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Fluorination of graphene has emerged as an attractive approach toward manipulating its physical, chemical, and electronic properties. To this end, we have demonstrated the viability of sulfur hexafluoride plasmas to fluorinate graphene as a safer alternative to the commonly reported techniques of fluorination that include exposures to fluorine and xenon difluoride gas. Incorporation of fluorine moieties on graphene after SF_6 plasma-treatment was confirmed by x-ray photoelectron spectroscopy. Modifications in the valence band states of graphene after plasma-treatment were characterized by ultraviolet photoelectron spectroscopy. Increase in work function of plasma-treated graphene demonstrates the ability of plasma-assisted fluorination to modify the electron emission characteristics of graphene. Raman spectroscopy reveals that the majority of carbon atoms in graphene retain their sp^2 hybridization after the plasma-treatment. © 2012 American Vacuum Society. [http://dx.doi.org/10.1116/1.3688760]

I. INTRODUCTION

Graphene is considered a possible successor to silicon for post-CMOS electronics. Thus the ability to engineer its properties is critical to the realization of graphene-based electronics. Toward this end, chemical functionalization of graphene has emerged as an attractive method to manipulate its physical, chemical, and electronic properties. Typical applications of chemical functionalization include band gap opening via functionalization with oxygen,[1–3] hydrogen,[4] and fluorine[5,6] and the production of graphene sheets by reduction of graphite oxide.[7–15] Recently, fluorinated graphene has garnered significant attention as a wide band gap semiconductor and a high-quality insulator.[16] Fluorination of graphene therefore offers the ability to tune its electronic properties. Derivation of graphene sheets from graphite fluoride has also been demonstrated.[17] Since fluorination of graphene increases its hydrophobicity[18,19] biomedical applications of graphene could be enabled.

Graphite fluoride was first synthesized in 1934 by exposing graphite to molecular fluorine;[20] extensive literature on the fluorination of other graphitic structures such as buckyballs[21] and carbon nanotubes[22–24] is available. The techniques currently used to produce fluorinated graphene include exposure to fluorine gas at high temperature[5,25] (400–600 °C) and to xenon difluoride (XeF_2) at room temperature.[6,25,26] However, fluorine gas is toxic and corrosive, and XeF_2 hydrolyzes readily to form HF when exposed to air.

Plasma-assisted fluorination using benign sources of fluorine such as sulfur hexafluoride (SF_6) can provide a safer and convenient alternative to F_2 and XeF_2 sources. Moreover, plasma etching using SF_6 is employed extensively in the fabrication of integrated circuits. Fluorination of graphene using SF_6 plasmas has been demonstrated. In particular, electron beam generated plasmas have been successfully used to fluorinate single-layer graphene film grown on copper and then transferred to Si/SiO_2 substrate.[27] The fluorinated graphene film was subsequently characterized using x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, but the effect of fluorination on the electronic properties was not reported. Moreover, electron-beam technology requires high vacuum

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conditions, which can ultimately limit the industrial application of this method. Most recently, Yang, *et al.* reported Raman studies characterizing the results of SF_6 plasma treatment of few-layer (1–3) graphene flakes, which were exfoliated from bulk graphite, in a reactive ion etch (RIE) reactor.[28] However, their work does not provide a description of chemical bonding in the resultant material and thus direct evidence of fluorination. Furthermore, the effect of SF_6 plasma treatment on the electronic properties is not discussed.

The work discussed in this paper investigates the SF_6 RIE plasma fluorination of both multilayer (~20 layers) and single-layer graphene films, which were grown epitaxially on the carbon-face silicon carbide (SiC). Plasma fluorination of large-area epitaxial graphene films grown on SiC[29] offers a means of controlling electronic properties during device processing. In addition, the use of multilayer graphene allows a more fundamental study of the extent of fluorination as a function of relative rates of epitaxial graphene fluorination and etching. Plasma-treated graphene films have been characterized by Raman spectroscopy, x-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy (UPS). Raman spectroscopy is used to verify that the sp^2 configuration of carbon atoms in graphene is not destroyed by plasma treatment while XPS confirms the incorporation of fluorine atoms in the SF_6 plasma-treated samples, where fluorination is limited to one or two layers at the surface and the concentration of fluorine can be changed by simply varying the plasma treatment time. UPS characterization reveals the modification in the valence electronic states and work function of graphene after the SF_6 plasma-treatment, which may facilitate the application of graphene in optoelectronic devices. The thickness of graphene films grown on the carbon-face SiC can be controlled;[30] this unique growth characteristic has been exploited to fabricate a single or bilayer fluorinated graphene on top of both the insulating substrate (SiC) and a conductive graphene film of desired thickness. The ability to generate a fluorinated graphene/graphene interface offers an approach to the formation of layered structures with graded or structured electronic properties that can be employed for device fabrication.

