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Effect of ultraviolet light irradiation and ion collision on the quality of multilayer graphene prepared by microwave surface-wave plasma chemical vapor deposition

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ABSTRACT

We successfully synthesized graphene by microwave surface-wave plasma chemical vapor deposition (CVD) and investigated the effect of UV light and ion collision from the plasma exposure during graphene synthesis. The graphene obtained here was multilayer graphene consisting of approximately 5 layers according to cross-sectional transmission electron microscopy results. The quality of the graphene was compared between the case where UV light was irradiated from the plasma and the case where the UV light was blocked by a grid-inserted CVD configuration. Quality was evaluated by Raman scattering spectroscopy. There were more defects in the graphene prepared with irradiation of UV light than with blocking of UV light. Furthermore, we investigated the effects of ion collisions that occurred in the plasma, but they had no effect on graphene quality. These results suggest that during graphene synthesis, UV light from the plasma affects its crystallinity. The electrical conductivity, optical transmittance and mobility of the transferred graphene films were measured to clarify the effects of UV light irradiation.

1. Introduction

Graphene is electrical conductive, optical transparent, mechanically strong, and chemically stable [1]. Because of these unique characteristics, graphene is expected to be used in transparent electrodes [2–4], wiring materials [5], mechanical sensors [6], high speed electronic devices [7], chemical sensors [8], and solar cells [9]. Various methods for synthesizing graphene have been attempted, including exfoliation of graphene [10], thermal chemical vapor deposition (CVD) methods [11], SiC sublimation methods [12], and graphene oxide methods [13].

We have targeted the synthesis of high-quality multilayer graphene consisting of approximately 5 layers by microwave surface-wave plasma CVD because it can be developed into a roll-to-roll process for synthesizing large-area sheets for industrial applications. There have been many reports of graphene synthesis by microwave surface-wave plasma CVD, and it is known that this method produces many more defects than thermal CVD does and that improvement of the growth process is necessary [14].

To address these shortcomings, we propose a growth method using two grids by which ultraviolet (UV) light is blocked and only carbon radicals are able to pass through. This paper describes the effects on graphene of using these grids and presents the results of plasma emission spectroscopy, Raman scattering spectroscopy, and transmission electron microscopy (TEM). In addition to the effects of UV light irradiation, the effects of ion collisions from the plasma exposure on the quality of the graphene are investigated. To clarify the effects of UV light irradiation, the electrical conductivity, optical transmittance, and carrier mobility of CVD graphene films transferred onto flexible substrates were characterized.

2. Materials and methods

2.1. Synthesis of multilayer graphene

Fig. 1 shows a schematic diagram of the setup for microwave surface-wave plasma CVD used in this research. Fig. 2 shows photographs of the grids for blocking the UV light and a schematic diagram of their relative placement. Copper plates (1 mm thick) with dimensions of 100 mm × 100 mm were used for the grids. The grid holes have a diameter of 5 mm and a pitch of 10 mm, and the grids were arranged such that the centers of the holes were offset by 10 mm between

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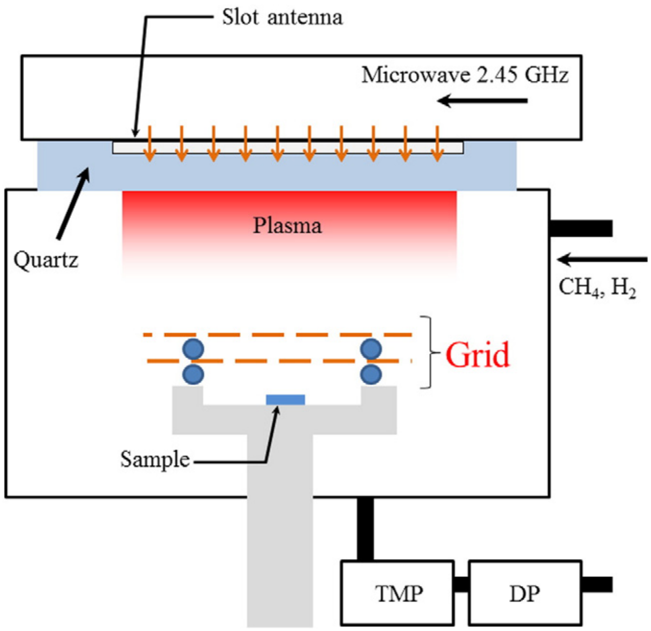

Fig. 1. Schematic diagram of setup for microwave surface-wave plasma CVD (DP: dry pump; TMP: turbo molecular pump).

the upper and lower grids. The distance between the grids was 6 mm, and the distance between the lower grid and the sample was 6 mm.

