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Spatially resolved chemical analysis of photodecomposition and doping effect of fluoropolymer-covered graphene

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We have studied the photo-decomposition of fluoropolymer-covered graphene and its effects on the electrical properties of embedded graphene using spatially resolved X-ray photoemission spectroscopy. From the comparative approach to the photo-decomposition and chemical analysis, we clearly prove that the fluorine atoms are desorbed from the sample surface by photon irradiation, resulting in a change of difluoride into a monofluoride form. As this photo-induced chemical modification proceeds, the dipole field changes strongly, which is responsible for the field-driven Dirac point realignment of the graphene layer. The desorption temperature of the photo-modified fluoropolymer was similar to that without photon irradiation (286 °C; ~ 0.047 eV); this similarity means that photo-modification did not cause chemical interactions between the fluoropolymer and graphene. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.5003167>]

Chemical doping of graphene to modulate its electrical properties has been of key interest for its application to electronic devices.^{1–8} Halogenation of graphene can change its local chemical and structural characteristics, which directly affects its electronic properties.⁹ Chemical absorption of oxygen, hydrogen, or fluorine on the graphene surface changes its hybridization from sp^2 to sp^3 and generates structural defects.^{9–12}

It is reported that laser irradiation of fluoropolymer (Cyclic Transparent Optical Polymer: CYTOP) covered graphene causes a notable amount of Dirac point shift of the embedded graphene layer.^{9,13} Recently, photo-driven modulation of electronic properties has been one of the strong candidate techniques for nano-scale device development.^{14–17} For this purpose, understanding the photo-induced details of the chemical process is the inevitable step for tailoring the electronic properties of graphene. In the fluoropolymer covered graphene, the active fluorine atoms produced by photon-irradiation are attributed to play an important role in modulating the electronic properties of graphene¹⁷ but are challenging for probing experimentally with chemical resolution.

In this work, the photo-driven chemical changes of CYTOP were investigated on the time-scale and compared with the adjacent non-irradiated area using scanning photoemission electron microscopy (SPEM) measurements. Spectroscopic data taken in time steps evidently show the gradual change in the fluorine valence of CYTOP by photons and desorption of fluorine atoms from the sample surface rather than chemical bonding with the underneath graphene. The thermal desorption experiment shows that the photo-modified CYTOP does not make notable changes in its interaction with the graphene layer. The large shift of the spectroscopy as a consequence of fluorine desorption reveals that

the strong dipole-field change of the fluoropolymer is enough to modulate the Dirac point of graphene.

Multi-layer graphene (10 ML on average) samples were grown by vapor deposition on 25 μm -thick copper foil in a quartz tube furnace, with CH_4 and H_2 as feed gases. The furnace was heated without gas flow for 30 min at 90 mTorr. The copper foil was preheated at 950 °C for 30 min. To obtain a large single-crystal copper surface, H_2 gas was supplied to the furnace at 150 mTorr and 33 cm^3/min (sccm). After preheating, a gas mixture of $\text{CH}_4:\text{H}_2 = 200$ sccm:33 sccm was supplied under ambient conditions for 10 min to synthesize graphene, and then, the furnace was cooled to room temperature at 10 °C/min under 33 sccm H_2 flow. CYTOP (3M, Inc.) was spin-coated onto the graphene on the copper foil and heated on a hot plate to 160 °C for at least 20 min to cure the fluoropolymer. Then, the unnecessary graphene formed on the other side of the Cu foil was removed by O_2 plasma etching. The sample was then immersed in 1 M FeCl_3 aqueous solution at room temperature for 15 h to etch away the remaining copper foil. The remaining layer of CYTOP and graphene (CYTOP-G) was carefully dipped into a deionized water bath 9 times to remove any residual etchant. The CYTOP-G sheets were then transferred onto an Si substrate. Bulk CYTOP was removed by immersion in a PF-5056 (performance fluid; 3M, Inc.) bath at room temperature for 5 min after the transfer procedures. Then, the sample was transferred into the preparation chamber (base pressure 5×10^{-10} Torr) and annealed at 180 °C for 10 h to degas and to release stress prior to analysis. Spatially resolved spectroscopic data were acquired at the SPEM beamline at NSRRC in Taiwan. Thermal desorption experiments and related spectroscopic analysis were performed at the 4D PES beamline of the Pohang Accelerator Laboratory in Pohang, South Korea.