II. EXPERIMENT

A. Material

Epitaxial graphene (EG) is grown on silicon carbide (SiC) via sublimation of silicon atoms by high-temperature (~1600 °C) annealing.[31] The samples used in this study were grown on the carbon-face of 4 H-SiC in an RF furnace. On carbon-face SiC, graphene film thickness can be controlled; in this work, fluorination of three multilayer (~20 layers) EG samples that were grown simultaneously and a single-layer EG sample were studied. Multilayer EG samples described in this manuscript were grown by Professor Walt A. de Heer's group who has established that these multilayer graphene layers do not grow as AB stacked layers in graphite; instead, these graphene layers contain a high density of rotational stacking faults which cause the adjacent layers to decouple electronically.[32]

B. Method

The samples were exposed to SF_6 plasma generated in an RIE (reactive ion etcher) system. This RIE system (Plasma-Therm RIE) operates at a radio-frequency (rf) of 13.56 MHz and has an electrode diameter of 11 in. An rf power of 50 W and an SF_6 partial pressure of 100 mTorr were used for all experiments. In order to minimize sputtering and structural damage to the surface of graphene, pure SF_6 gas was used; no other carrier gas was introduced into the system. All experiments have been carried out at room temperature.

C. Characterization

The samples were characterized by XPS/UPS (Axis Ultra[DLD], Kratos Analytical) to determine elemental composition, confirm the existence of fluorine-carbon bonds, measure the thickness of the films, and investigate the valence-band states. The fluorinated samples were depth-profiled by argon ion-bombardment (3 keV) in a different XPS system (Thermo Scientific K-Alpha). All XPS spectra were collected using monochromatized AlKα radiation (energy = 1486.6 eV) and UPS spectra were collected using He I radiation (energy = 21.2 eV).

Raman spectroscopy was used to investigate the change in graphitic structure of the EG after exposure to SF_6 plasmas. All Raman spectra presented in this paper were obtained with a confocal Raman microscope (JY Horiba LabRam HR800) using 532 nm laser excitation.

III. RESULTS AND DISCUSSION

The ability of SF_6 plasma treatment to control degree of fluorination and work function of EG film was investigated by exposing multilayer EG to SF_6 plasmas for 30, 60, and 90 s under identical plasma conditions. Single-layer EG was subsequently plasma-treated for 30 s to demonstrate that single-layer EG can be successfully fluorinated by SF_6 plasma-treatment.

A. Multilayer graphene

1. X-ray photoelectron spectroscopy

The presence of fluorine in samples exposed to SF_6 plasmas is confirmed by the appearance of an F 1s peak at ~688 eV in the XPS survey spectra of fluorinated samples as shown in Fig. 1. The fluorine-to-carbon (F/C) ratio obtained from XPS analysis, as seen in Fig. 2, does not increase monotonically with the treatment time. The F/C ratio after a 60 s plasma-treatment is higher than the F/C ratio after a 30 s plasma-treatment, but this ratio decreases when the treatment time increases from 60 to 90 s. The film thickness (see Fig. 3) calculated from the relative intensities of the graphene and SiC peaks in the C 1s spectra[33] shows that graphene etching during a 30 s plasma treatment is negligible while approximately one layer of graphene is etched during 60 and 90 s plasma treatments.

