DC Biasing Effects on Properties of Carbon Nanowalls by Microwave Surface-Wave Plasma Chemical Vapor Deposition and Towards Transparent Electrode

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We synthesized carbon nanowalls on a Si substrate by microwave surface-wave plasma chemical vapor deposition. The Raman scattering I_D/I_G ratio was changed by altering the DC bias applied to the growth substrate and the decrease in I_D/I_G with increasing DC bias appears to arise from the growing length of the carbon nanowalls. The ultrasonically separated carbon nanowalls in ethanol exhibited strong 2D-peak intensity and significant graphitization. A graphite layer of approximately 10 nm grew parallel to the substrate initially, and the carbon nanowalls grew on top of that. When the nanowalls were dispersed in ethanol and spin-coated onto PET, they exhibited a transmittance of 81% and a sheet resistance of 52 kΩ/□ without reduction treatment used in the graphene oxide.

Key words: Carbon Nanowalls, CVD, Ultrasonic, Raman, TEM

1. INTRODUCTION
The superior properties of carbon nanowalls, including high specific surface area [1-3] and excellent electric field emission [4], mean that they are expected to have many commercial applications, for example, in electrode materials in rechargeable batteries [5, 6], catalyst supports in fuel cells [7, 8], electric field and electron emission sources [9, 10], gas storage materials [11, 12], and gas sensors [13].

The crystallinity of carbon nanowalls is improved by using microwave surface-wave plasma chemical vapor deposition (CVD) and applying a DC bias to the growth substrate. Carbon nanowalls can be peeled off the substrate and dispersed in ethanol, and they can be used as a substitute for graphene oxide. Unlike graphene oxide, carbon nanowalls do not require reduction with chemicals such as hydrazine, which is very dangerous.

In this study, we investigated the DC bias dependence of carbon nanowalls fabricated by microwave surface-wave plasma CVD and the dispersion of carbon nanowalls in ethanol for spin-coating onto polyethylene terephthalate (PET).

2. EXPERIMENTAL METHODS
2.1 Synthesis
Figure 1 shows a schematic of the microwave surface-wave plasma CVD equipment consisting of an external DC power supply that applied a DC bias to the substrate stage, which was electrically isolated from the CVD unit by a quartz plate. Si was used as the growth substrate.

The CVD unit was evacuated to 5 × 10⁻⁵ Pa by a dry pump and a turbo molecular pump, and then a plasma was formed. The carbon nanowalls were synthesized by applying 2.45 GHz microwaves at 1000 W at a substrate temperature of 650 °C and a flow of 35 sccm C₂H₂, 35 sccm Ar, and 200 sccm H₂ at 15 Pa. The growth time was 15 min. The distance between the quartz...

Table 1 Sample fabrication parameters.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Substrate temperature (°C)</th>
<th>DC bias (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>650</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>650</td>
<td>20.0</td>
</tr>
<tr>
<td>3</td>
<td>650</td>
<td>30.0</td>
</tr>
<tr>
<td>4</td>
<td>650</td>
<td>36.5</td>
</tr>
</tbody>
</table>

Figure 1 Schematic of microwave surface-wave plasma CVD equipment. (DP: dry pump; TMP: turbo molecular pump)

Figure 2 Carbon nanowalls suspended in ethanol.
plate and substrate stage was 40 mm. Table 1 shows the experimental parameters used in this research.

2.2 Separation and liquid dispersal of carbon nanowalls
The Si substrate bearing the carbon nanowalls was placed in a beaker of ethanol, and it was ultrasonicated at 42 kHz for 1 min. The carbon nanowall was separated from the substrate, and samples for characterization were obtained by evaporating the ethanol to a concentration of approximately 10 wt %. Figure 2 shows a photograph of the separated carbon nanowalls in ethanol (the black dots are nanowall aggregates). Next, the liquid dispersion (1 mL) was spin coated at 1500 rpm onto oxygen plasma-treated PET (20 × 20 mm).