CYTOP-G was irradiated by X-rays (614 eV, $\lambda \sim 2$ nm; beam diameter: 0.4 mm, 2.5 mW/cm^2) in the center region of the sample as described in Fig. 1(a). Upon irradiation, the

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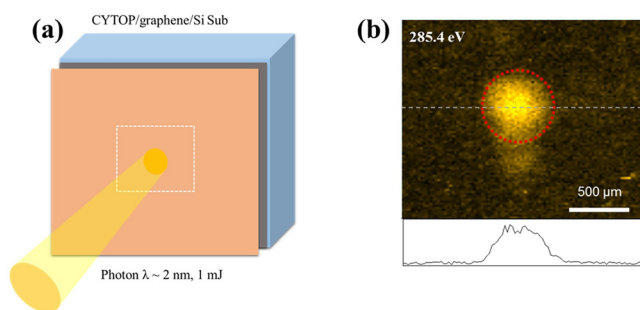


FIG. 1. (a) Schematic of photon irradiation on the CYTOP doped few-layer graphene/Si substrate. Gray dotted rectangle: area scanned using SPEM. (b) SPEM image by intensity at $E_b = 285.4$ eV. Bottom inset: intensity profile along the dashed line in the image.

chemical feature of C 1s began to get affected abruptly; the change was complete after 2 h 45 min. On this surface, spatially resolved photoelectron intensities at a binding energy of $E_b = 284.5$ eV were scanned using a focused X-ray beam to a 20 nm spot size by a Fresnel zone plate [Fig. 1(b)]. Electron intensities show strong contrast between irradiated [red circle in Fig. 1(b)] and non-irradiated regions, implying that the irradiation induces significant chemical modification of the sample surface. The boundary of the irradiated region was indistinct due to the Gaussian profile of the photon distribution.

For the same region of interest, SPEM images acquired through 16-binding energy channels ($E_b = 283$ – 295 eV in increments of 0.8 eV) are shown in Fig. 2. The C 1s intensity difference between irradiated and non-irradiated regions directly shows the comparative chemical status at each binding energy. The brightest center region in the images of binding energy between 284.6 and 286.2 eV results from the

exclusive presence of carbon monofluoride induced by the photo-decomposition of carbon difluoride. This chemical transformation leads to the reversed contrast in the energy range of 289.4–291.8 eV in which C 1s of carbon difluoride is.

To identify the chemical evolution during irradiation, high resolution C 1s core level spectra were measured over the duration of irradiation [Fig. 3(a)]. The bottom spectrum in Fig. 3(a) is from the as-introduced sample and is decomposed into five peaks: sp^2 (284.70 eV), CF (286.96 eV), O-CF (289.67 eV), CF_2 (291.66 eV), and O- CF_2 (293.09 eV) [Fig. 3(b)].¹⁸ The stoichiometric ratio of carbon atoms belonging to each chemical form of CYTOP was 1:1:2:1 (Table I), which agrees well with the intensity ratio of 0.75:1.00:2.24:1.02 of the four elementary C 1s peaks in Fig. 3(b). The deviation from ideal stoichiometry could be a result of contamination.

