We successfully synthesized a thin graphite film by microwave surface-wave plasma chemical vapor deposition and investigated the effect of UV light from the plasma during the film synthesis. The quality of the film was compared between the case where UV light was irradiated from the plasma and the case where the UV light was blocked. The quality was also evaluated by Raman scattering spectroscopy. There were more defects in the thin graphite film prepared with UV light irradiation than with the UV light blocked. These results suggest that during the synthesis of the thin graphite film, UV light affects its crystallinity. However, charged particles from the plasma had no effect on the quality.

Cross-sectional transmission electron microscopy revealed that the thin graphite film consisted of approximately 20 layers.

Key words: Thin graphite film, Graphene, Chemical vapor deposition, UV light, Raman scattering, Transmission electron microscopy

1. INTRODUCTION
Graphene, which consists of a few layers of graphite sheets, has attracted much attention [1-13]. Commercially available graphite sheets are several micrometers thick. In this work, we propose a method for creating thin graphite films that consist of several tens of layers of graphite sheets and have thickness intermediate between few-layer graphene and several-micrometer-thick graphite sheets.

We focused on the synthesis of thin graphite film by microwave surface-wave plasma chemical vapor deposition (CVD) because it can be developed into a roll-to-roll process for synthesizing large areas for industrial applications. There have been many reports of graphene synthesis by microwave surface-wave plasma CVD. This method produces many more defects than hot CVD does, and 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 can pass through. This paper describes the effects on the graphene of using these grids to block UV light. Furthermore, we show experimentally that the effects of charged particles from the plasma can be ignored.

2. EXPERIMENTAL METHODS
2.1 Synthesis
Figure 1 shows a schematic diagram of the setup for microwave surface-wave plasma CVD used in this research. Figure 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 × 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 the upper and lower grids. The distance between the grids was 6 mm, and the distance between the lower grid and sample was 6 mm. Copper foil (35 μm thick) with dimensions of 20 × 20 mm was used for the growth substrate and annealed in advance for 2
Synthesis of Thin Graphite Film by Microwave Surface-Wave Plasma Chemical Vapor Deposition

Sample fabrication parameters

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Grids</th>
<th>Substrate temperature (°C)</th>
<th>Deposition time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Not installed</td>
<td>800</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Installed</td>
<td>800</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>Installed</td>
<td>700</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Installed</td>
<td>600</td>
<td>20</td>
</tr>
</tbody>
</table>

Thin graphite film 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 CH₄ and 100 sccm H₂ at approximately 15 Pa while maintaining the substrate temperature at 600, 700, or 800 °C. The distance between the quartz plate and substrate stage was 60 mm. Because the growth rate depended on whether the grids were present, the growth time was set to 1 min without the grids and 20 min with the grids. Table 1 shows the experimental conditions in this research. Furthermore, to investigate the effects of charged particles from the plasma, thin graphite films were grown using the same parameters as Sample 2 but with a DC voltage in the range of -70 to 70 V applied to the grid. The grid and stage were insulated from each other.

2.2 Transfer

Figure 3 shows the thin graphite film 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

The crystallinity of the obtained thin graphite film was evaluated by Raman scattering spectroscopy using 532 nm excitation light and 250 mW injection power (inVia, Renishaw). The thin graphite film on PET was cut into dimensions of 1.0 × 10⁻⁴ A by applying an AC magnetic field (ResiTest 8400, TOYO Corporation). Figure 4 shows the external appearance and attachment of the sample used for Hall measurements. Sheet resistance measurements 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, JEOL) was performed on the thin graphite film 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, JEOL).

3. RESULTS AND DISCUSSION

3.1 Plasma emission

Figure 5 shows the emission spectrum of the plasma in this experiment. Hα, Hβ, Hγ, CH, and C₂ have peaks at 656, 486, 434, 431, and 516 nm. The spectrum shows that the hydrocarbon CH₄ decomposed to create decomposition products such as CH* and C₂* and carbon radicals. It is also clear that UV light below 400 nm was generated. It is known that C-C bonds, which form the main backbone of organic materials, have a binding energy of 3.82 eV, which corresponds to a UV wavelength of 325 nm. The emission spectrum in Fig. 5 shows that much of the light is at or below 325 nm, and can thus break C-C bonds.

3.2 Raman spectra

Figure 6 shows a comparison of Raman scattering between the cases with and without the grids installed. The peak near 1350 cm⁻¹ indicates defects in the thin graphite film. This part of the spectrum is called the D-band. The part of the spectrum near 1590 cm⁻¹ is called the G-band, and this is where the peak originating from sp² carbon appears. The D-band peak is larger for the 800 °C synthesis than for the 700 °C synthesis. It is thought that the higher substrate temperature increased the crystallinity which shows that UV light hindered crystal growth.

Figure 7 shows Raman scattering results for the thin graphite film synthesis. Hα, Hβ, Hγ, CH, and C₂ have peaks at 656, 486, 434, 431, and 516 nm. The spectrum shows that the hydrocarbon CH₄ decomposed to create decomposition products such as CH* and C₂* and carbon radicals. It is also clear that UV light below 400 nm was generated. It is known that C-C bonds, which form the main backbone of organic materials, have a binding energy of 3.82 eV, which corresponds to a UV wavelength of 325 nm. The emission spectrum in Fig. 5 shows that much of the light is at or below 325 nm, and can thus break C-C bonds.
synthesis was successful. The behavior of the D-band peak differs according to the presence or absence of the grids, thus clearly indicating that UV light has an effect during thin graphite film synthesis.

