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A study of defects induced by femtosecond laser on monolayer graphene

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Abstract

Defects induced by a femtosecond laser on monolayer graphene deposited on SiO_2/Si substrate has been studied by Raman spectroscopy. Under subthreshold irradiation condition, dependence of the D, G, and 2D Raman spectrum with various laser pulse energy was evaluated. The $I(D)/I(G)$ ratio was seen to increase with the growth of laser energy. The increase of the D' (intravalley phonon and defect scattering) peak at 1620 cm^{-1} appeared in defective graphene. The maximum concentration of defects were found for the 1 nJ pulse energy with the scan speeds of 0.1 mm/s. The growth of the full width at half maximum of D line and G line with increasing of the pulse energy were observed as well as the area ratio of D and G peaks.

Keywords: Laser, Graphene, Defects

1. Introduction

Graphene is atomic thick sheet of carbon arranged in a honeycombed lattice. It has extraordinary physical and chemical properties and is regarded as one of the most promising materials for advanced electronic application [1, 2]. The optical properties of the graphene lattice offer potential applications in optoelectronic devices and sensors [3]. Unlike traditional silicon manufacturing there is no advanced manufacturing route for graphene, which is still in its infancy, lasers offer one solution to fill this manufacturing gap. Laser based graphene processing has currently been explored in different conditions to produce ablation [4, 5], oxidation [6], reduction [7] and functionalisation [8, 9]. Specifically considering the effects of defects, both the nature and amount have a strong influence on the chemical and physical properties of graphene [10]. Control of the location of defects by ultrafast lasers provides a new method of graphene-based materials with novel properties [10]. In this paper we take the work further by analysing the defects using Raman spectrometry to gain greater understanding on how these are generated by the laser light matter interaction.

2. Experiment methods

The single layer graphene was grown (by the Cambridge Graphene Centre) on a 25 µm copper by chemical vapour deposition methods and then transferred onto 280 nm SiO_2 (on silicon) substrate with area 4 cm^2.

Laser processing was undertaken using an Amplitude Systèmes Satsuma, 1030 nm, 280 fs (verified using APE PulseCheck USB) at room temperature in air. The laser was circularly polarised and focused by an NA=0.35 objective lens (12 OI 09, Comar Optics) with a focal length of 12.7 mm to a spot diameter of 4.16 µm. Processed area was controlled through the motion of a high-precision translation stage.

Graphene was processed by irradiating with a range of pulse energies, the power fine-tuned with a diffractive attenuator (TOPAG DA10-800). The pulse energies were set at, 2 nJ, 1 nJ, 0.4 nJ, 0.2 nJ and 0.1 nJ, with process speed fixed at 0.1mm/s.

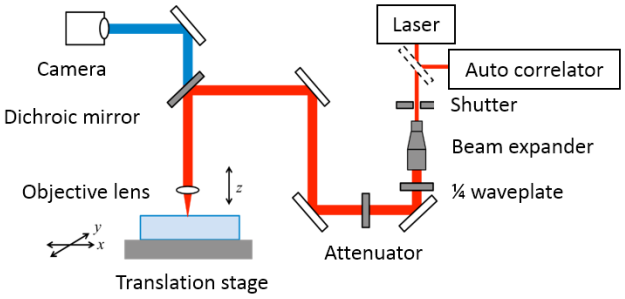

Figure 1. Experimental setup of femtosecond laser machining system.

3. Results and analysis

The cut areas of irradiated samples in a 5 µm x 5 µm were examined by Raman spectroscopy, using 514 nm laser excitation with a 100x objective. The Raman laser spot size was estimated to be 0.7 µm. The laser power maintained lower than 1 mW to prevent damage to the graphene [11]. The main features in Raman spectra of carbons are so-called G and D peaks, which lie at around 1580 cm^{-1} and 1360 cm^{-1}[12]. The G peak is due to the bond stretching of sp^2 atoms [12]. It is independent of excitation energy [12]. When the carbon systems reduced, disorder effects can be seen at defect locations or at graphene edges. D peak and D' peak (1620 cm^{-1}) are commonly observed in the sp^2 disordered carbon systems [13]. Unlike G peak, D and D' band are dispersive; varying with photon excitation energy [13]. The D peak is connected with an intervalley scattering process from K point to K' point in the Brillouin zone while the D' band is connected with an intravalley scattering around the K point or the K' point [12,13]. Fig. 2 shows results from the irradiation area, intense D and D' peaks are present. These peaks decreased with the reduction of laser pulse energy, demonstrating that the laser could introduced defects on monolayer graphene. When the pulse energy was 2 nJ ablation occurred and the G peak disappeared. The $I(D)/I(G)$ ratio was seen to increase with the growth of laser energy, Fig. 3. The maximum concentration of defects was found to be with 1 nJ pulse energy. When the pulse energy

