EUV induced defects on few-layer graphene

A. Gao,1 P.J. Rizo,2 E. Zoehout,1 L. Scaccabarozzi,2 C.J. Lee,1 V. Banine,2 and F. Bijkerk1,3
1) POM-Dutch Institute for Fundamental Energy Research, Edisonbaan 14, 3439 MN Nieuwegein, the Netherlands.
2) ASML, De Run 6501, 5504 DR Veldhoven, the Netherlands.
3) MESA+ Institute for Nanotechnology, PO Box 217, University of Twente, 7500 AE, Enschede, the Netherlands.

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We use Raman spectroscopy to show that exposing few-layer graphene to extreme ultraviolet (EUV, 13.5 nm) radiation, i.e. relatively low photon energy, results in an increasing density of defects. Furthermore, exposure to EUV radiation in a H2 background increases the graphene dosage sensitivity, due to reactions caused by the EUV induced hydrogen plasma. X-ray photoelectron spectroscopy (XPS) results show that the sp2 bonded carbon fraction decreases while the sp3 bonded carbon and oxide fraction increases with exposure dose. Our experimental results confirm that even in reducing environment oxidation is still one of the main source of inducing defects.

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I. INTRODUCTION

Graphene is a single planar sheet of sp2 bonded carbon atoms which are closely packed in a honeycomb-like crystal structure. It is the basis of many carbon-based materials, e.g., stacked into graphite, rolled into carbon nanotubes or wrapped into buckyball.1–3 Graphene has unique physical properties, such as quantum electronic transport, a tunable band gap, extremely high mobility, high elasticity, and electromechanical modulation.4–8 This makes graphene a promising material for many applications, including graphene transistors, electronic circuits, and solar cells, as well as other applications in biology and chemistry.9–10 However, one of the key requirements for such applications is the control of defects, such as vacancies, dislocations or adatoms. The electronic properties of graphene are greatly affected by the presence of defects because they can act as scattering centers for electrons, reducing sheet conductivity.9 Defects associated with dangling bonds can enhance the chemical reactivity of graphene.11 Likewise, the presence of defects reduces the thermal conductivity of graphene.12

The unique properties make graphene an attractive candidate for applications in radiation-rich environment. However the presence of defect may affect its performance. Therefore, it is critical to understand the radiation-induced damage in graphene. Zhou et al.13 reported that soft x-rays can easily break the sp2 bond structure and form defects in graphene that is weakly bound to the substrate. Hicks et al.14 also studied multilayer graphene, grown on SiC, before and after 10 keV x-ray irradiation in air. They concluded that defects were generated due to surface etching by reactive oxygen species created by x-rays. In this paper, we focus on defect generation in graphene, induced by exposure to 13.5 nm (EUV) radiation under a variety of background conditions. We compare the rate at which defects are induced by EUV in a vacuum condition, and the rate at which defects are induced by exposure to EUV in a background of molecular hydrogen. We show that, defects are introduced in both cases, though at different rates. Surprisingly, our data also show that, even in a reducing environment, oxidation is still one of the main sources of EUV induced defects. The experimental results are important for illustrating the damage-creating mechanisms upon photon interaction as well as designing graphene-based components for EUV lithography systems.

II. EXPERIMENTS

Graphene samples in this report were produced by the Graphene Supermarket. A few layers of graphene were grown on 25 × 25 mm2 Ni/Si substrate with chemical vapor deposition method. The number of layers of graphene varies from 1 to 7, with an average of 4 over the sample. Three groups of experiments were performed: 1) a pristine sample served as a reference (refer to Sref) and was not exposed; 2) a sample was exposed to EUV irradiation (SEUV) without molecular hydrogen in the background gas; 3) a sample was exposed to EUV irradiation in a 5 × 10−2 mbar H2 background (SEUV+H2). The other experimental settings are summarized in table I. Graphene samples were irradiated by an EUV source (Philips EUV Alpha Source 2) with a repetition rate of 1 kHz and an average dose of 0.1 mJ/cm2 per pulse. Raman spectra were collected with a home-built system. In this system, a 532 nm diode-pumped solid state laser is used to excite the samples with an illumination spot of 3.5 × 0.1 mm2 and a power density of 200W/cm2. The collection efficiency of the detector system was calibrated using the HG-1 Mecury Argon Calibration Light Source and AvaLight-D(H)-S Deuterium-Halogen Light Source. 2D Raman intensity maps were acquired by collecting

