Study of EUV induced defects on few-layer graphene

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Abstract
Defects in graphene greatly affect its properties[1-3]. Radiation induced-defects may reduce the long-term survivability of graphene-based nano-devices. Here, we expose few-layer graphene to extreme ultraviolet (EUV, 13.5nm) radiation and show there is a power-dependent increase in defect density. We also show that exposure to EUV radiation in an H_2 background increases graphene's dosage sensitivity. This may be due to reactions caused by the EUV induced hydrogen plasma. The nature of the defects was studied with X-ray photoelectron spectroscopy (XPS), which showed that the sp^3 bonded carbon and oxide fractions increase with exposure. The experimental results are important for understanding the defect-creating mechanisms upon photon interaction as well as designing graphene-based components for EUV lithography systems.

Graphene samples grown on $25x25mm^2$ Ni/Si substrate by CVD were obtained from Graphene Laboratories, Inc. Each sample had 1 to 7 layers, with a spatial average of 4. The samples were exposed to EUV, and for comparison purposes, hydrogen radicals, under conditions summarized in table 1. Raman spectroscopy and XPS were used to study the defects in graphene. Fig. 1 shows the Raman spectra of the five samples. The spectrum for the sample exposed to EUV in a hydrogen background (S_{EUV+H2}) has the highest D peak intensity. The spectra for the samples exposed to atomic hydrogen (S_H) and EUV irradiation (S_{EUV}) show slightly lower D peak intensities. The pristine sample (S_{ref}), and the one exposed to molecular hydrogen (S_{H2}) have the lowest D peak intensities. An increased D peak intensity indicates increased defect density.

Fig. 2 and Fig. 3 show the D/G ratio dependence on the EUV power for S_{EUV} and S_{EUV+H2}. In Fig. 2, the D/G ratio maps of the S_{EUV} and S_{EUV+H2} show clear differences between exposed and unexposed areas. The two maps also coincide with the EUV intensity profiles, as shown in Fig.2. The relationship between D/G ratio and EUV power is plotted in Fig. 3. For S_{EUV+H2}, the D/G ratio first grows as the EUV power increases, then saturates. It seems, however, for S_{EUV}, that the D/G ratio shows a linear dependence on EUV power.

After Raman spectroscopy, the samples were examined by XPS. Fig. 4 shows the curve fitting results. There are four components for the graphene samples: carbide, sp^2 bonds, sp^3 bonds and –COH. Their concentrations are shown in table 2. For the S_H, S_{EUV} and S_{EUV+H2}, the sp^2 concentration decreases while the sp^3 concentration increases, indicating a sp^2 phase to sp^3 phase transformation. In the case of S_{EUV} and S_{EUV+H2}, the increase of –COH concentration suggests that graphene may be reacting with background water. However, for S_{EUV+H2}, oxidation is more prevalent than sp^3 formation, despite what might be expected to be a reducing environment. We speculate that the added H_2, together with EUV radiation, created more OH radicals from the background water.

The Raman and XPS results reported here show that there are defects induced on graphene after EUV irradiation, which are reflected by an increase of D peak intensity. EUV irradiation, in the absence of hydrogen, introduces defects, both through oxidation with the residual water background, and, more directly, by breaking sp^2 bonds. Bonding-breaking defects are caused by EUV photons, energetic electrons and ions. In a hydrogen atmosphere, oxidation is still significant, due to the formation of OH groups by hydrogen and water plasma, generated during EUV irradiation.

References

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Figures

Table 1 Exposure conditions

	S_{ref}	$S_{H2(molecular)}$	$S_{H(atomic)}$	S_{EUV}	S_{EUV+H2}
EUV(hr)	0	NA	NA	8	8
H_2(mbar)	0	$5x10^{-2}$	$5x10^{-2}$*	0	$5x10^{-2}$
Background(mbar)	$6x10^{-7}$	$6x10^{-7}$	$6x10^{-7}$	$6x10^{-7}$	$6x10^{-7}$

**Atomic hydrogen was generated by injecting $5x10^{-2}$ mbar molecular hydrogen into the chamber and flowing the gas over a tungsten filament held at 2000°C.*

Table 2 Atomic concentration of the four components for different samples

	carbide(%)	sp^2(%)	sp^3(%)	-COH(%)
S_{ref}	5.7	79.3	9.0	5.0
$S_{H(atomic)}$	3.6	73.2	16.3(↑7.3)	6.9(↑0.9)
S_{EUV}	5.5	69.1	16.1(↑7.1)	9.2(↑3.3)
S_{EUV+H2}	4.2	67.7	14.7(↑5.8)	13.3(↑7.4)