Upon irradiation, the intensity of the peaks starts to change abruptly, with those of monofluoride increasing and those of difluoride decreasing. The energy positions of the peaks are concurrently shifted toward the low binding energy side; the changes reach saturation at 2 h 45 min. The peak located at 284.7 eV is attributable to carbon atoms with the sp^2 orbital of the graphene layer. The intensity of this peak increased accordingly due to the increase in the probing depth of photoelectrons as photon irradiation caused desorption of weakly bound contaminants. Compared to the initial spectrum, the spectrum after photon irradiation [Fig. 3(c)] was depleted in CF_2 and O- CF_2 bonds and enriched in CF and O-CF bonds. This change implies that photon-induced desorption of fluorine transformed the carbon difluoride bonds [Fig. 3(b), inset] into carbon mono-fluoride bonds [Fig. 3(c), inset]. The chemical formula of CYTOP after the complete conversion of difluoride into monofluoride gives a

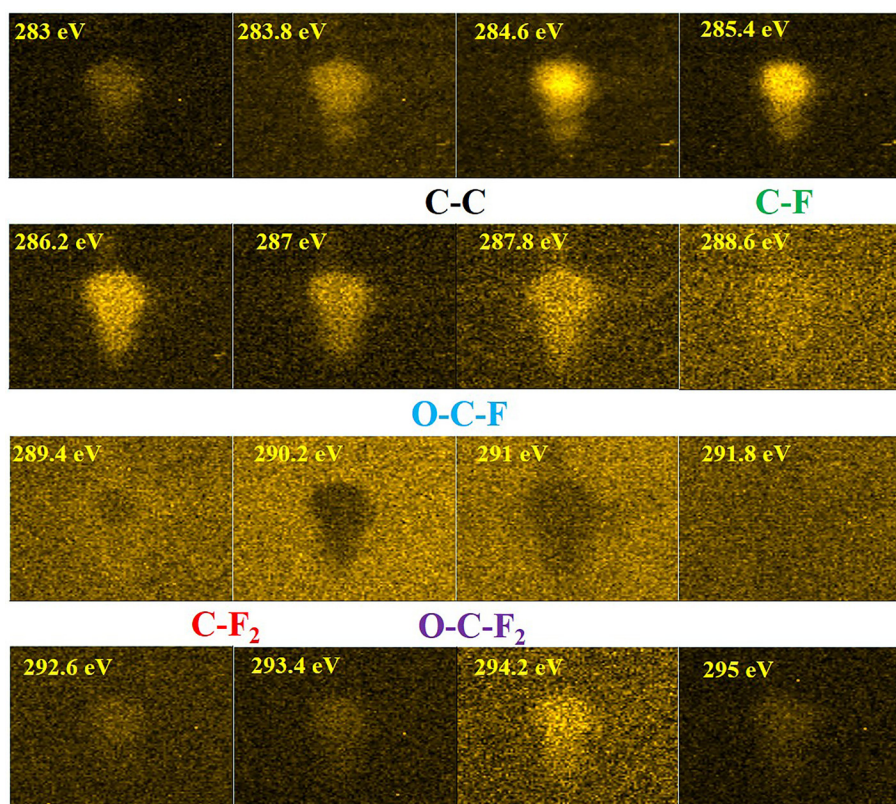


FIG. 2. SPEM images of the 2×2 mm area (pixel size: $20 \times 20 \mu\text{m}$ and pixel number: 100×100) acquired by spatially mapping the electron intensity from the sample after photon irradiation (number in the upper-left corner: E_b of the image).