Depth of fluorination was determined by *in situ* ion-bombardment to slowly remove graphene layers. After 15 s of argon ion-bombardment, the C/Si ratio of single and
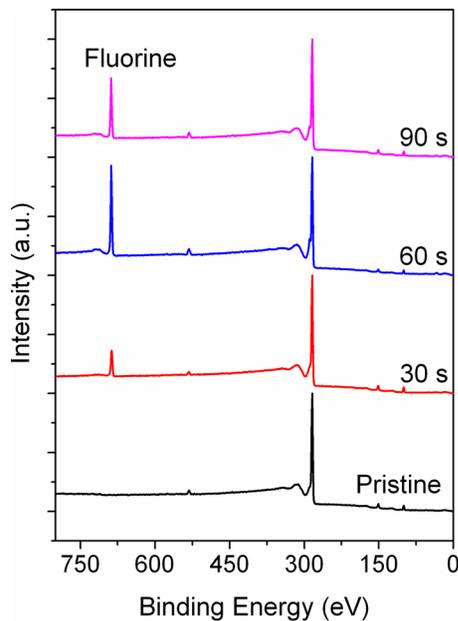
FIG. 1. (Color online) XPS survey spectra of SF$_6$ plasma-treated multilayer EG.

FIG. 3. Thickness of pristine and SF$_6$ plasma-treated multilayer EG.

three-layer thick EG films decreased from 1.9 to 1.0 and 3.0 to 1.9, respectively, thereby suggesting that one or two graphene layers were etched. In addition, the fluorine concentration is below XPS detectability in all plasma-treated samples after 15 s of ion-bombardment. These data indicate that graphene fluorination under the conditions used in this study is limited to one or two surface layers irrespective of the treatment time.

The observation that fluorine concentration does not increase monotonically with the exposure time and that fluorination is limited to only one or two surface layers suggests that plasma fluorination of graphene is governed by the relative rates of fluorination and etching. Since the etching of graphene is not reported during the fluorination of monolayer graphene in a nonplasma environment, the etching observed during the plasma fluorination can be attributed to ion-bombardment. The interplay between the fluorination
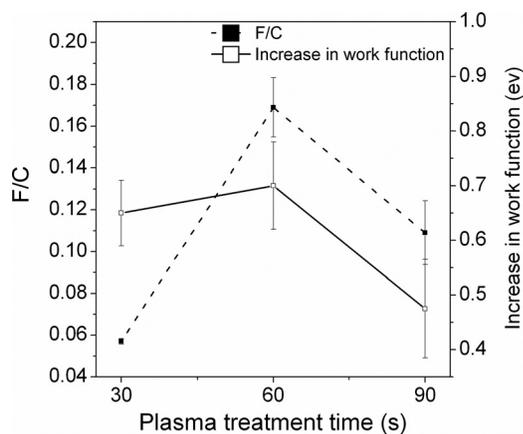
and etching observed in our work can be described as follows:

(1) During a 30 s plasma treatment, fluorination is dominant and etching is negligible.
(2) The observed increase in fluorine concentration between 30 and 60 s plasma treatment along with the removal of approximately one layer of graphene is indicative of simultaneous fluorination and etching. The increase in F/C ratio implies that the rate of fluorination is higher than the rate of etching.
(3) The F/C ratio decreases between 60 and 90 s of plasma treatment; this change in F/C ratio is smaller than the change in F/C ratio in the exposure interval from 30 to 60 s. This observation suggests that the rates of fluorination and etching are comparable.

For samples exposed to the SF$_6$ plasma for 30 s, a F 1s peak at $\sim$687.3 eV appears as shown in Fig. 4(a) which is characteristic of fluorine atoms bonded to carbon atoms in aromatic rings.[34] For samples exposed to SF$_6$ plasma for 60 and 90 s, the peaks in F 1s spectra [see Fig. 4(a)] are shifted by nearly 1 eV to 688.5 eV. A similar increase in the binding energy with an increase in degree of fluorination has also been reported in XPS studies of fluorobenzene.[35] The presence of carbon-fluorine bonds in 60 and 90 plasma-treated samples is corroborated by peaks at $\sim$289.5 eV, which is indicative of carbon-fluorine bond in aromatic rings,[35] in the corresponding C 1s spectra as seen in Fig. 4(b). Absence of a peak at a similar binding energy in the C 1s spectrum of 30 s SF$_6$ plasma-treated sample [see Fig. 4(b)], appears to contradict our earlier conclusion regarding the existence of fluorine-carbon bonds in the sample that was exposed to an SF$_6$ plasma for 30 s. However, this observation can be attributed to signal attenuation of the characteristic peak in C 1s spectra as a result of the lower F/C ratio as shown in Fig. 2.