** Arrows indicate the change in concentration relative to the reference sample.*

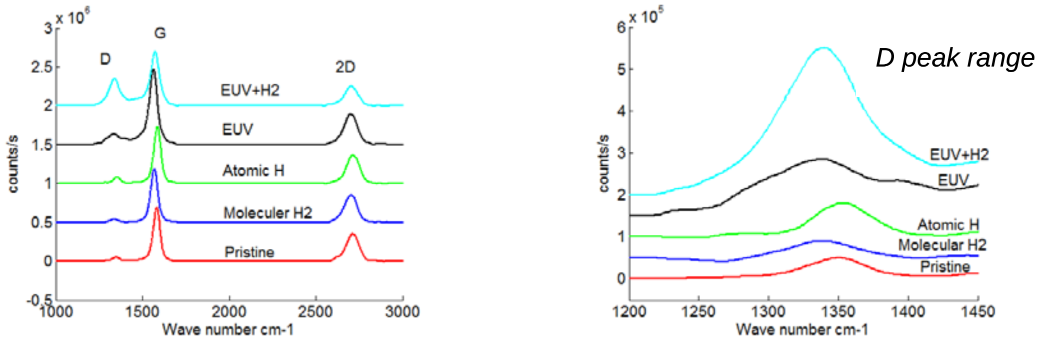
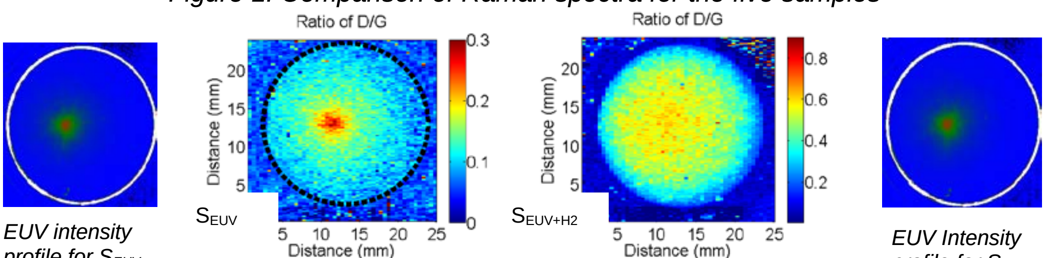


Figure 1. Comparison of Raman spectra for the five samples



EUV intensity profile for S_{EUV}

EUV Intensity profile for S_{EUV+H2}

Figure 2. D/G ratio map profile versus EUV intensity profile

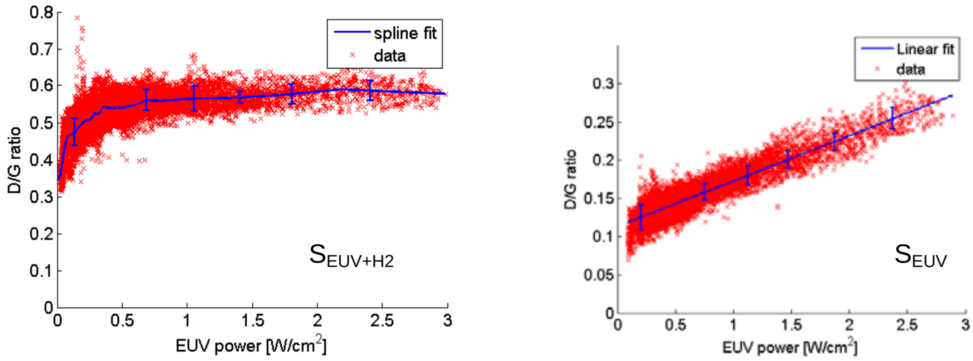


Figure 3. D/G ratio versus EUV power

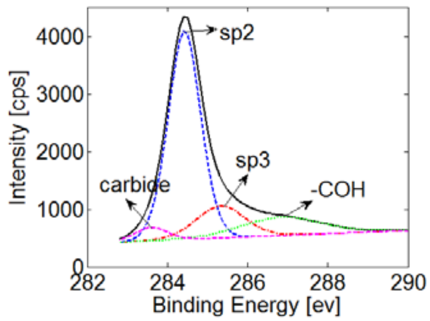


Figure 4. XPS curve fitting results for S_{EUV+H2}.