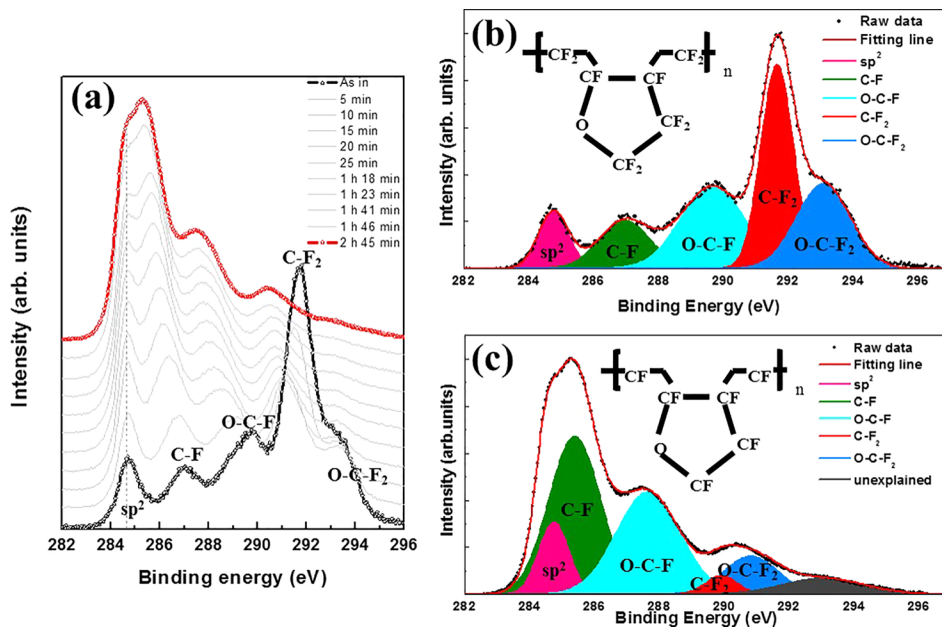


FIG. 3. (a) C 1s core level spectra of the CYTOP/graphene/Si sample as a function of photon irradiation time ($h\nu = 614$ eV). (b) C 1s spectra before and (c) after irradiation are deconvoluted into five peak components.

TABLE I. Stoichiometry and intensity ratio of each C 1s component of CYTOP doped graphene before irradiation.

Chemical component	CF	O-CF	CF ₂	O-CF ₂
Binding energy (eV)	287	289.7	291.7	293.1
Stoichiometry ratio	1	1	2	1
Intensity ratio (H)	0.75	1.00	2.24	1.02

CF:O-CF:CF₂:O-CF₂ stoichiometric ratio of 3:2:0:0, whereas the measured C 1s intensity ratio [Fig. 3(c)] was 2.62:1.68:0.29:0.42 (Table II). The small amount of remaining CF₂ and O-CF₂ is likely due to incomplete dissociation in the thickest areas of the non-uniform CYTOP layer.

The dipole moment of CYTOP can be estimated by summing all dipole moments of CF_x in CYTOP. As CF₂ is transformed into CF, the strong dipole moment of CYTOP decreases because CF has a lower dipole moment than CF₂. This reduced dipole field, combined with charge redistribution caused by chemical transformation, results in the gradual shift in E_b of the four main C 1s components toward the lower binding energy side for ~ 2 eV [Fig. 3(a) and Tables I and II]. There are two main effects which result in the electron binding energy shift, i.e., chemical or electrostatic shift. The simultaneous shift by the same amount of energy of core levels and the valence band originated from atoms exposed to the electrostatic field are well understood by an electrostatic shift.¹⁹ The shift in E_b of the four main C 1s toward the lower energy side is in good accord with Dirac point realignment

TABLE II. Stoichiometry and intensity ratio of each C 1s component after photon irradiation.

Chemical component	CF	O-CF	CF ₂	O-CF ₂
Binding energy (eV)	285.4	287.7	289.9	290.8
Stoichiometry ratio	3	2
Intensity ratio (H)	2.62	1.68	0.29	0.42

observed by Lee *et al.*¹⁸ Interestingly, the peak position of sp^2 from graphene underneath CYTOP did not show a notable energy shift despite a strong change in the CYTOP dipole field; this lack of change could be attributed to a mirror dipole field that forms at the Si surface under the graphene layer, which has permittivity ($\epsilon_{Si} = 11.68\epsilon_0$) that is strong enough to effectively compensate for the changed dipole field of CYTOP. As the depth increases from the top surface where there are dipoles, the field decreases due to the depolarization effect and should be nearly zero at the metallic graphene surface to satisfy the boundary condition.¹⁹ However, if the graphene is on the SiO₂ surface, the sp^2 peak of graphene could be shifted by an amount similar to that of the four main C 1s peaks because the atomic scale graphene-layer does not have sufficient charge to neutralize the dipole field. Despite these changes, irradiation induced no meaningful chemical interaction between graphene and CYTOP.

