Process Optimization for Synthesis of High-Quality Graphene Films by Low-Pressure Chemical Vapor Deposition

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Low-pressure chemical vapor deposition (LPCVD) is a simple and useful method for the large-area synthesis of graphene films. Here, we have investigated how to adjust and optimize process conditions for the synthesis of single-layer graphene films by LPCVD. Through our experimental procedure, uniform and high-quality graphene films could be grown on Cu foil at 1000°C for 20 min with an H2 flow rate of 20 sccm, CH4 flow rate of 40 sccm, total pressure of 1.7 Torr, and a fast cooling rate (>10³°C/s). In a Raman spectrum measured from synthesized graphene film, we found that the full width at half-maximum (FWHM) of a symmetric 2D peak centered at 2682.5 cm⁻¹ was 34 cm⁻¹ and the 2D-to-G intensity ratio was 1.35. © 2012 The Japan Society of Applied Physics

1. Introduction
Graphene, a one-atom-thick sp²-bonded carbon planar sheet, has gained much attention owing to its unique physical properties since isolated graphene sheets were actually found by mechanical exfoliation in 2004. It has been proposed as a potential material for various electronic applications such as flexible transparent electrodes, logic devices, high-frequency transistors, and memory devices. To fabricate devices by the existing process technology used in the semiconductor industry, it is essential to synthesize large-area graphene films. Various methods have been developed for this; but it is well known that low-pressure chemical vapor deposition (LPCVD) technology is the most useful method for large-area synthesis of graphene films. By LPCVD, graphene films can be grown on several transition metals that are used as catalysts for the decomposition of precursor materials and provide a geometrical fit for the growth of graphene. Even though graphene films are grown on the metals, the number of graphene layers and the growth mechanism differ depending on the type of metal. For example, in the case of Ni, graphene films are predominantly composed of three to four layers of graphene and grown by carbon segregation and precipitation because of the high solubility of carbon in Ni. On the other hand, graphene films grown on Cu are mainly composed of single-layer graphene. Because of the extremely low solubility of carbon in Cu, graphene films are grown on Cu by surface adsorption. Therefore, to prepare thin and uniform graphene films, LPCVD growth on Cu is a promising method. Even though there are various reliable processes for the growth of graphene films, it was difficult to realize the synthesis of graphene films in the early days. Thus, it is necessary to optimize reproducible experimental conditions adapted to the arranged settings.

In this study, we investigated how to adjust process conditions and grow high-quality graphene films on Cu by LPCVD. In addition, we have researched the effect of process conditions, including flow rates of gases in each step, reaction time, and cooling rate.

2. Experimental Procedure
2.1 Synthesis of graphene films
Graphene films were grown on 25-μm-thick Cu foil (Alfa Aesar 13382) at low pressure in a furnace with a 1-in. quartz tube. The Cu foils were cut into 1 cm² pieces and loaded onto a quartz boat. Before starting the experiments, we purged oxygen by introducing Ar into the tube.

The temperature rose from room temperature to 1000°C in 1 h and was held constant to anneal Cu foil for 30 min with a constant flow rate of H2. The annealing is an essential step to remove native oxide on the surface of Cu foil and increase grain size to ~100 μm. This large grain size allows the synthesis of high-quality and uniform graphene films because multilayer graphene is generally grown on the grain boundary. In this step, we performed experiments under various flow rates of H2 to find the optimum rate. This was a fundamental experiment to make the surface of Cu foil smooth. A smooth surface was also an important condition for synthesizing high-quality graphene films. The flow rate of H2 was changed from 2 to 20 sccm. After the annealing steps, we inspected the surface by optical microscopy.

After the flow rate of H2 was chosen, CH4 was introduced into the tube to supply the precursor material. In this step, the variables to be considered were the flow rate of CH4 and reaction time, so we carried out experiments under several flow rates of CH4 for several reaction times. After the growth step, a quartz boat with a magnetic bar was moved into a cool zone (~150°C). Graphene film/Cu foil was cooled quickly (>10³°C/s) to room temperature without changing the flow rates of H2 and CH4 used in the growth step. When the temperature of the furnace reached 200°C, 200 sccm of Ar was introduced into the tube to purge the remaining H2 and CH4. After the synthesis of graphene films, the films were transferred onto SiO2/Si wafer to evaluate the quality or uniformity of the films by optical microscopy, Raman spectroscopy, and atomic force microscopy (AFM).

