

Plasma oxidation of thermally grown graphenes and their characterization

Byeong-Joo Lee, Goo-Hwan Jeong*

Department of Advanced Materials Science and Engineering, Kangwon National University, Chuncheon, Gangwon-do 200-701, Republic of Korea

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ABSTRACT

We report the plasma oxidation of thermally synthesized graphenes and their characterization using Raman spectroscopy and atomic force microscope (AFM). A graphene was synthesized by thermal chemical vapor deposition with methane and transferred onto trench substrate to make suspended configuration in order to exclude substrate effects. The air plasma treatment at 0.4 W for 5 min and property characterization were alternately performed to address the effect of oxidation. After the oxidation, a drastic change in Raman spectra was observed, which implies that considerable structural changes occurred in the graphene. Interestingly, we observed from the Raman and AFM analyses that the number of layers can be reduced by the controlled plasma oxidation treatment. The results may open the possibility of graphene formation from graphite sheets through the precise control of plasma treatment conditions.

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1. Introduction

Since its discovery in 2004, graphene has been attracted significant attention due to its outstanding properties [1–3] and potential applications to electronic device, sensors, nano-electromechanical systems, transparent conductive films, and composites [4–7]. In general, the fine structures of graphene, such as the layer numbers, edge structures, defects, and chemical doping, are major factors to determine the physical properties of graphene. Thus, the researches on not only the controlled growth of graphene but also their chemical doping or functionalization are being intensively carried out to exploit the potential uses.

A chemical vapor deposition (CVD) [8,9] has been conceived as the most suitable for a large area production with a high structural integrity, and most CVD works have concentrated on the thickness uniformity over the substrates, which is the most important factor for aforementioned applications. In addition, the graphene functionalization has also been investigated to open the inherent closed electronic bandgap of the graphene, which will be extremely useful for electronic and optical applications. From this background, there has been a number of researches and the doping with hydrogen [10,11], nitrogen [12,13], or oxygen via gas phase [14] and plasma [15–17] has been known to have a function of modulation on the graphene electronic structures. Especially, the plasma-assisted

graphene oxidation has great potential for not only functionalization but also structural design by selective etching through the control of plasma parameters such as plasma density, temperature, and potential. However, the effects of plasma treatment on the probable structural or morphological changes and their influences on graphene properties should be performed further.

In order to investigate the detailed changes of graphene structure, we here perform the plasma oxidation of CVD-synthesized graphenes and report their results focusing on the structural and optical properties. For a comparison, a mechanically exfoliated graphene was also examined using the same plasma batch. As a result of the plasma oxidation, we observed a drastic change in Raman spectra, which implies that structural changes occurred in the graphene. Interestingly, according to the results of Raman and AFM analyses, we found that the number of layers can be reduced by the controlled plasma oxidation treatment. This is very important from the fact that we could make thin-layered graphenes, which are more applicable in various fields, through the plasma-assisted post-treatment with precisely controlled plasma conditions.

2. Experimental

For the CVD synthesis and transfer of graphene, we described in detail elsewhere [9]. Briefly, we used Ni thin films (300-nm thick) as catalytic layer and installed the substrate on the center of CVD furnace (1 inch diameter). The chamber was pumped down to 6.5×10^{-2} mbar and filled with Ar (500 sccm) and H₂ (500 sccm) gases to atmospheric pressure. After heating up to synthesis

* Corresponding author. Tel.: +82 33 250 6268; fax: +82 33 250 6260.
E-mail address: ghjeong@kangwon.ac.kr (G.-H. Jeong).

temperature of 1000 °C, the mixture of CH₄ (5 sccm) and H₂ (1500 sccm) was introduced to the chamber for 5 min. After the synthesis, the chamber was cooled with the rate of 4 °C/min. The synthesized graphene was transferred to trench substrate to make suspended configuration in order to exclude substrate effects. On the other hand, we also prepared mechanically exfoliated graphene to compare the oxidation behavior.

The prepared graphenes were plasma treated using dc plasma CVD system, which has unsymmetrical parallel electrodes geometry to concentrate the plasma ions. After installation of the samples on the cathode substrate, the chamber was filled with air and the plasma was ignited by applied bias of 400 V. The plasma power was maintained at 0.4 W during 5-min treatment. The plasma oxidation and property characterization were alternately performed to investigate the changes of graphene properties. For the graphene analysis, we used optical microscopy, Raman spectroscopy (Aramis, Horiba Jobin), transmission electron microscopy (TEM, JEM 2100F, JEOL), and atomic force microscopy (AFM, XE-70, Park System).

3. Results and discussion

The optical images of exfoliated and transferred graphenes onto trench substrates were shown in Fig. 1(a) and (b), respectively. In general, the number of graphene layers can be distinguished by the contrast difference in optical images. The CVD-grown samples were consisted of mono-, bi-, and multi-layered graphenes with a few micrometer domain sizes. Fig. 1(c) and (d) are Raman spectra from Fig. 1(a) and (b), respectively, and the colors of the Raman profile mean the acquisition points at the same colored dots in Fig. 1(a) and

(b). We obtained intensive peaks around 1350, 1600, and 2700 cm⁻¹, which are defined as the defect-induced D-band, the graphitic C–C vibration-related G-band, and the G'-band as overtone of the D-band, respectively. In general, the intensity ratio of the D and G-bands (ID/IG) increases with an increase of the structural disorder in the examined graphene. In addition, the intensity ratio of the G- and G'-band (IG/G') has been known to below 1 in mono-layered graphene. On the other hand, as the number of graphene layer increases, the value of IG/G' increases over 1 and the profile of G'-peak was changed from single Lorentzian profile to unsymmetrical shape [18,19]. To directly observe the graphene structures, we transferred the synthesized graphenes onto TEM grid and their results are shown in Fig. 1(e) and (f), which correspond to monolayer and few-layer graphene, respectively. Finally, we confirmed that the microscopic observation results are well coincided with the Raman results. Thus, we have performed the 2-dimensional Raman mapping to get more generalized areal information on oxidation effects.