C 1s spectra of both pristine and fluorinated EG are dominated by the peak at $\sim$284.5 eV, which is characteristic of graphitic carbon.[36] There is no shift in the position and width of this peak after plasma treatment, which indicates that the

FIG. 2. F/C ratio and increase in work function of SF$_6$ plasma-treated multilayer EG.

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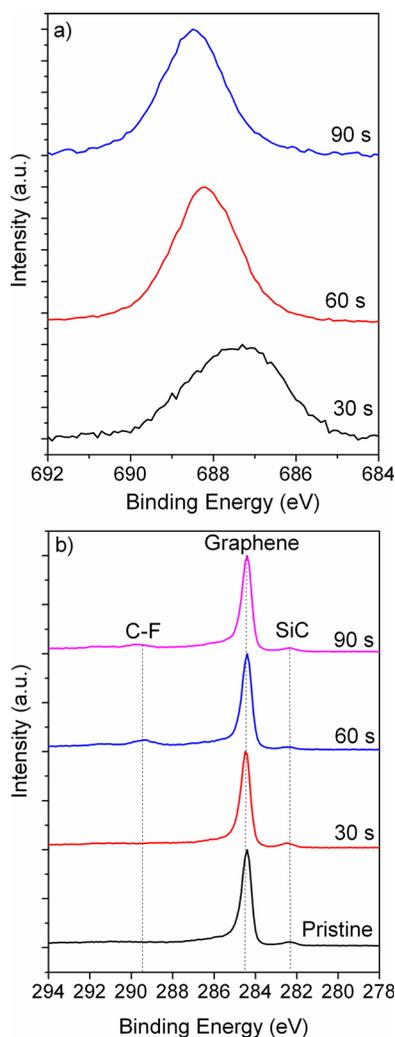
FIG. 4. (Color online) XPS F 1s (a) and XPS C 1s (b) spectra of SF$_6$ plasma-treated multilayer EG.

FIG. 5. (Color online) Raman spectra of SF$_6$ plasma-treated multilayer EG.

chemical environment of the graphitic carbon was not altered significantly in spite of the incorporation of fluorine moieties. The peak at ~ 282.3 eV is characteristic of carbidic carbon-carbon atoms bound to silicon atoms in the silicon carbide substrate.[36]

2. Raman spectroscopy

The Raman spectrum of graphene is dominated by the features of graphitic carbon, the G and D peaks at ~ 1580 and ~ 1350 cm^{-1}, respectively. The G peak, a bond-stretching vibration of a pair of sp^2-hybridized carbon atoms, is Raman active in both a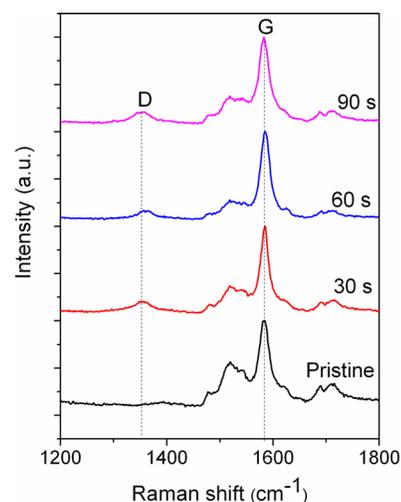romatic rings and olefinic chains.[37] The D peak is a breathing vibration of a 6-member aromatic ring. The D peak becomes Raman active only in polycrystalline graphite and its intensity is inversely proportional to the effective crystalline size.[37] Raman spectra of all EG samples before and after plasma-treatment, as shown in Fig. 5, consist of G peak around 1583 cm^{-1}. Retention of the G peak at ~ 1583 cm^{-1} in the Raman spectrum of fluorinated EG films as seen in Fig. 5 suggests that the sp^2-hybridized carbon skeleton of graphene remains intact after plasma exposure. The emergence of the D peak at ~ 1350 cm^{-1} is an indication of the polycrystallinity of fluorinated graphene. Ion-bombardment during plasma treatment most likely results in the formation of smaller graphite domains, which enhances the Raman activity of the D peak. In addition to the graphite phonon modes, several SiC characteristic bands at ~ 1480, 1520, 1620, 1688, and 1718 cm^{-1} appear in the Raman spectra of both plasma-treated and pristine EG. Other than the appearance of the D peak, no overall changes are observed in the Raman spectra after plasma treatment. The position and width of a single Lorentzian peak fitted around the G mode after the plasma treatment does not undergo significant changes as shown in Table I. In addition, there is no splitting of the G peak, which is an indication that bond alteration has not occurred. These observations suggest that little to no change in the energy of bond-stretching vibration of sp^2 sites after the plasma treatment takes place; such results imply that the chemical environment of the sp^2 graphene sites was not altered significantly by the plasma treatment. These Raman studies are consistent with our earlier conclusion from XPS characterization that the sp^2 hybridized carbon skeleton of graphene remains intact upon plasma fluorination.

