

Growth Characteristics of Graphene Film by Chemical Vapor Deposition Method Using Nozzle Gas Injection*

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Graphene has attracted much attention due to its many unique properties and potential applications. It is considered that a chemical vapor deposition (CVD) method is a promising for growth method of graphene. We have examined growth characteristics of graphene by means of a low-pressure alcohol catalytic CVD (LP-ACCVD) method. Here nozzle gas injection is used to supply carbon source gas to a substrate. This method enables efficient supply of carbon source gas to a substrate for the growth of graphene. Therefore, an efficient growth and lowering of the growth temperature of graphene is expected. [DOI: 10.1380/ejssnt.2015.265]

Keywords: Carbon; Graphene; Chemical vapor deposition; Nozzle gas injection; Low pressure alcohol catalytic CVD; Iron

I. INTRODUCTION

Graphene, a two-dimensional material composed of carbon atoms in a honeycomb lattice, has recently attracted much attention because of its many unique properties, such as large specific surface area [1], high charge carrier mobility [2] and high thermal conductivity [3]. Several methods for synthesis of graphene have been proposed [4-6]. Among those methods, a chemical vapor deposition (CVD) method is the most promising one [7]. However controllability of the graphene growth by the CVD methods, e.g. control of the number of layer, enlargement of the domain size, enhancement of growth rate, are not sufficient at present and are still to be improved.

In this study, a low-pressure alcohol catalyst CVD (LP-ACCVD) method was used for the graphene growth. This method enables prompt removal of by-product that is produced by the decomposition of precursor. The by-product inhibits the growth of graphene and its prompt elimination is desirable for the efficient graphene growth. We have confirmed that a nozzle gas injection LP-ACCVD method, which uses a nozzle with small diameter (< 1 mm) for efficient supply of the precursor to a substrate, enables efficient growth of single-wall carbon nanotubes [8]. In addition, iron (Fe) was used as a catalyst film. In CVD growth of graphene, copper or nickel is usually used as a catalyst layer [9]. On the other hand, it is considered that efficient graphene growth is possible by Fe catalyst layer owing to its high solubility of carbon [10]. We have examined the growth characteristics of graphene in the condition of different growth temperatures by the LP-ACCVD method, using ethanol gas as a carbon source and Fe as a catalyst layer.

II. EXPERIMENTAL

P-type Si (100) wafers with SiO₂ layer (300 nm in thickness) were used as substrates for the graphene growths.

The catalyst film was deposited onto the substrate by vacuum evaporation method. Fe film of 60 nm in thickness was used as a catalyst layer. The substrate after the catalyst deposition was introduced into a cold-wall type high vacuum chamber shown in Fig. 1. This chamber was evacuated by the turbo molecular pump and the base pressure was $< 1 \times 10^{-4}$ Pa. The substrate was placed on the substrate heater and the carbon source gas (ethanol) was irradiated onto the substrate via the stainless steel nozzle with a 0.50 mm inner diameter. The CVD process was carried out with the process timing chart shown in Fig. 2. Then the temperature was raised to growth temperature of 750°C. The irradiation of ethanol gas to the substrate

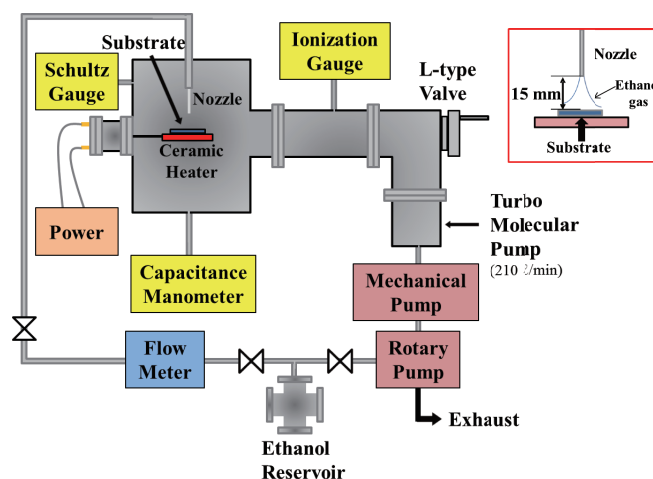


FIG. 1. Schematic drawing of LP-ACCVD apparatus.