2.3 Characterization
The crystallinity of the carbon nanowalls was evaluated by Raman scattering (inVia, Renishaw) by using excitation light with a wavelength of 532 nm. The morphology of the carbon nanowall grown on the Si substrate was observed by scanning electron microscopy (SEM; JSM-6510LA, JEOL) with the sample stage in the horizontal position (0°) and tilted position (70°). The morphology of the separated carbon nanowall was also observed by planar transmission electron microscopy (TEM; JEM-2100F, JEOL). The growth morphology of the carbon nanowall was evaluated by fragmentation by focused ion beam (FIB; JIB-4500, JEOL) and cross-sectional TEM. The sheet resistance was measured by the four-probe method (RG-7C, NAPSON) and the transmittance (V-570, JASCO) was measured by using transmitted light with a diameter of 10 mm.

3. RESULTS AND DISCUSSION
3.1 Raman spectra
Figure 3(a) shows Raman scattering as a function of DC bias. Figure 3(b) shows the dependence of $I_D/I_G$ on DC bias.
Samples that were detached by ultrasonication were used. In all the Raman spectra of the carbon nanowalls, two main bands are present, one around 1580 and another around 1350 cm$^{-1}$, respectively. The former corresponds to the G band (after graphite), corresponding to the $E_{2g}$ mode of graphite [14, 15]. The latter corresponds to the D band (after defect), arising from the disorder due to the finite crystallite size [14-17]. In addition, a weak band is observed around 1620 cm$^{-1}$. This band appears when many graphene sheet edges are present [18]. The structure of carbon nanowalls has been investigated in detail by Raman scattering [2, 19]. We compared those results and the result of this experiment. According to a report by Kurita et al. [2], carbon nanowall length is related to $I_D/I_G$, where $I_D$ is the intensity of the D band peak and $I_G$ is the intensity of the G band peak: as the carbon nanowalls become longer, $I_D/I_G$ decreases. They found that for carbon nanowalls of length 1.71, 0.95, and 0.56 μm, $I_D/I_G$ was 0.77, 1.58, and 2.66 respectively. Figure 3(b) shows the relationship between $I_D/I_G$ and DC bias. In these experiments, we found that $I_D/I_G$ varies between 1.67 and 0.35. Looking at the SEM images discussed below, the lengths of the carbon nanowalls prepared at DC bias of 36.5 V was 3 to 5 μm. In other words, the decrease in $I_D/I_G$ with increasing DC bias appears to arise from the growing length of the carbon nanowalls. It is thought that the Ar$^+$ ions are driven out of the plasma as the DC bias is increased, promoting the carbon nanowall growth.

Furthermore, given that the D' band (around 1620 cm$^{-1}$) also became smaller as the DC bias was increased, the number of graphene sheet edges was reduced. In other words, this indicates that the graphene sheets were becoming larger. In all the samples, a 2D band peak (double-resonant) was found around 2700 cm$^{-1}$, showing that the carbon nanowalls had graphitized [20].

3.2 SEM observation

Figures 4(a) and 4(b) show planar SEM images of Sample 4 (DC bias: 36.5 V). The carbon nanowalls grew as if they were wrapping around spaces about 5 μm in size. Furthermore, in the SEM images with the sample tilted at 70° in Figs. 4(c) and 4(d), the carbon nanowalls grew with no breaks in a meandering pattern.

3.3 TEM observation

Figure 5 shows planar TEM images of the carbon nanowall...
bias: 36.5 V). The wall height was around 650 nm (Fig. 6(a)) and during the initial growth stage, the nanowalls grew with the graphene (0002) plane parallel to the substrate (Fig. 6(b)). Periodicity consisting of 6 layers was found over a 2-nm-thick lattice strip, and each layer was about 0.33 nm thick. This corresponds to the spacing between the (0002) planes in graphite. After about 10 nm of graphene had grown parallel to the Si substrate, the graphene growth changed to the [0001] direction perpendicular to the substrate (Fig. 6(c)).