TABLE I. Position and width of a single Lorentzian peak fitted around the G mode (see Fig. 5) of multi-layer EG films before and after plasma treatment.

Treatment time (s)	G peak position (cm^{-1})		G peak width (cm^{-1})	
	Before plasma treatment	After plasma treatment	Before plasma treatment	After plasma treatment
30	1583 ± 0.5	1584 ± 1.0	17 ± 2.5	17 ± 1.2
60	1583 ± 2.0	1585 ± 0.8	20 ± 1.7	16 ± 1.4
90	1584 ± 0.4	1583 ± 0.6	21 ± 4.0	19 ± 2.1

3. Ultra-violet photoelectron spectroscopy

The effect of SF_6 plasma treatments on the electronic properties of graphene was investigated using UPS. Figure 6 indicates that the UPS spectrum of EG before plasma treatment consists of peaks at ∼3.0 eV (labeled A) and ∼13.6 eV (labeled B) below the Fermi level (labeled E_F) which can be attributed to photoelectrons emitted from the 2p-π and the mixed 2s-2p hybridized states, respectively.[38] Retention of both peaks in the UPS spectra of plasma-treated samples suggests that the sp^2-hybridized carbon skeleton of graphene is preserved after the plasma treatment. A feature at ∼10 eV (labeled as C) appears in the UPS spectra of samples plasma-treated for 60 and 90 s, which can be attributed to the photoelectrons emitted from the fluorine 2p-like states.[38] Emergence of this peak after plasma-treatment confirms the existence of fluorine containing moieties while its absence in the sample that was plasma-treated for only 30 s can be explained by the lower fluorine concentration.