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a) Electronic mail: a.gao@differ.nl.
A typical Raman spectrum of graphene has three prominent features, i.e., D, G, and 2D peaks, located at 1350 cm\(^{-1}\), 1580 cm\(^{-1}\), and 2700 cm\(^{-1}\) respectively. The G peak is a first order Raman scattering process, corresponding to an in-plane stretching of \(sp^2\) bonds. The D band is due to the breathing modes of six-atom rings, and requires a defect for activation. The 2D peak is the second order of the D peak. Since the 2D originates from a process where momentum conservation is satisfied by two phonons with opposite wavevectors, defects are not required for their activation, and are, thus, always present. 

![Fig. 1: (color online) Comparison of the whole Raman spectra and intensity. The pristine sample has the lowest D peak intensity. Note that the spectra are separated by an offset of \(5 \times 10^5\) counts/s.](image)

TABLE I: Experimental settings summary. Two parameters vary among different experiments: exposure time to EUV radiation and/or \(H_2\) pressure.

| Sample                  | \(S_{EUV}\) | \(S_{EUV+H_2}\) |
|-------------------------|-------------|-----------------|
| Exposure time (hr)      | NA          | 8               |
| \(H_2\) pressure (mbar) | NA          | 0               |
| Chamber pressure (mbar) | NA          | \(1 \times 10^{-8}\) |

Raman signal over the central \(2 \times 0.1\) mm\(^2\) area. The transverse distance between two data points was set to 500 \(\mu m\), and along the longitudinal direction, the data points were collected continuously. XPS was measured by monochromatic Al-K\(\alpha\), Thermo Fisher Theta probe with a footprint of 1mm diameter.

III. RESULTS AND DISCUSSION

A. Raman analysis

Besides the single spectrum comparison, 2D scans for the two samples \(S_{EUV}\) and \(S_{EUV+H_2}\) were made to map the ratio of the D and G integrated intensities (shown in Fig. 2). In Fig. 3, the two samples \(S_{EUV}\) and \(S_{EUV+H_2}\) were partially covered with a metal mask. The spatial intensity distribution of EUV light is indicated in Fig. 2a and Fig. 2d. Fig. 2c shows that the D/G ratio maps of the samples \(S_{EUV}\) and \(S_{EUV+H_2}\), indicating the formation of \(sp^2\) clusters or chains. Furthermore, there is another possible source for defects generation: secondary electrons from the Ni substrate, producing EUV radiation. These electrons can be expected to have an energy less than 50 eV with a peak distribution between 2 and 5 eV. Low energy electrons are not expected to create vacancy type defects. However, low energy electrons (7 eV) have been reported to dissociate adsorbed water and initiate oxide formation on metal surfaces. This remains to be investigated.

Fig. 2b clearly coincides with the EUV intensity profile for pristine sample to 1598 cm\(^{-1}\) for both \(S_{EUV}\) and \(S_{EUV+H_2}\), indicating the formation of \(sp^2\) clusters or chains. Furthermore, there is another possible source for defects generation: secondary electrons from the Ni substrate, produced during EUV radiation. These electrons can be expected to have an energy less than 50 eV with a peak distribution between 2 and 5 eV. Low energy electrons are not expected to create vacancy type defects. However, low energy electrons (7 eV) have been reported to dissociate adsorbed water and initiate oxide formation on metal surfaces. This remains to be investigated.