The growth process of carbon nanowalls has been reported by several groups [21-23]. We compare those reports with the results of this study. Each of the groups reported that the carbon nanowalls curled in the perpendicular direction after approximately 20 nm of initial layers had formed parallel to the substrate. This concept is shown in Fig. 7. In the report by Zhu et al. [21], the curl was induced by the plasma sheath electric field. In this research as well, an electric field was actively formed on the substrate surface by the DC bias. The curvature of the wall shown in Fig. 6(c) is attributed to the effect of this electric field. Furthermore, according to a report by Kondo et al. [22], the initial layers contain a large amount of amorphous carbon. Here, the initial layers of the substrate surface layers were graphitized (Fig. 6(b)). Dangling bonds on the substrate surface are thought to have been reduced by reducing collisions with Ar+ ions when the DC bias was applied, thus contributing to the formation of the graphite layers.

Furthermore, in Fig. 6(c), intermediate layers were found between the carbon nanowalls and Si substrate. According to a report by Krichno et al. [24], a thin graphite layer of approximately 8 nm grew parallel to the Si substrate, covering it and inducing carbonization of its surface. In the present study as well, a graphite layer of approximately 10 nm grew parallel to the substrate, and the carbon nanowalls grew on top of that. The intermediate layer in Fig. 6(c) is thought to be carbonization of the Si substrate.

### 3.4 Transmittance and sheet resistance

Table 2 shows the transmittance and sheet resistance of each of the samples spin-coated onto PET. The samples were fabricated by adjusting the concentration so that the transmittances were similar. The PET surface was made hydrophilic by oxygen plasma treatment to prevent poor coverage. Sample 4 (DC bias: 36.5 V) gave the best sheet resistance, which is consistent with the Raman scattering results.

Figure 8 shows the dependence of transmittance on the sheet resistance of nanocarbon materials, including that of the nanowalls prepared in this study. The nanocarbon materials used for comparison are reduced graphene oxide [25-27], thermal CVD graphene [28], and multiwalled carbon nanotubes [29]. When compared at a transmittance of 80%, we can see that the obtained performance is almost the same as that of reduced graphene oxide reported by Eda et al. [25] and multiwalled carbon nanotubes reported by Lee et al. [29].

### Table 2 Transmittance and sheet resistance of the samples.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>DC bias (V)</th>
<th>Transmittance at 550 nm (%)</th>
<th>Sheet resistance (Ω□)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>83</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>20.0</td>
<td>84</td>
<td>106</td>
</tr>
<tr>
<td>3</td>
<td>30.0</td>
<td>82</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td>36.5</td>
<td>81</td>
<td>52</td>
</tr>
</tbody>
</table>

Figure 8. Dependence of transmittance on sheet resistance of nanocarbon materials.
materials in these studies were flake- and needle-shaped, and had essentially the same form as the carbon nanowalls in this study. Since our aim was to obtain conductive films without reduction treatment, we have achieved our initial aim.

However, there is a severe performance gap with thermal CVD graphene [28]. Whereas thermal CVD graphene forms a continuous uniform film, there is a possibility that our carbon nanowall did not form in the same way on the PET substrate surface since we fabricated the transparent conductive film as flake-shaped carbon nanowalls by spin-coating. Further improvements are needed in the method for forming transparent conductive films.

4. CONCLUSION

We grew carbon nanowalls on a Si substrate by using microwave surface-wave plasma CVD. The crystallinity of the carbon nanowalls was improved by applying a positive voltage to the Si substrate. We found that Raman I_D/I_G varies between 1.67 and 0.35 due to the growing length of the carbon nanowalls depending on DC bias. About 10 nm of graphene grew parallel to the substrate during the initial growth stage, and the graphene growth changed to the [0001] direction perpendicular to the substrate to form carbon nanowalls. The crystallinity of the carbon nanowalls were spin-coated onto PET, and the best sheet resistance of 52 kΩ/□ and transmittance of 81% (550 nm) were obtained for nanowalls grown at a DC bias of 36.5 V.

Acknowledgements

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5. REFERENCES