



# UV-irradiation induced defect formation on graphene on metals



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## ABSTRACT

Defects in graphene are of great interest as they are considered to provide various intriguing physical and chemical properties to graphene. We have investigated defect formation in graphene induced by UV-irradiation under various atmospheres. We have found that graphene can be damaged by UV-irradiation in vacuum. The defect formation by UV-irradiation was accelerated under ammonia ambience, while no additional effect was observed for UV-irradiation in nitrogen. The noticeable enhancement of defect formation could be attributed to a radical reaction where reactive species generated by photodissociation reaction of ammonia attacks the chemical bond of graphene. The UV-irradiation under ammonia ambience causes not only defect formation but also nitrogen doping to graphene. Incorporation of nitrogen atoms seems to occur rather locally to form graphitic carbon nitride domains.

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## 1. Introduction

Graphene, a one-atom-thick sheet composed of  $sp^2$  carbon atoms arranged in a honeycomb lattice, has been attracting tremendous attention due to its fascinating properties [1]. Defects in graphene, such as vacancies, disorders, non-hexagonal-rings and doped impurities, have also been investigated because they are considered to affect various physical and chemical properties. Defects would form scattering centers for carriers which deteriorate the electric conductivity and the carrier mobility of the graphene [2]. In contrast to such a negative effect, defects in graphene give rise to some intriguing phenomena. Graphene with defects has been reported to exhibit Kondo effect in which local magnetic moments at the defect sites interact with conduction electrons at low temperatures [3]. On the other hand, defects might provide a reaction site at which doping of heteroatoms is likely to occur. Nitrogen doping to graphene has been considered to relate with the oxygen reduction reactivity, which is expected to contribute to the development of platinum free catalyst for a future fuel cell [4]. Thus, the deep understanding of defects is essential not only for fundamental science but also for application to industry.

The studies on defects in graphene have been reported theoretically and experimentally. In most of the experiments high energy electron beams or ion bombardment has been used to create defects in graphene [2,3,5]. On the other hand, photo-irradiation has been less employed to induce defects in graphene. Photo-irradiation has a potential to be a deliberate way of inducing defects in graphene because generation of electron-hole pairs by ultraviolet (UV) have been observed recently [6]. Actually formation of defects

was observed for the graphene under UV-irradiation [7]. In addition to the defect formation photo-irradiation in various atmospheres might cause chemical reaction in graphene. Liu et al. have reported that photo-irradiation to graphene in a toluene solution of benzoyl peroxide excites the optical transition in graphene and triggers a chemical reaction, leading to a subsequent chemical modification of graphene [8].

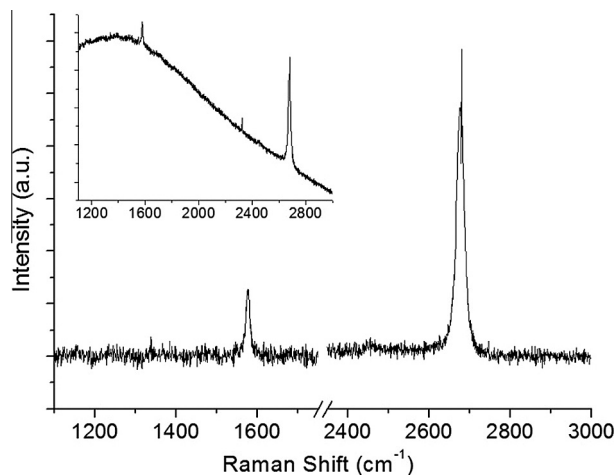
In the present Letter, we have investigated the defect formation and chemical reaction in graphene by UV-irradiation. We used a deuterium lamp as a light source and the graphene grown on a Cu foil was UV-irradiated under various atmospheres (vacuum, nitrogen, and ammonia). We observed a notable dependence of defect formation on ambient gas species. On the basis of the experimental results we discussed the mechanism for the defect formation through UV-irradiation.

## 2. Experimental

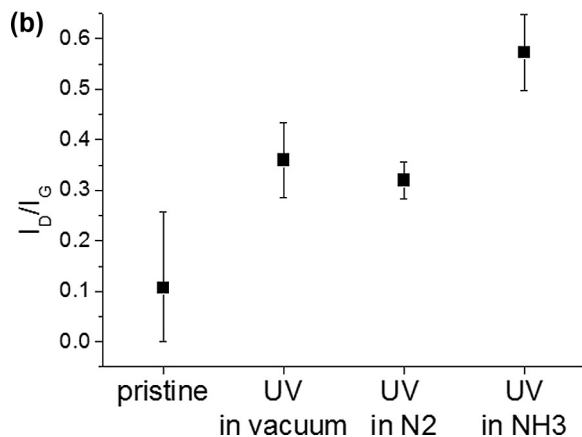
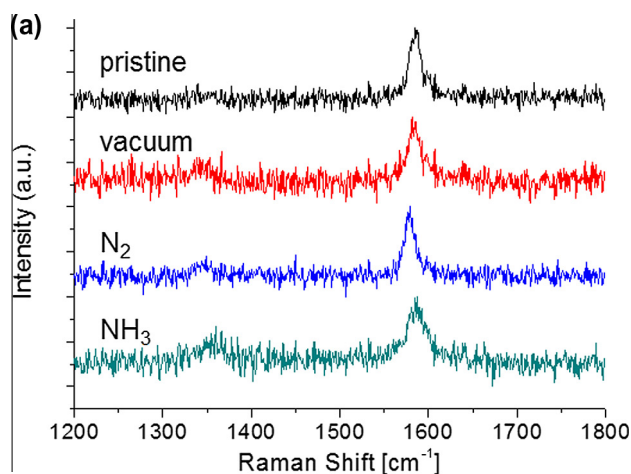
Graphene was formed on a copper foil by a conventional CVD process using a high temperature infrared furnace (MILA-5000, UL-VAC-RIKO, Inc.) [9]. The copper foil was heated at 1000 °C under hydrogen gas of 10 Pa in the furnace to clean the surface. Methane and hydrogen gases were then supplied to the furnace. The total pressure was kept at 100 Pa, and the flow rates of methane and hydrogen were set at 70 and 4 sccm, respectively. The formation of graphene was confirmed by Raman spectroscopy, which was measured by a JASCO NRS-3100 utilizing a 532 nm laser as an excitation source. Figure 1 shows a typical Raman spectrum of graphene on a copper foil, which was obtained after subtracting a fluorescent background from the copper foil. There appear G band and 2D bands at 1576 and 2680  $\text{cm}^{-1}$ , respectively [10]. The intensity ratio (7.3) of 2D to G and the narrow peak width of 2D band