Fig. 2 presents the result of planar Raman mapping before and after the 5-min plasma oxidation of the mechanically exfoliated sample, the same sample of Fig. 1(a). As shown in Fig. 2(a)–(c), the sample has no D-band intensity over the whole area [Fig. 2(a)], but the G-band intensity gradually increases from mono to multilayer graphenes [Fig. 2(b)]. On the other hand, the intensity of the G'-band was enhanced from multi to monolayer graphene [Fig. 2(c)].

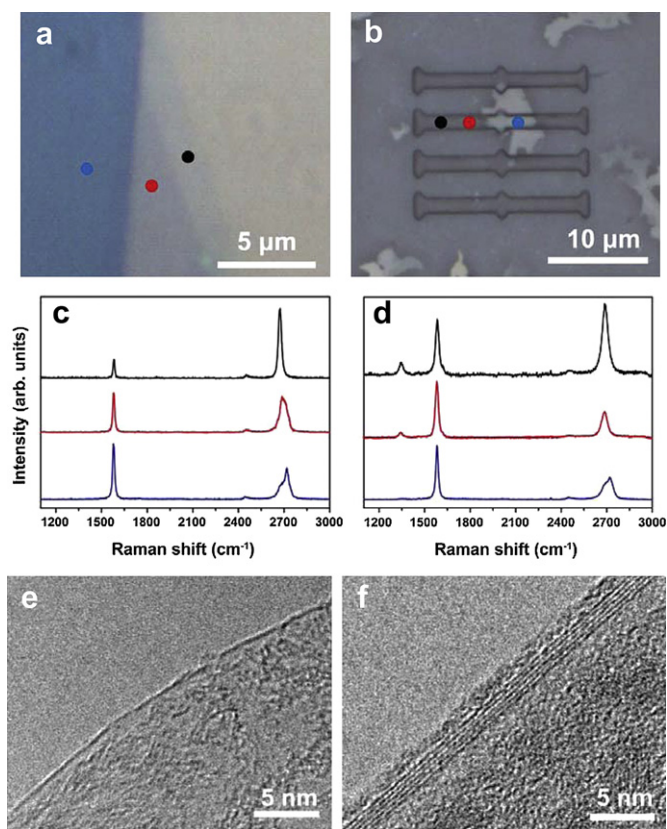


Fig. 1. Optical microscope images of (a) exfoliated and (b) synthesized graphene. Raman spectra obtained from the (c) exfoliated and (d) synthesized graphenes. (e) and (f) show TEM images of the synthesized graphenes.

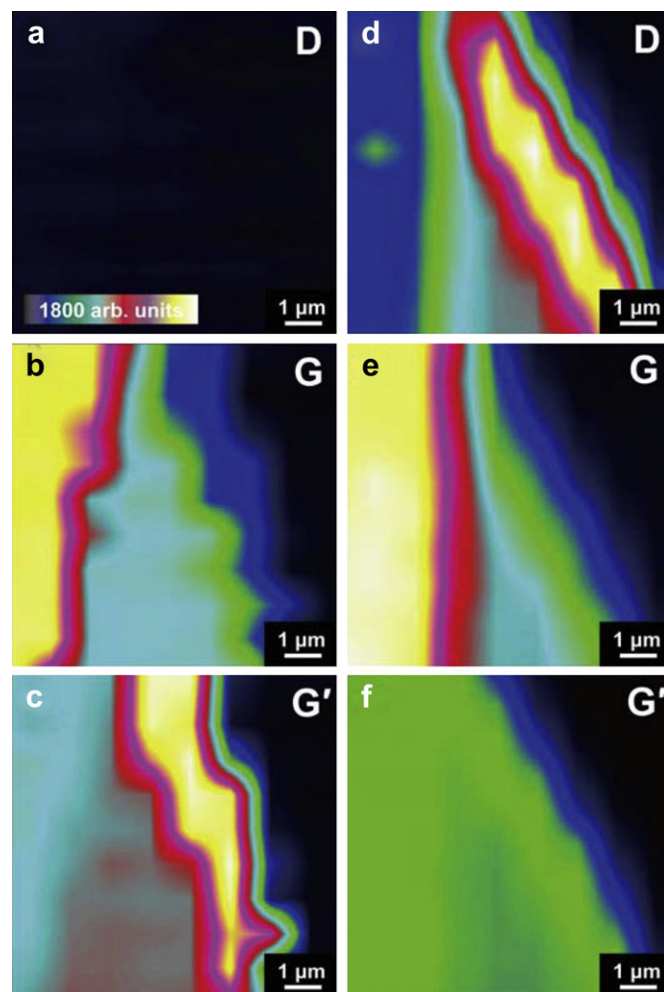


Fig. 2. Raman mapping images of D-, G- and G'-bands of exfoliated graphene (a–c) before and (d–f) after plasma oxidation for 5-min.

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