From UPS spectra, the work function of graphene can be estimated by subtracting the width of the photoelectron spectrum from the photon energy. The work function of multilayer EG prior to the SF_6 plasma-treatment is estimated to be 4.4 ± 0.05 eV. The decrease in the width of the photoelectron spectra after an SF_6 plasma-treatment (see Fig. 6) indicates that the work function has increased; this increase is quantified in Fig. 2. Since the work function is the energy difference between the Fermi and the vacuum level and no shift in the Fermi edge was observed, the increased work function can be attributed to the creation of a surface dipole by adsorption of the highly electronegative fluorine containing moieties. An electrical double layer with a negatively charged outer surface is generated, which produces a dipole field at the surface that opposes electron escape from the surface, thereby increasing the work function.[39]
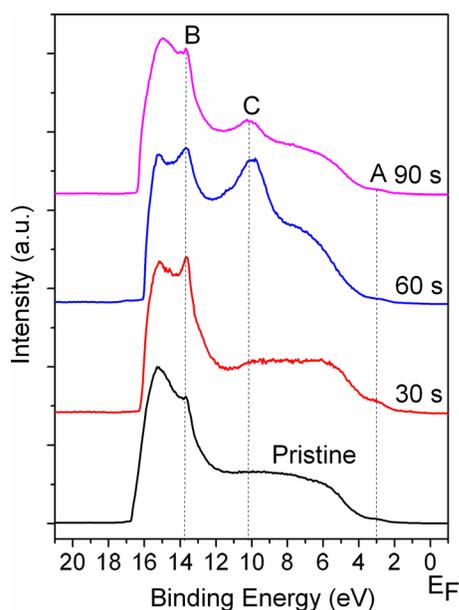
Plasma-treatment involves ion bombardment of sample surfaces; the surface defects created by the ion bombardment have been reported to induce changes in work functions.[39–42] Because a number of parameters (e.g., crystal orientation, measurement technique, ion-bombardment energy) affect work function measurements, these results do not establish a quantitative relationship between surface defects and the change in work function. Since the synergy between the effects of fluorine adsorption and the surface defects generated by ion bombardment governs the sign and magnitude of change in the work function, plasma-treatment time does not correlate directly with the increase in work function (see Fig. 2). The relationship between the change in work function of graphene and plasma treatment time can be elucidated by isolating the two effects, fluorine adsorption and surface defects, from each other and studying each effect separately; these studies are in progress. Nevertheless, the observed increase in work function after the plasma-treatment of EG indicates the utility of SF_6 plasma treatments for modification of the electron emission characteristics of graphene. Furthermore, retention of the characteristic features of graphene in the valence-band spectra corroborates our previous conclusions drawn from XPS and Raman studies that the sp^2 hybridized carbon skeleton of graphene survives the plasma-treatment.

B. Single-layer graphene

The experiments described above on multilayer EG demonstrated that graphene films can be fluorinated with negligible etching with a 30 s plasma treatment time. Therefore, a plasma treatment time of 30 s was used to demonstrate that single-layer EG films can be fluorinated by exposure to SF_6 plasmas. Preservation of the G peak in the Raman spectrum [Fig. 7(a)] of EG film after plasma treatment suggests that the graphene film is not etched and the sp^2-hybridized carbon skeleton survives the plasma treatment. Emergence of the D peak in the Raman spectrum [Fig. 7(a)] accounts for the polycrystallinity generated by ion bombardment. Fluorine content in the plasma-treated sample is ∼8%; the peak at ∼687 eV in the F 1s spectrum [Fig. 7(b)] and the peak at ∼288.5 eV in the C 1s spectrum [Fig. 7(c)] suggest the existence of carbon-fluorine bonds. From the UPS spectra [Fig. 7(d)], a 0.4 eV increase in work function after the plasma-treatment is estimated.