Energetic electrons are known to break carbon bonds forming defects in graphene. Furthermore, graphene hydrogenation occurs due to presence of a hydrogen plasma. These combined effects lead to a higher defect density on the sample exposed to EUV in a hydrogen background. There is also a G peak shift from 1583 cm\(^{-1}\) for pristine sample to 1598 cm\(^{-1}\) for both \(S_{EUV}\) and \(S_{EUV+H_2}\), indicating the formation of \(sp^2\) clusters or chains. Furthermore, there is another possible source for defects generation: secondary electrons from the Ni substrate, produced during EUV radiation. These electrons can be expected to have an energy less than 50 eV with a peak distribution between 2 and 5 eV. Low energy electrons are not expected to create vacancy type defects. However, low energy electrons (7 eV) have been reported to dissociate adsorbed water and initiate oxide formation on metal surfaces. This remains to be investigated.
(b) EUV+H

(c) EUV+H

B. XPS analysis

Quantitative information on the relative concentrations of different C bond types in the sample were obtained by analyzing the C1s peak of the XPS spectrum. The curve fitting results for the C1s spectrum of \( S_{EUV+H_2} \) are shown in Fig. 4a. There are four components in the C1s spectrum: the first peak at binding energy 283.4 eV, which is attributed to carbide formation with the underlying Ni layer, the second peak at binding energy 284.4 eV, corresponds to the \( sp^2 \) bonds in graphitic like carbon, the third peak, at binding energy 285.3 eV, corresponds to carbon bonds with \( sp^3 \) hybridization, and the fourth peak, at binding energy 286.8 eV, is assigned to hydroxyl group. The appearance of \( sp^3 \) carbon and C-OH both indicate the generation of defects in graphene. Oxidation occurs when graphene reacts with the residual water during exposure. At the same time, oxidation will generate at least one \( sp^2 \) bond as well. The \( sp^3 \) bonds can also be introduced by hydrogen plasma generated under EUV irradiation. In Fig. 4b, for both the \( S_{EUV+H_2} \) and \( S_{EUV} \) sample, we can see that C element (the \( sp^2 \) bonded carbon) concentration drops by 5-9% and O element concentration increases by 5-8% compared with that in pristine sample. The concentration change of different bonds versus EUV power with respect to the pristine sample are plotted in Fig. 4c and Fig. 4d. In the case of \( S_{EUV} \), the \( sp^2 \) concentration decreases less in the higher power range than in the lower power ranges. It appears that under EUV irradiation, besides breaking \( sp^2 \) bonds and forming \( sp^3 \) and C-OH bonds, there is also a transformation from C-OH phase to \( sp^2 \) phase, since the C-OH concentration change drops to almost zero. This transformation can be induced by local heating due to EUV irradiation. However, this transformation does not indicate that the converted \( sp^2 \) bonds are forming an ordered ring structure like in the undistorted graphene network, since, in the Raman spectrum, \( I(D)/I(G) \) (Fig. 3a) increases in higher EUV power range. In contrast, for \( S_{EUV+H_2} \), the transformation to \( sp^2 \) is neglectable. Because hydrogenation can be the dominant effect, the converted \( sp^2 \) bonds will be hydrogenated in the end. Besides forming C-OH (oxidation), forming C-H bond (hydogenation) will generate C-C (\( sp^3 \)) bonds as well. The \( sp^3 \) concentration increases slowly at low intensities (lower than 0.5W/cm^2) and saturates at higher powers, which coincide with the \( I(D)/I(G) \) ratio map in Fig. 5b. However, comparing \( S_{EUV+H_2} \) with \( S_{EUV} \), even with the same amount of \( sp^2 \), \( sp^3 \), and C-OH, they show different \( I(D)/I(G) \) values, indicating that there is no
unique quantitative relationship between I(D)/I(G) ratio and sp$^3$ or C-OH content. The contribution from C-H or C-OH solely to I(D)/I(G) has yet to be investigated. Nevertheless, the XPS data clearly show that the defects were generated by EUV photons, including hydrogenation, and oxidation even in a reducing environment (H$_2$).

IV. CONCLUSION

The Raman results reported here show that there are defects induced in graphene after EUV irradiation, which is reflected by an increase of the D peak intensity. The defects are caused by breaking sp$^2$ bonds by EUV photons, oxidation due to the formation of OH groups, hydrogenation due to hydrogen plasma generated during EUV irradiation. The XPS results confirm that, after EUV irradiation, the concentration of sp$^2$ bonds in graphene decreases while the concentration of sp$^3$ bonds and C-OH bonds increases, clearly indicating defects generated in graphene. EUV irradiation introduces defects both through oxidation with the residual water background, and more effectively by hydrogenation due to the presence of hydrogen plasma.

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