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Full Length Article

Effects of ultraviolet nanosecond laser irradiation on structural modification and optical transmission of single layer graphene

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ABSTRACT

Structural modifications and optical transmission change of single layer graphene (SLG) on transparent SiO_2 substrate induced by nanosecond 355 nm laser irradiation were systematically studied by scanning electron microscopy (SEM), laser-excited Raman, X-ray photon spectroscopy (XPS) and UV–vis transmission spectra. In this study, to avoid damage to graphene, the selected irradiation fluence was set to be smaller than the laser damage threshold of SLG. Laser-driven formation of nano-dots, carbon clusters and spherical carbon morphologies were clearly presented using SEM magnification images, and the formation mechanism of such structures were discussed. Raman spectra revealed formation of D' peak and the continuously increasing of I_D/I_G intensity ratio with the concurrent increase of laser fluence, indicating the increase in amount of structural defects and disordering in SLG. XPS results disclosed that the oxygen content in SLG increases with laser fluence. The formation and relative content increase of C═O, C—O—C and O—C═O bonds in SLG induced by laser irradiation were also revealed by XPS. Laser-driven micro-structure modifications of crystalline graphene to nano-crystalline graphene and photo-chemical reactions between graphene and O_2 and H_2O in air environment were suggested to be responsible for the Raman and XPS revealed modifications in SLG. It is worthy to point out that the above mentioned structural modifications only caused a slight decrease (<2% @ 550 nm) in the optical transmittance of SLG. These results may provide more selections for the batch processing of large scale graphene aiming at modifying its structure and thus taiorling its properties.

1. Introduction

Graphene has been attracting considerable attention because of its outstanding electric [1], optical [2,3], mechanical [4] and thermal [5] properties. These properties make graphene good candidates for many applications such as field effect transistors, transparent conducting electrodes, non-linear optical components, photodetectors and thermal management materials.

For the application of graphene-based devices, the processing or modification of graphene is an important issue. Laser irradiation treatment is a very good solution for the processing [6–9] and modification [10–12] of such thin films like graphene. Compared with other methods, laser treatment has unique advantages. For example, the processing precision can be very high, and the treatment location can be arbitrarily selected according to specific requirements by controlling the laser beam paremeters. Also, unnecessary contamination can be avoided during laser-based processing. Due to the practical importance, investigating the laser-induced effects on graphene is very necessary. Recently, influence of CW laser [13,14] and short pulsed femtosecond laser [15–17] as well as nanosecond laser [18–21] irradiation on graphene has been reported. These results showed that the damage threshold, structure modification and the properties of graphene were closely related to the laser parameters (e.g. wavelength, pulse duration and pulse energy), the type of the substrate and the characteristics of graphene. However, most of these studies focused on the laser-induced damage effect or laser-induced chemical modifications on graphene, while little attention was paid to the low energy laser-induced modifications rather than damage on pure single layer graphene (SLG), especially in the case of nanosecond laser irradiation. Therefore, more investigation is needed to extend understanding on this point, so that the specific properties of SLG can be tailored through modifying its microstructure.

In this paper, we present a study of the structural modifications of SLG during nanosecond pulsed laser irradiation at fluence lower than its damage threshold using sacnning electron microscopy (SEM), Raman spectrum and X-ray photoelectron spectroscopy(XPS). Also, the optical transmittance variation of SLG with

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Table 1
The tested LIDT and the irradiated laser fluence for SLG samples.

Sample Name	*a*	*b*	*c*	*d*	*e*	Tested LIDT
Laser fluence (mJ/cm^2)	0	10.5	31.6	51.8	70.3	78.0

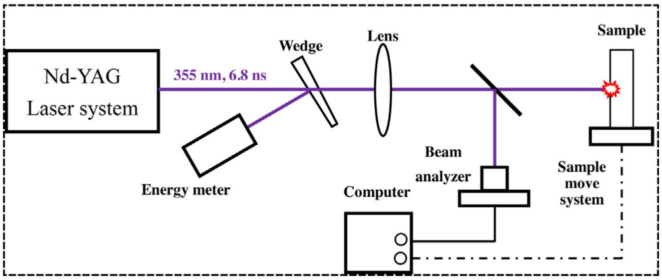

Fig. 1. Experimental setup of the pulsed UV laser beam irradiation system.

laser irradiation fluences is measured and analyzed. Additional features of our work include: (1) the 355 nm ultra-violet laser is used by considering the relatively strong absorption of graphene at this wavelength, which possibly means higher treatment efficiency than using lasers with longer wavelengths; (2) the SLG used is on the transparent fused silica substrate, as is rarely reported.

2. Experiment

SLG was prepared by chemical vapor deposition method on high purity copper foil and then transferred onto a foreign substrate. UV grade Corning 7980 fused silica with dimensions of $25.4 \times 25.4 \times 2\,\mathrm{mm}^3$ was used as the substrate. The substrate was first carefully polished using CeO_2 slurry and the surface roughness was controlled to be less than 1 nm. Then the substrate was washed thoroughly with distilled de-ionized water and absolute ethanol to rinse off any dusts and particles induced by polishing and storage. After that, poly methyl methacrylate (PMMA) was spin-coated on the surface of graphene on copper foil. The copper substrate was dissolved in a warm (70 °C) etchant solution (30% $FeCl_3$ and 5% HCl) and rinsed in deionized water. Then the PMMA-based graphene was transferred onto the as-polished fused silica substrate. Finally, the PMMA cover layer was completely removed in warm (70 °C) dimethylethylene solution and then dried.

