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Citation: Appl. Phys. Lett. 111, 121601 (2017);
View online: https://doi.org/10.1063/1.5003167
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Published by the American Institute of Physics

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

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(Received 26 April 2017; accepted 3 September 2017; published online 18 September 2017)

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]
The 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)]. 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
CF:O-CF:CF2:O-CF2 stoichiometric ratio of 3:2:0:0, whereas the measured C1s 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 CFX 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 Eb of the four main C 1s components toward the lower binding energy side for /C24/C_{14}^2e V[ 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 However, if the graphene is on the SiO2 surface, the sp2 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 /C14^180°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 ~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).

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

<table>
<thead>
<tr>
<th>Chemical component</th>
<th>CF</th>
<th>O-CF</th>
<th>CF2</th>
<th>O-CF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>287</td>
<td>289.7</td>
<td>291.7</td>
<td>293.1</td>
</tr>
<tr>
<td>Stoichiometry ratio</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Intensity ratio (H)</td>
<td>0.75</td>
<td>1.00</td>
<td>2.24</td>
<td>1.02</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Chemical component</th>
<th>CF</th>
<th>O-CF</th>
<th>CF2</th>
<th>O-CF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>285.4</td>
<td>287.7</td>
<td>289.9</td>
<td>290.8</td>
</tr>
<tr>
<td>Stoichiometry ratio</td>
<td>3</td>
<td>2</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Intensity ratio (H)</td>
<td>2.62</td>
<td>1.68</td>
<td>0.29</td>
<td>0.42</td>
</tr>
</tbody>
</table>
between pentacene molecules.\textsuperscript{20} This means that the photodecomposition of the fluoropolymer does not induce chemical doping of the graphene layer.\textsuperscript{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.

This work was supported by the National Research Foundation of Korea (NRF) (Grant No. NRF-2015M2A2A6A01045343) through the Ministry of Science, ICT, and Future Planning, Korea. Experiments at PLS-II were supported by MSIP-R. O., Korea. JRA was supported by the National Research Foundation of Korea (NRF) (Grant No. 2016M2B2A902944596).


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