Figure 7 shows Raman scattering results for the thin graphite films synthesized at substrate temperatures of 600, 700, and 800 °C with the grids installed. The 2D-band peak was observed in the spectrum for the 700 °C synthesis but not the 600 °C synthesis, indicating that thin graphite films can be created at 700 °C or higher. The D-band peak was smaller for the 800 °C synthesis than for the 700 °C synthesis. It is thought that the higher substrate temperature increased the crystallinity through increased mobility of carbon radicals, resulting in bonds reforming at appropriate sites.

The ratio $I_D/I_G$ of the Raman scattering spectra was used to evaluate the crystallinity of the thin graphite film. Furthermore, the crystal grain size can be estimated by using the following equation [15].

$$L_a(\text{nm}) = (2.4 \times 10^{-10})\lambda^4(I_D/I_G)^{-1}$$

Here, $L_a$ is the crystal size of the thin graphite film, $\lambda$ is the wavelength of the excitation laser, $I_D$ is the height of the D-band peak, and $I_G$ is the height of the G-band peak.

Table 2 shows the $I_D/I_G$ ratios and crystal sizes of the samples obtained in this research. The crystallinity varied depending on the growth temperature and the presence or absence of the grids. Growth at a substrate temperature of 800 °C with the grids installed clearly gave the best thin graphite film crystallinity. The crystal size of Sample 2 (UV light blocked) was approximately threefold that of Sample 1 (UV light present), which shows that UV light hindered crystal growth.

3.3 Physical properties

The transmittance, sheet resistance, and Hall measurement results for the samples are summarized in Table 3. As the substrate temperature was increased, the sheet resistance
Synthesis of Thin Graphite Film by Microwave Surface-Wave Plasma Chemical Vapor Deposition

decreased and the mobility increased. Furthermore, the mobility was significantly lower and the sheet resistance was much larger in the thin graphite film prepared without the grids installed than in that with the grids installed. These results were attributed to the threefold larger grain size of the thin graphite film prepared with the grids installed, which meant that the thin graphite film had fewer grain boundaries and less carrier scattering. In Fig. 8(a), the crystal size is large and the number of scattering events at grain boundaries is small. For comparison, Fig. 8(b) shows a schematic for the case where the crystal size is 1/3 of that in Fig. 8(a). The mobility would be lower owing to the larger number of scattering events.

3.4 TEM observation

Figure 9 shows a planar TEM image and electron diffraction diagram for Sample 2. The diffraction spots exhibit a clean hexagonal shape, indicating that the multiple layers of the thin graphite film are cleanly stacked. No halos originating from amorphous structure were found, indicating that the crystallinity was good.

Figure 10 shows a cross-sectional TEM image of Sample 2. Multiple layers of stacked graphite can be seen. The thickness of the multiple layers is approximately 6.7 nm, and it was estimated from the thickness of a single layer of graphene (0.34 nm) that around 10 layers were present. From the transmittance measurements, the transmittance was 65% (at 550 nm), and back-calculating from the absorption of a single layer (2.3%) gave an estimate of around 15 layers. Because the transmittance measurement uses the average value for transmitted light within a diameter of 10 mm, a difference equivalent to 5 layers is expected to occur.

3.5 Application of DC voltage to the grid

In plasma CVD, the film properties of thin films are modified by ion collisions. The electron temperature is lower in microwave surface-wave plasma CVD than in other types of plasma CVD, and the ion damage from the plasma is smaller. In the experiments in Section 3.2 and 3.3, we could not remove the effects of ion collisions. In this section, we present the results of applying a DC bias to the grids, which were insulated from the substrate stage, and we discuss the effects of ions from the plasma.

Figure 11 shows the I_D/I_G ratio from Raman scattering measurements for the thin graphite film grown with a DC bias applied to the grids, which were insulated from the substrate stage. Although the DC bias was varied between -70 and 70 V, the I_D/I_G ratio remained virtually unchanged. If ions from the plasma are present near the growth substrate, the H- ions are expected to be accelerated and reach the substrate, thereby interfering with the growth of sp² carbon and increasing the I_D/I_G ratio. Regardless of the UV light being blocked by the grids and the application of a DC bias for accelerating the ions, the I_D/I_G ratio did not change. This experimentally demonstrates that the effects of ions are small.

Furthermore, we discuss the sheath potential that accelerates charged particles. The sheath potential can be expressed as shown in Eq. (2) [16].

\[
\phi = -\frac{k_e e}{e} \ln \left( \frac{N_e}{N_0} \right)
\] (2)

Here, \( \phi \) is the sheath potential, \( k \) is the Boltzmann constant, \( T_e \) is the electron temperature, \( e \) is the charge of an electron, \( M_e \) is the mass of an electron. The electron temperature in microwave surface-wave plasma CVD with the same configuration as this experiment is 3 eV [17, 18]. However, in regular plasma CVD, it has been reported to be around 10 eV [18]. If we assume that the parameters other than the electron temperature are the same, then the sheath potential is proportional to the electron temperature. This means that a threefold difference in sheath potential occurs between microwave surface-wave plasma CVD and other types of CVD. This is also supported by the sheath potential calculation, where the effect of ion collisions from the plasma is also smaller compared with that in other types of CVD.

4. CONCLUSION

The plasma light from the microwave surface-wave plasma CVD used in this research contained UV light with wavelengths below 325 nm. By blocking the UV light originating from the plasma, defects in the thin graphite film could be reduced and the crystal size could be improved threefold. Furthermore, the thin graphite film consisted of approximately 20 layers. We also showed experimentally that the effects of charged particles from the plasma can be ignored.

5. REFERENCES


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