To understand the possible change in surface adsorption energy of mono-fluoride after photon irradiation, we performed a thermal desorption experiment on samples with (point A) and without (point B) photon treatment. Data at both A and B were acquired on the different position of the same sample surface which had been pre-heated at 180 °C for 10 h before the desorption experiment in a preparation chamber (base pressure: 5×10^{-10} Torr). Prior to the desorption experiment, photon irradiation at point A was conducted in the same condition as in Fig. 3. The fluorine 1s peak at point A decreased and broadened after irradiation [Fig. 4(a), red]; the area under the peak was reduced by $\sim 50\%$, which is more than expected (38%) by stoichiometric consideration of difluoride decomposition into monofluoride. Considering the low adsorption energy of CYTOP on the surface, the difference may occur because some CYTOP molecules desorb as a result of the thermal effects of photon irradiation. The blue spectra in both Figs. 4(a) and 4(b) are taken after the sample was annealed at 286 °C for 20 min; these show abrupt desorption of fluorine atoms on both points. Note that the desorption temperature of 286 °C corresponds to $E_b = 0.047$ eV, which is lower than Van der Waals interaction energy (~ 1.2 eV)

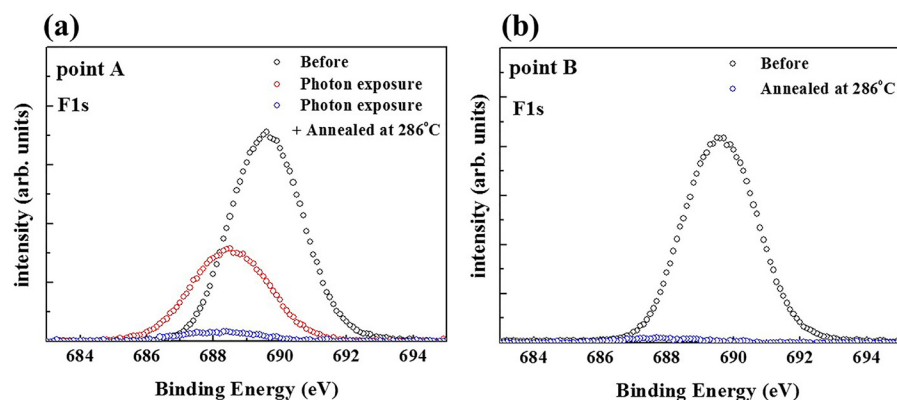


FIG. 4. F 1s spectra before and after annealing at 286 °C for 20 min taken from position A with photon irradiation ($h\nu = 620$ eV for 2 h 45 min) (a) and from position B without photon irradiation (b).

between pentacene molecules.²⁰ This means that the photo-decomposition of the fluoropolymer does not induce chemical doping of the graphene layer.² The small amount of remaining fluorine is acceptable considering the inconsistent thickness of CYTOP.

Chemical analysis using spatially resolved photoemission spectroscopy shows that focused soft x-ray irradiation (614 eV) causes fluorine decomposition resulting in contrast changes in the C 1s spectromicroscopy image. The comparative study of high resolution photoemission spectra extracted from several regions of interest reveals that, in contrast to expectation, graphene remains chemically intact during CYTOP decomposition by photons. Our findings show that it is the enhanced dipole moment of photo-modified CYTOP, rather than the formation of carbon fluoride on the graphene surface, that induces a large shift in the Dirac point of graphene.

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