The as-prepared SLG samples were irradiated with a nanosecond pulse laser (Nd-YAG Q-swithched solid laser). The wavelength was 355 nm and the pulse length (full width at half maximum, FWHM) was ~6.8 ns. The incident laser energy of each shot was measured by a Ophir calorimeter in front of the test sample with a wedge. The beam profile was measured with an Ophir & Spiricon beam analyzer. The temporal and spatial profile of laser beam was both near Gaussian with a $1/e^2$ diameter of 10 mm at the sample plane. Prior to laser irradiation experiment, the laser-induced damage threshold (LIDT) of the prepeared SLG samples was tested strictly according to Interanational Standard ISO 11254. Using the R-on-1 method, the tested LIDT for the as-produced SLG samples was 78 mJ/cm^2 at 355 nm. Thus, in order to avoid distinct laser-induced damage, the examined laser energy density in this study was set as 0, 10.5, 31.6, 51.8, 70.3 mJ/cm^2, respectively (seen in Table 1). To study the effect of laser fluence, for one SLG sample, only one pulse of laser shot was irradiated. The setup of the laser irradiation facility was depicted in Fig. 1.

Sacnning electron microscopy (SEM) was used to observe the typical morphological variations of SLG induced by laser irradiation. Raman and XPS spectra were employed to annalyze the structural modifications and surface functional groups of SLG samples. Raman spectra were performed with a Fourier-transform mode of Renishaw Raman system, using a 514 nm Ar$^+$ laser as excitation light source with a power of 5 mW. The diameter of the excited laser beam was about 2 mm, and thus the laser power density on the sample plane was about 0.158 W/cm^2. This low level power density won't induce destroy to graphene during Raman test. All Raman spectra were obtained in the 90° scattering configuration. The Raman spectra were measured over the range from 1000 to 3500 cm^{-1}. XPS spectra were acquired on a thermal electron ESCALAB 250 system. The X-ray source was a monochromatic Mg Ka (1253.6 eV) beam with an analysis area of ~3 mm^2 on sample surface. The optical transmittance of samples were characterized by the UV–vis NIR optical transmission spectra.

3. Results and discussions

Fig. 2 systematically presented the morphology modifications of graphene induced by laser pulse at different fluence. Fig. 2(a,b) showed the morphology of pristine state graphene. It demonstrated good surface quality, though some isolated nano-scale cracks/wrinkles were also observed. Fig. 2(c–f) clearly presented the morphology of SLG after laser irradiation. Unlike the folds [15] and nanometer-scale patterning [22] induced by femtosecond laser ablation, it is interesting to observe that nano-scale spherical carbon was formed on the SLG surface after UV nanosecond laser irradiation. Particularly, discrete carbon clusters looking like flower buds were observed for the graphene irradiated by laser pulse at 10.5 mJ/cm^2. When the laser fluence increased to 31.6 mJ/cm^2, nanometric-sized carbon balls were discovered. Larger size spherical carbon could be seen in images of Fig. 2e (51.8 mJ/cm^2) and Fig. 2f (70.3 mJ/cm^2). Besides, a small amount of folds and nano-scale holes presented on the surface of graphene irradiated by high laser fluence of 70.3 mJ/cm^2. The morphology modification revealed that graphene surface experienced high temperature, material melting, gasification and carbon atom re-deposition processes during irradiation-induced photon energy absorption. In detail, nanosecond laser irradiation caused photon energy deposition and transient temperature rise on graphene layer. Then, the irradiated graphene gasified quickly, producing carbon plasma with high temperature and high density. At the end of laser pulse, the cooling process began and deposition of carbon atoms/ions on graphene surface occurred, resulting in nano-sized carbon with different morphologies. The morphology of deposited nano-carbon depended on several factors such as the density and diffusion of carbon plasma as well as the property of the substrate. The density of carbon plasma was closely related with the laser fluence. Due to relatively large surface tension of the graphene and the difficulty in diffusion of carbon atoms, spherical carbon was easily formed during the condensation process.

Fig. 3 simultaneously presented morphologies of three types of carbon on the surface of laser-irradiated graphene, i.e. nano-sized dots, carbon clusters and spherical carbon. It was inferred that the spherical carbon was formed by the growth of small size nano-dots and carbon clusters.

Fig. 4 showed Raman spectra of the pristine state and laser irradiated SLG. The pristine graphene showed typical G peak (1585 cm^{-1}) and 2D peak (2700 cm^{-1}) belonging to SLG. The G band corresponds to the strethching virbration mode, E_{2g} phonon at the Brillouin zone center [23]. The *2D* band, which is also called *G'* in literature, originates from a second order Raman process involving a double resonance (DR) scattering event between *K* and *K'* points [24]. After laser irradiation, structural disorder-induced D peak (1350 cm^{-1}) immediately appearred, revealing defects and disorder created in graphene [25]. When the laser fluence increased to 50.8 mJ/cm^2, another defect-related D' peak (1620 cm^{-1}) appeared. Also, G peak broadened obviously at laser fluence of 70.3 mJ/cm^2.