In addition to confirming the viability of SF_6 plasma to fluorinate single-layer EG film, results on this single-layer EG film also allows further insight into the experiments on multilayer EG films. From the XPS, UPS, and Raman studies of multilayer EG, we inferred that the sp^2 configuration of graphene remains intact after the plasma treatment and the fluorination is limited to one or two surface layers. Such conclusions lead to the question of whether these spectroscopic studies are influenced by the contribution of the EG layers underneath the surface modified layer. XPS and Raman studies of single-layer EG clarify this issue. Retention of the G peak in the Raman spectrum [Fig. 7(a)] and the graphene peak in C 1s spectrum [Fig. 7(c)] of the single-layer EG without any significant change in the peak position and
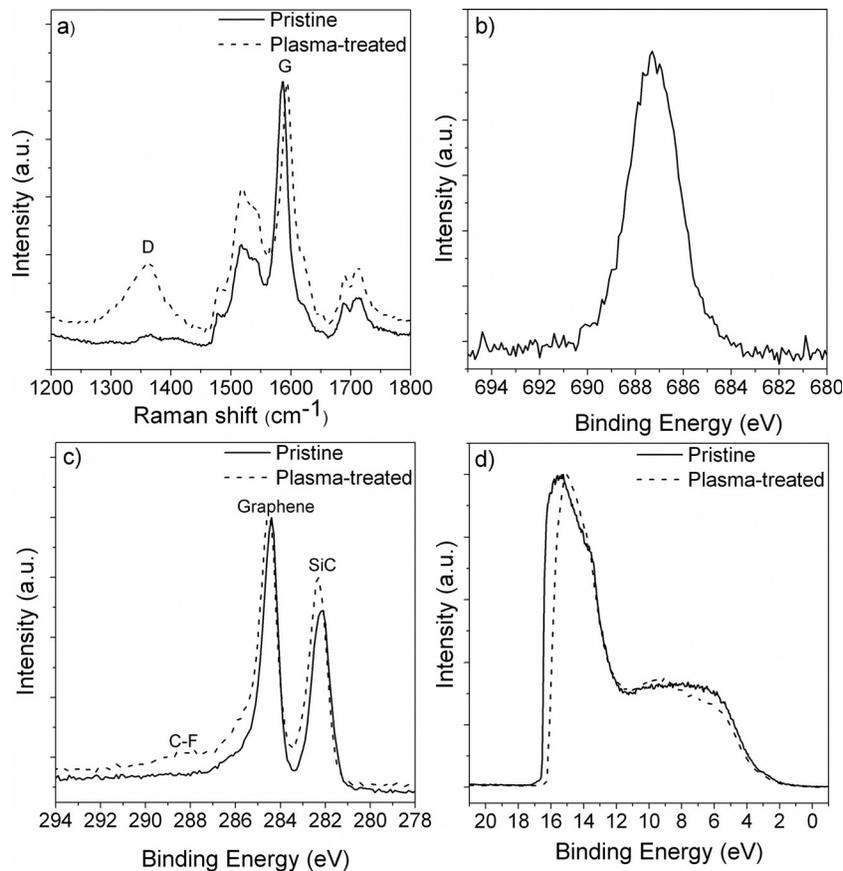

FIG. 6. (Color online) UPS spectra of SF_6 plasma-treated multilayer EG.

FIG. 7. Raman (a), XPS F 1s (b), XPS C 1s (c), and UPS (d) spectrum of SF_6 plasma-treated single-layer EG.

width validate the conclusions drawn from our studies of multilayer EG. Furthermore, our conclusions pose another intriguing question concerning the existence of carbon-fluorine bond—if the sp^2 configuration of graphene is not disrupted by plasma-treatment, then how is fluorine bonded to carbon atoms? A plausible scenario is the confinement of fluorination to the carbon atoms at the edges of graphite domains generated by ion-bombardment. If carbon-fluorine bonds exist only at the edges, the basal plane of graphene does not undergo chemical modification which is manifested in the spectroscopic characterization of plasma-treated samples. A subsequent question emerges on whether the carbon-fluorine bonds lead to sp^3 rehybridization of carbon atoms at the edges of graphite domains. The observed shift of work function requires a surface dipole perpendicular to the basal plane of graphene which is not possible if the carbon-fluorine bonds are coplanar with the basal plane of graphene. Therefore, the carbon atoms at the edges most likely rehybridize to sp^3 configuration and the carbon-fluorine bonds are out of plane.

IV. SUMMARY AND CONCLUSIONS

Due to the ubiquitous presence of plasma technology in the semiconductor industry, plasma-enabled processing of graphene may facilitate the integration of the technological infrastructure of the semiconductor industry into graphene-based electronics. Toward this end, this study demonstrates

that an SF_6 RIE plasma can fluorinate both multilayer and single-layer EG films without disruption of sp^2 hybridized carbon framework of EG. Fluorine content in the sample can be altered by simply varying the plasma treatment time and the fluorination is limited to only one or two surface layers. In addition, we have demonstrated the ability of plasma-assisted fluorination to modify the electron emission characteristics of graphene; therefore, SF_6 plasma treatment facilitates the application of graphene as an electrode for optoelectronic devices. The ability to control the thickness of EG on carbon-face SiC was exploited to fabricate one or two layers of fluorinated graphene both on top of the insulating substrate (SiC) and on a conductive graphene film of desired thickness. Since the semiconducting properties of fluorinated graphene have been reported previously, a fluorinated graphene/graphene interface also offers the possibility of fabricating bottom-gated epitaxial graphene devices.

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