Copper foil (35 μm thick) with dimensions of 20 mm × 20 mm was used for the growth substrate and annealed in advance for 2 h at 1000 °C in an Ar + H_2 (3%) atmosphere in order to control the surface properties.

Graphene synthesis was performed by evacuating the CVD apparatus using a dry pump and turbo molecular pump down to a vacuum of approximately 5×10^{-5} Pa and then creating a plasma by applying 2.45 GHz microwaves at 1000 W with a flow of 6 sccm CH_4 and 100 sccm H_2 at approximately 15 Pa while maintaining the substrate temperature at 800 °C. The distance between the quartz plate and substrate stage was 60 mm. Since the growth rate differed depending on whether the grids were present, the growth time was set to 1 min without the grids and 10 min with the grids. Furthermore, to investigate the effects of ion collisions, growth was conducted while applying a DC bias from an external device with the grids insulated from the substrate stage. Table 1 shows the experimental conditions used in this research.

Table 1
Sample fabrication parameters.

Sample no.	Grids	Substrate temperature (°C)	Deposition time (min)	DC bias (V)
1	Not installed	800	1	0
2	Installed	800	10	0
3	Installed	800	10	−70–70

2.2. Graphene transfer onto flexible substrate

Fig. 3 shows the graphene transfer process used here. A polyethylene terephthalate (PET) film with adhesive layer was attached at 90 °C using a laminator, and then the copper was wet-etched using a 10 wt% aqueous solution of iron nitrate. After the copper had completely dissolved, the sample was rinsed in distilled water and the various measurements were performed.

2.3. Characterization methods

The crystallinity of the obtained graphene was evaluated by Raman scattering spectroscopy using 532 nm excitation light (inVia, Renishaw). The graphene on PET was cut into dimensions of 10 mm × 10 mm and Hall measurements were performed with a current of 1.0×10^{-4} A by applying an AC magnetic field (ResiTest 8400, TOYO Corporation). Fig. 4 shows the external appearance and attachment of the sample used for Hall measurements. Sheet resistance measurement using the four-probe method (RG-7C, NAPSON) and transmittance measurements (V-570, JASCO) were performed. Transmittance measurements were evaluated using transmission light. Planar transmission electron microscopy (TEM; JEM-2100F, JOEL) was performed on the graphene after wet etching of the Cu foil to evaluate the crystallinity. The number of layers was measured by TEM observation after milling the samples with a focused ion beam (JIB-4500, JOEL).

3. Results and discussion

3.1. Graphene growth with and without the grid

In plasma CVD, UV light and ions from the plasma are problems. It is difficult to investigate these two factors at the same time. In this section, we mainly investigate the effects of UV light depending on the presence or absence of the grids. We discuss the ion damage in Section 3.2, where we show that the effects of ion damage can be ignored.

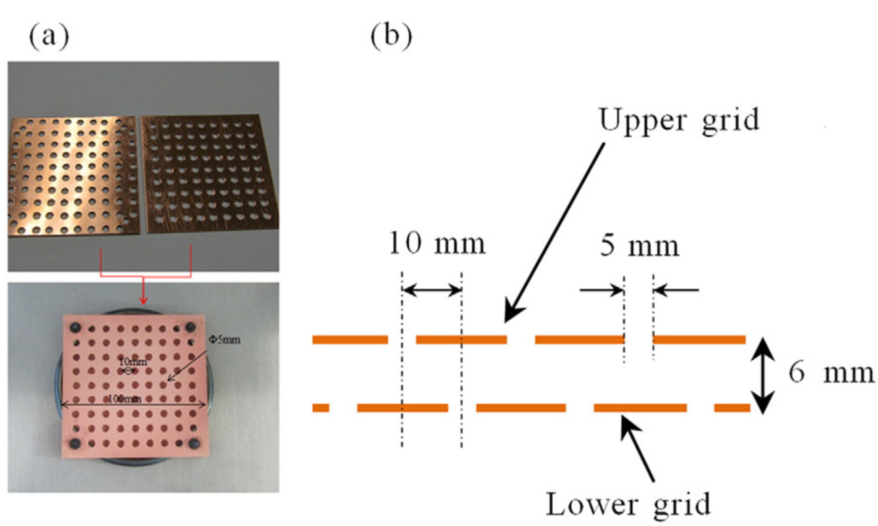

Fig. 2. (a) Photos of the grids (top view). (b) Schematic diagram of the relative positions of the upper and lower grids (cross-sectional view).