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Effects of ultra-violet laser irradiation on graphene

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ABSTRACT

Graphene can be applied for transparent electrodes instead of indium tin oxide (ITO). For patterning of ITO, the maskless laser process was reported as a simple and fast process. Raman spectra and electrical resistances of graphene were measured before and after ultra-violet laser irradiation to investigate the possibility of maskless laser process. The Raman spectrum was affected by laser irradiation (>3 MW/cm^2), indicating defects generation. The resistance was more sensitive to laser irradiation than the Raman spectrum.

1. Introduction

Graphene has been attracting much attention of researchers since it was isolated from graphite [1]. From the viewpoint of practical application to electronic devices, one of the most interesting properties of graphene is the extremely high room-temperature carrier mobility up to 2×10^5 cm^2/V s [2,3], which may realize very high speed transistors. Another promising application of graphene is transparent electrodes in solar cells, touch-screen panels, and flat panel displays [4–7] which utilize high transmittance (more than 90%) and high conductivity of graphene.

Comparing the above two practical applications of graphene, i.e. channel material in transistors and transparent electrodes, the latter seems to be put into practical use in the nearer future, because there remains several problems to be solved to realize high-speed transistors using graphene such as controlling the band gap [8,9], suppression of the extrinsic scattering [2,3], and fabrication process of small transistor with short gate length. Concerning graphene transparent electrodes, on the other hand, trial products were already reported [4–7] and the mass fabrication technology is one of the most relevant matter of interest.

Indium tin oxide (ITO) is quite famous and widely used material for transparent electrodes. For patterning of ITO, the maskless laser process was reported as a simple and fast process comparing to the conventional lithography process with resist and masks [10,11].

In this paper, Raman spectra and electrical resistances of graphene were measured before and after ultra-violet (UV) laser irradiation in order to investigate the possibility of the maskless laser process of graphene.

2. Experimental

Graphene samples were prepared by the mechanical exfoliation from highly ordered pyrolytic graphite using a scotch tape [1]. The substrate was silicon, the surface of which was thermally oxidized. Thicknesses of the graphenes used in the present work were 2–3 nm, which were measured by an atomic force microscope (AFM) and correspond to roughly 3–6 layers of graphene. The samples were irradiated by a KrF excimer laser with a wavelength of 248 nm (5.0 eV). The pulse width was 20 ns. Since the laser photon energy is chosen to be larger than the C–C bond energy (~3.6 eV), the direct C–C bond breaking in graphene can be expected. The laser power used in the present work ranged 0–3.8 MW/cm^2. Such a large power should raise the temperature and may cause ablation of material, which is another possible mechanism of the laser process. In the case of carbon nanotubes, it was reported that the laser irradiation with the same wavelength and the similar power densities affect the morphology and the field-emission properties [12–15].

The Raman spectra were measured at room temperature using an incident laser wavelength of 488 nm before and after UV laser irradiation. Room-temperature electrical resistances were measured in the 4-terminal configuration which was prepared by the electron-beam lithography and lift-off technique.

To observe changes in the Raman spectra, the graphene samples were irradiated by 500 laser pulses at 100 Hz with a particular laser power density. After measuring the Raman spectra, the samples were irradiated by 500 more laser pulses with an increased laser power density. This procedure was repeated with increasing laser power density up to 3.8 MW/cm^2.

3. Results and discussion

Fig. 1a and b shows the scanning-electron-microscope (SEM) photographs of a graphene before and after laser irradiation with

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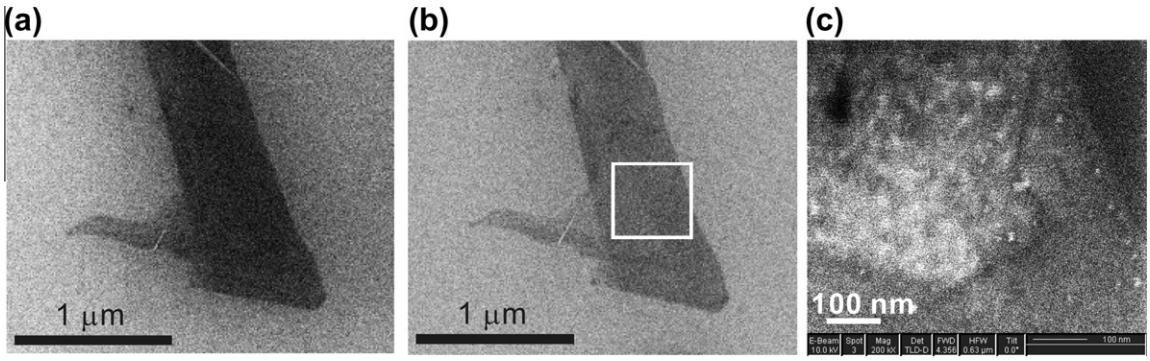

Fig. 1. SEM micrographs of graphene before (a) and after (b) laser irradiation with a power density of 3.8 MW/cm^2. (c) An enlargement of the white square in (b).

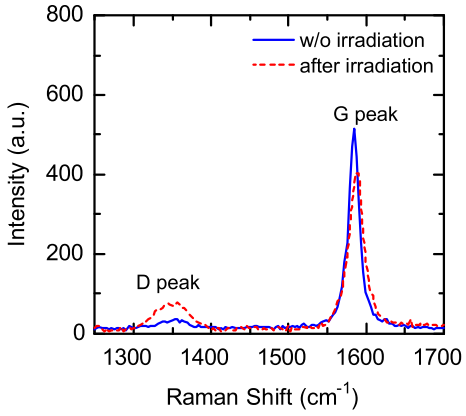

Fig. 2. Raman spectra of graphene before and after laser irradiation with a power density of 3.8 MW/cm^2.