2.2 Transfer of graphene films
AZ 5214E was spin-coated on the graphene film/Cu foil surface and baked to harden the photoresist. Afterwards, iron(III) chloride (FeCl3) was used to etch Cu foil. Cu foil could be etched without removing graphene films on the back of the Cu foil because the films are naturally removed during spin-coating and baking. In addition, graphene films are difficult to grow on the back adjoining the quartz boat. AZ 5214E/graphene films floated on FeCl3 were moved onto de-ionized water to keep the surface of graphene films clean. After 30 min, the films were transferred onto SiO2/Si...
wafer by the scooping-up technique and dried in room ambient overnight. To keep graphene films unbroken and eliminate the remaining AZ 5124E on the films, AZ 5214E was spin-coated onto AZ 5214E/graphene films again. Finally, AZ 5214E layers were removed in acetone at 55°C for 1 h.

2.3 Inspection of graphene films
By optical microscopy, we could identify the uniformity of synthesized graphene films because the contrast differs depending on the number of graphene layers. Raman spectroscopy (532 nm laser wavelength, 100× objector) could be used to evaluate the quality of graphene films and the number of graphene layers. AFM (Veeco Dimension 3100) was used to measure the height of graphene films from substrates and observe the surface of graphene films.

3. Results and Discussion
3.1 Heating and annealing steps
In heating and annealing steps, we performed experiments with increasing flow rate of H2. Figure 1 shows optical images of Cu foil after the annealing steps performed with (a) 2, (b) 4, (c) 15, and (d) 20 sccm of flowing H2. The pressure was 72, 100, 500, and 900 mTorr, respectively. (e) Optical image of the smooth surface (marked with a circle) and the rough surface (marked with an arrow) of Cu foil covered with graphene film after the optimum growth step. (f) Optical image of graphene film transferred onto SiO2. The indicated points correspond to the arrow and circle in (e). Scale bars are 25 μm in (a)–(d).

Fig. 1. (Color online) Optical images of Cu foil after the annealing steps performed with (a) 2, (b) 4, (c) 15, and (d) 20 sccm of flowing H2. The pressure was 72, 100, 500, and 900 mTorr, respectively. (e) Optical image of the smooth surface (marked with a circle) and the rough surface (marked with an arrow) of Cu foil covered with graphene film after the optimum growth step. (f) Optical image of graphene film transferred onto SiO2. The indicated points correspond to the arrow and circle in (e). Scale bars are 25 μm in (a)–(d).

3.2 Growth step
In this step, CH4 was introduced into the tube with 20 sccm of flowing H2. We performed experiments with increasing reaction time and flow rate of CH4. We compared nine graphene films grown with 20 sccm of flowing H2 and 30, 40, and 50 sccm of CH4 for 20, 30, and 40 min, as shown in Figs. 2. Table I shows the uniformity of graphene films evaluated by optical microscopy and Raman spectroscopy. The initial flow rate of CH4 and reaction time were 30 sccm and 20 min, respectively. Under these conditions, Cu foil was not fully covered with graphene film, as shown in Fig. 2(a). Bare areas on Cu foil could be filled with single-layer graphene when we increased the flow rate of CH4 while keeping the reaction time unchanged. As a result, uniform single-layer graphene films were grown with 40 or 50 sccm of flowing CH4 for 20 min, as shown in Figs. 2(b) and 2(c). However, when reaction time was increased, bilayer graphene islands on single-layer graphene film or multilayer graphene film were synthesized, as shown in Figs. 2(e)–2(i). These results were contrary to the self-limiting growth of graphene on Cu. Figure 3(a) shows

Fig. 2. (Color online) Optical images of graphene films grown with 20 sccm of flowing H2 and various flow rates of CH4 for several reaction times. Flow rate of CH4: (a, d, g) 30 sccm, total pressure of 1.5 Torr; (b, e, h) 40 sccm, total pressure of 1.7 Torr; (c, f, i) 50 sccm, total pressure of 2.0 Torr. Reaction time: (a–c) 20 min; (d–f) 30 min; (g–i) 40 min. Insets in (a) and (d) are enlargements of areas within white dotted squares. Scale bars are 25 μm.
Table I. Uniformity of graphene films observed by optical microscopy and the number of graphene layers evaluated by Raman spectroscopy.