reached 2 nJ, the graphene was ablated and G peak disappeared. When the pulse energy is lower than 2 nJ, the D and D' peak grew accordingly with the increase of the pulse energy. Further analysis of defects was given by studying A (D)/A (G) and full width half maximum (FWHM) of D lines and G lines. The ratio of A (D)/A (G) increased with growth of pulse energy under the ablation threshold. A similar increasing trend also occurred in the FWHM of D line and G line as well as the area ratio of D and G peaks.

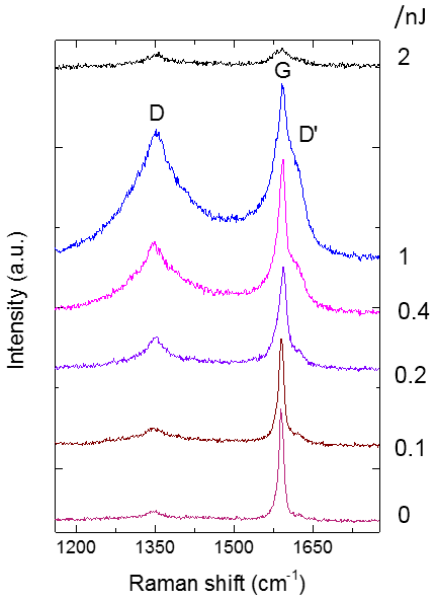

Figure 2. Raman analysis of laser irradiated area.

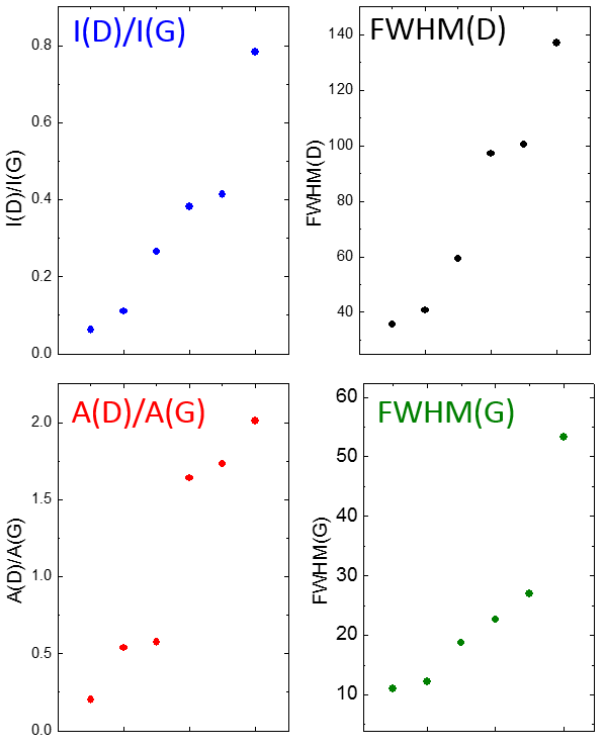

Figure 3. Defect analysis of laser irradiated area (from left to right: 0, 0.1 nJ,0.2 nJ,0.4 nJ,1 nJ,2 nJ).

4. Conclusion

A 280 fs fibre laser has been evaluated for patterning of monolayer graphene on a SiO_2/Si substrate. We have demonstrated direct femtosecond laser could be an effective technique to control the defects on the surface of graphene on 280 nm SiO_2 on silicon substrate in sub ablation threshold processing conditions.

Acknowledgements

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