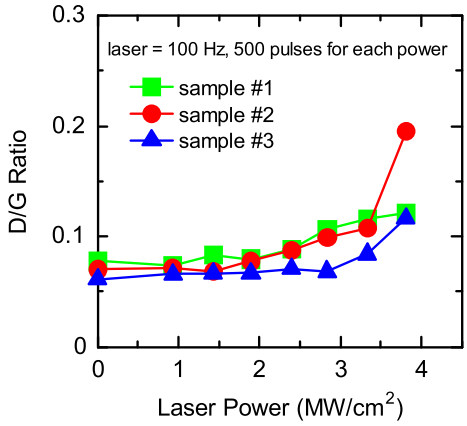

Fig. 3. D/G ratio of Raman intensity as a function of laser power density.

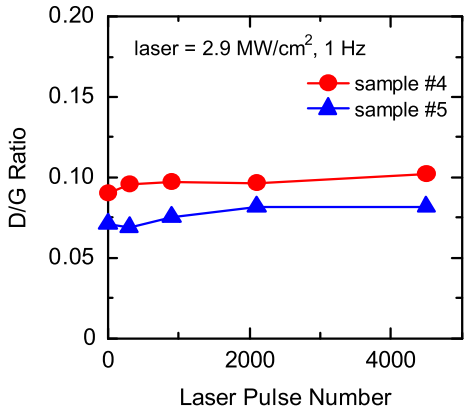

Fig. 4. D/G ratio of Raman intensity as a function of laser pulse number.

a power density of 3.8 MW/cm^2, respectively, while (c) is an enlargement of the white square in (b). The average thickness of the central part measured by AFM decreased from 2.6 nm (a) to 1.5 nm (b) by laser irradiation. As shown in Fig. 1c, the surface of the graphene became rough after laser irradiation. Although the graphene surface before laser irradiation with large magnification is not shown, it was quite smooth without any structures.

Fig. 2 shows the Raman spectra of graphene before and after laser irradiation with a power density of 3.8 MW/cm^2. The intensity of the G peak decreased by laser irradiation while that of the D peak increased. This is due to the defects induced by laser irradiation. The similar change in Raman spectra of graphene irradiated by electron beams was reported and discussed with respect to the defects in detail [16]. Although the G peak in Fig. 2 shows a small shift to the higher frequency after irradiation, the origin for the shift is presently unclear. The Raman intensity ratios of the D peak to the G peak (D/G ratios) are shown as a function of laser power density in Fig. 3. The laser irradiation with a power density less than approximately 3 MW/cm^2 hardly affected the D/G ratio.

As mentioned in the previous section, the mechanism for the laser process can be direct C–C bond breaking by photon energy or thermal ablation. In order to discuss the mechanism, the laser of 2.9 MW/cm^2 with a frequency of 1 Hz was used. The low frequency (1 Hz) comparing to the pulse width (20 ns) was chosen to avoid the thermal effect. Moreover, the laser with the power density of 2.9 MW/cm^2 hardly affected the D/G ratio as shown in Fig. 3. Therefore, only the effect of the direct C–C bond breaking by phonon energy can be investigated using these experimental parameters if the samples were irradiated during long time. Fig. 4 shows the D/G ratio as a function of number of laser pulse. The D/G ratio did not change even after irradiation of 4500 laser pulses. This indicates that the mechanism is not due to the direct bond breaking by photon but the thermal effect.

In order to discuss the change of electrical resistance of graphene irradiated by the UV laser, the laser with a power density of less than 1.5 MW/cm^2 was used because the laser of more than 1.5 MW/cm^2 destroyed the electrode fabricated on the graphene to measure the resistance. The resistance was measured after a single pulse irradiation, then the sample was irradiated by the next laser pulse with the larger power density. This procedure was repeated. The resistance increase was observed when the laser power density was 1.4 MW/cm^2. The second pulse with the same power density caused more increase of the resistance. The observed electrical resistance is shown in Fig. 5 as a function of laser

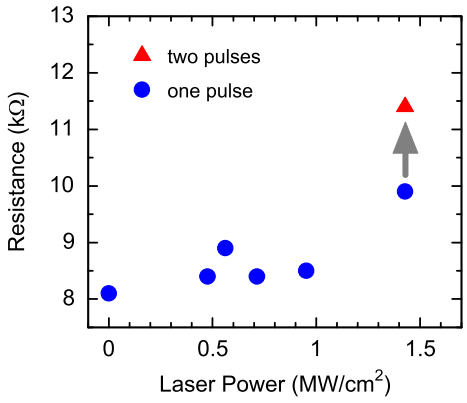

Fig. 5. Resistance as a function of laser power density.

power density. The laser irradiation with a power density of less than 1 MW/cm^2 hardly affected the resistance, while that of 1.4 MW/cm^2 increased the resistance.

4. Summary

In summary, Raman spectra and electrical resistances of graphene were measured before and after UV laser irradiation. The Raman spectrum was affected by laser irradiation with a power density of more than 3 MW/cm^2, indicating defects generation by laser irradiation. The resistance increased at the laser power density of 1.4 MW/cm^2, which means that the resistance is more sensitive to laser irradiation than the Raman spectrum. To achieve complete removal of graphene, larger laser power density than 3.8 MW/cm^2 is required, while electrical breakdown might be possible using smaller power density than that. Using such large power, a properly designed lens system to achieve fine focusing, and a computer-controlled two-axis stage or a computer-controlled mirror to scan laser beams, maskless patterning of large-area graphene transparent electrode in air can be achieved.

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