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>Flow rate of CH₄ (sccm) 30</th>
<th>40</th>
<th>50</th>
</tr>
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<tbody>
<tr>
<td>30</td>
<td>Single-layer graphene islands (not fully covered) on single-layer graphene film</td>
<td>Bilayer graphene islands on single-layer graphene film</td>
<td>Multilayer graphene film</td>
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<tr>
<td>40</td>
<td>Multilayer graphene film</td>
<td>Multilayer graphene film</td>
<td>Bilayer graphene islands on single-layer graphene film</td>
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Raman spectra of single- and bilayer graphene from the indicated points in Fig. 2(e) and a Raman spectrum of multilayer graphene from the point in Fig. 2(h). The number of graphene layers was verified by the full width at half-maximum (FWHM) of the 2D peak (~2690 cm⁻¹) and the $I_{2D}/I_G$ ratio. FWHM of the 2D peak increases with increasing number of graphene layers because a single-Lorentzian 2D peak in single-layer graphene splits into several components in bi- or multilayer graphene. In our case, the values were 36, 65, and 86.5 cm⁻¹ for single-, bi-, and multilayer graphene, respectively. In addition, the increase in graphene layers leads to a decrease in the $I_{2D}/I_G$ ratio because the intensity of the G peak (~1590 cm⁻¹) increases with increasing number of graphene layers. In general, it is well known that a high $I_{2D}/I_G$ ratio (>2) can be found in single-layer graphene. Even though, in our case, the $I_{2D}/I_G$ ratio (~1.14) in single-layer graphene identified by FWHM of the 2D peak was slightly lower than the general ratio, we observed a drop in the ratio caused by the increase in the number of graphene layers.

On the basis of the above results, in the growth step, we chose 40 sccm and 20 min as the flow rate of CH₄ and reaction time, respectively. Figure 3(b) shows a Raman spectrum of single-layer graphene film grown under these conditions. The 2D-to-G intensity ratio was 1.35, and a symmetric 2D peak was centered at 2682.5 cm⁻¹. In addition, FWHM of the 2D peak was 34 cm⁻¹, and there was no D peak. These characteristics of the Raman spectrum were similar to the results obtained by Li et al. Therefore, we found that high-quality, uniform single-layer graphene films could be grown by our process. Figure 3(c) shows an AFM image of the graphene film transferred onto the SiO₂.
Si wafer. The height of single-layer graphene from the substrate was 2.475 nm. This value is about 3.4 times higher than the height measured by Reina et al.\textsuperscript{30} This large value results from the gap between the graphene film and the substrate, and it means that the film and the substrate were not in complete contact. To verify this gap, it is necessary to observe high-resolution images of the side using a transmission electron microscope in future work.

3.3 Cooling step

After the growth step, graphene films loaded on the quartz boat were quickly moved into a cool zone using a magnetic bar. Such a fast cooling rate was important for growing uniform single-layer graphene films because additional or unwanted reactions must not occur on the surface of graphene films after the growth step. When the films were naturally cooled (~0.5 °C/s) after the furnace was turned off, multilayer graphene films were grown on Cu foil, as shown in Fig. 4(b).

4. Conclusions

We have developed a method of finding the optimum process conditions and growing high-quality and uniform graphene films on Cu foil by LPCVD. In the heating and annealing steps, we chose 20 sccm as the flow rate of H\textsubscript{2} to make the surface of Cu foils clean and smooth, we needed such a high flow rate of H\textsubscript{2}. In the growth step, to synthesize continuous and uniform single-layer graphene films, we chose 40 sccm and 20 min as the optimum flow rate of CH\textsubscript{4} and reaction time, respectively. When the flow rate of CH\textsubscript{4} and reaction time were excessively increased, multilayer graphene films or bilayer graphene islands on single-layer graphene films were grown. In the cooling step, to keep graphene films uniform, graphene films on Cu foil were cooled to room temperature quickly (~10 °C/s). As a result, high-quality, uniform single-layer graphene films could be grown through our process. To prepare graphene films for electronic applications, this experimental procedure will be useful and notable.

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