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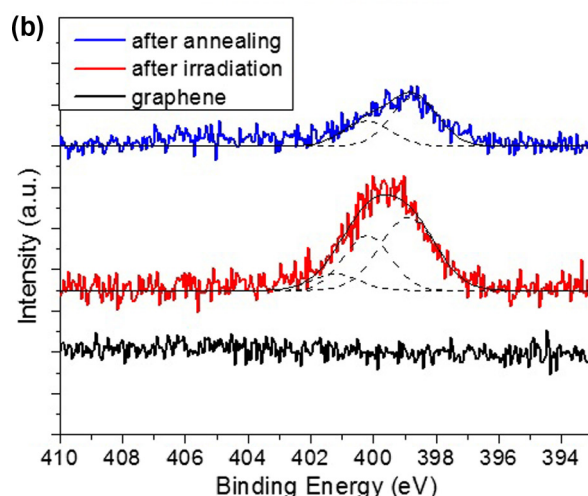
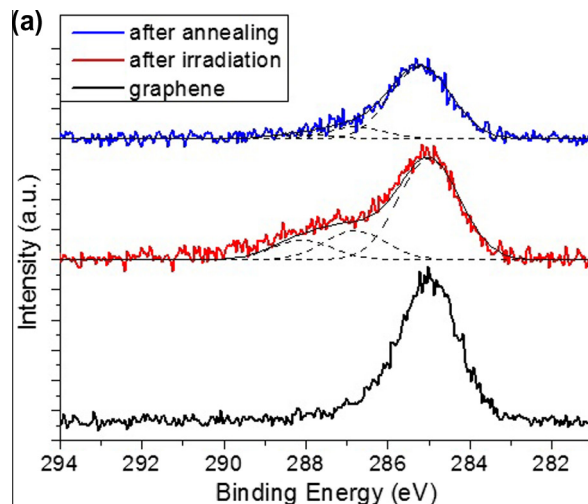
**Figure 1.** Raman spectrum of graphene grown on a copper foil. The raw spectrum before subtracting a background is shown in the inset.



**Figure 2.** (a) Raman spectra of graphenes on a copper foil UV-irradiated under various atmospheres. (b) Intensity ratio ( $I_D/I_G$ ) after UV-irradiation.

(the full width at half maximum is  $21 \text{ cm}^{-1}$ ) indicate formation of a single layer graphene on a copper foil [11]. The uniform coverage of graphene on Cu was confirmed by both Raman spectroscopy and scanning electron microscopy (SEM). The SEM image was shown in the [Supplementary information](#).

UV-irradiation to graphene was performed at room temperature with a deuterium lamp (L2D2, 30 W, Hamamatsu Photonics K.K.) in various atmospheres. The UV spectrum shows a maximum



**Figure 3.** XPS spectra of the graphene on a copper foil UV-irradiated under ammonia ambience. (a) C 1s peak, (b) N 1s peak.

between 150 and 200 nm and the effective power on the graphene surface was an order of  $0.1 \text{ mW/cm}^2$ . The base pressure in the irradiation chamber was an order of  $10^{-5} \text{ Pa}$ . The ambient pressure during UV-irradiation was kept at 10 Pa for each gas and the irradiation was carried out. The samples were characterized with Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). XPS measurements were performed with an X-ray source (Thermo VG Scientific XR3E2) and a hemispherical energy analyzer (SPECS, PHOIBOS-100). An Al  $K\alpha$  excitation source ( $h\nu = 1486.6 \text{ eV}$ ) was used and the energy of the spectrometer was calibrated using Au  $4f_{7/2}$ , Ag  $3d_{5/2}$ , and Cu  $2p_{3/2}$  peaks.

### 3. Results and discussion

#### 3.1. Raman and XPS spectra of graphene UV-irradiated in various ambiances

Graphenes grown on a copper foil through CVD process were irradiated by UV light under various ambient conditions: vacuum ( $<1.0 \times 10^{-5} \text{ Pa}$ ), nitrogen (10 Pa) and ammonia (10 Pa). [Figure 2a](#) shows the representative Raman spectra of graphenes after UV-irradiation for 2 h. We could assume the amount of defect increases almost proportionally up to the time of 2 h [12]. The evolution of the D bands ( $\sim 1350 \text{ cm}^{-1}$ ) was observed for the UV-irradiated graphenes. No significant change was observed in G band

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