with the graphene but rather intercalate to the C–SiC interface is also evident from C 1*s* core level spectra shown in Fig. 2(b). The

top spectrum is from the buffer layer before fluorination and exhibits two peaks (S_1, S_2), which arise from the bonding of the carbon atoms in the buffer layer to the SiC substrate, at ~ -285.55 and -284.75 eV,¹⁷ and a peak at ~ -283.7 eV due to the bulk SiC. Upon exposure to fluorine, buffer layer peaks S_1, S_2 are largely suppressed, and a new peak (G) at ~ -284.05 eV appears, attributed to the formation of the graphene layer. Its separation to the carbon peak from the SiC bulk is much smaller than for graphene on buffer/SiC samples (~ -284.74 eV),¹⁷ which is related to the fact that the graphene is strongly doped. The C $1s$ spectrum in Fig. 2(b) (lower) also shows none of the C–F peaks of perfluorographene¹² or any peaks in the range 285 to 290 eV expected for C–F bonding,^{12,25} for that matter. This provides strong evidence that the fluorine does not bond covalently to the graphene layer. The buffer layer peaks are still present after fluorination, indicating that only partial fluorination of the sample has occurred. Thus the buffer layer is transformed into a single layer of graphene by intercalation, similar to the effect of hydrogen observed in quasifreestanding samples.^{4,5} Similar results (not shown) on thicker initial films have shown that the fluorine interacts with monolayers and bilayers of graphene on buffer layer/SiC, to produce highly p -doped bilayer and trilayer graphene, respectively, by converting their buried buffer layers to graphene. Although a detailed interpretation of the binding energy shifts reported above is difficult without considering local field effects, a qualitative picture emerges of an interfacial fluorine layer, chemically bound to Si atoms, which is fully ionic owing to charge transfer from both the Si and from the graphene C atoms. Comparison of the peak areas of the F $1s$ and the C $1s$ graphene peak [peak G in Fig. 2(b)], and applying the correct photoemission cross-section ratio,²⁶ gives (Graphene C)/F atomic ratio of ~ 4.6 . As we have shown that the F bonds to the surface Si not the graphene C then the important ratio is $\text{Si}_{\text{surface}}/\text{F}$ atomic ratio (~ 1.7), implying a 60% fluorination of the sample.

In summary, using core and valence band photoemission we demonstrate that fluorine interaction with the carbon buffer layer on SiC leads to the formation of a strongly p -doped graphene layer that is decoupled from the substrate through intercalation, shifting the Dirac crossing point to 0.79 eV above the Fermi energy. This is the strongest p -type doping ever observed in graphene, and the fact that the intercalated structure is stable against ambient conditions suggests its use in applications. Moreover, the doping process may be patterned, which could lead to laterally structured n – p – n devices.

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