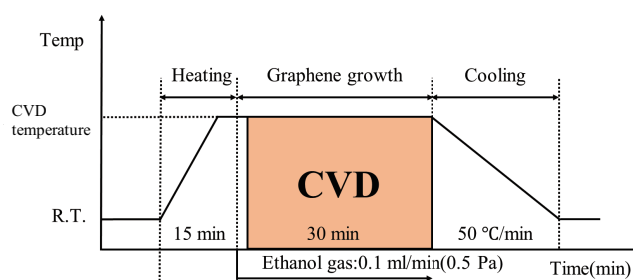


FIG. 2. Timing chart of LP-ACCVD process.

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was carried out in a pressure of 0.5 Pa for 30 min. After the irradiation, the temperature of the substrate was lowered with a constant cooling rate of 50°C/min.

The graphene grown in this study was characterized by an optical microscope (OM) and Raman scattering spectrometer. The excitation wavelength and the power of the laser were 532 nm and 2.5 mW, respectively. The spot size of the laser on the sample was about 1 μm .

III. RESULTS AND DISCUSSION

The dependence of the growth of the graphene on the CVD temperature was first examined. Here the CVD processes were carried out at various the temperatures between 600°C and 800°C and the growth characters of the graphene were examined. Figure 3(a) shows Raman spectra on the sample substrates after the CVD processes. The Raman spectra were acquired on randomly selected twelve different positions on the sample substrates. The spectra shown here are the representative ones on the samples. In these spectra, D, G and 2D band peaks are confirmed. The peaks observed at $\sim 1350\text{ cm}^{-1}$ originate from defects in the graphene and called D-band, and the peaks observed at $\sim 1590\text{ cm}^{-1}$ originate from a graphitic structure with sp^2 carbon bond and called G-band. The peaks appear at $\sim 2700\text{ cm}^{-1}$, called 2D-band, is also a specific one to the graphene structure [11]. It can be confirmed that the peak intensity of G-band depends on the CVD temperature and decreases at the higher CVD temperature. The D-band peaks are also found in the spectra. Those intensities are large at the lower temperature and decreases as the temperature increases. Enlarged 2D band peaks are shown in Fig. 3(b). The peak positions and the full width at half maxima (FWHMs) of the 2D peaks measured at the twelve different positions on the sample substrates are summarized in Table. I. The peak positions and the FWHMs varied with the different po-

sitions on the sample surface. The CVD temperature of 750°C shows the lowest Raman shift ($2697 \pm 3\text{ cm}^{-1}$) and the smallest FWHM ($32 \pm 6\text{ cm}^{-1}$). These value increases at the higher and lower CVD temperature than 750°C. This indicates that the CVD temperature of 750°C gives the smallest number of the graphene layer on the surface [12].

Figures 4 are OM images and Raman mapping images of the surface of the substrates after the CVD processes. The Raman mapping images show the two-dimensional distribution of the 2D and G band intensity ratio (I_{2D}/I_G) and the G- and D-band intensity ratio (I_G/I_D) on each substrate. The I_{2D}/I_G ratio can be used as a measure of the thickness of the graphene. The larger I_{2D}/I_G ratio indicates the thinner graphene layer [9]. The I_G/I_D ratio can be used for the evaluation of the domain size of the graphene as described later. The morphology gradually changes as the CVD temperature rises. It can be confirmed that the change of the Raman mapping images corresponds to the morphology changes in the OM images. Fine structure with many small spots is seen on the surface of the samples prepared at 600°C. The size of the spots gradually increases as the temperature increases. The size of the spots seen in the mapping gradually increases as the CVD temperature increases. These changes indicate that the domain of the graphene gradually increases as the CVD temperature rises.

To examine the growth characteristics more quantitatively, we examined the I_{2D}/I_G and I_G/I_D peak intensity ratios in the Raman spectra at the twelve different points that were randomly selected on the sample as described above. The peak intensities (i.e. peak area) of D-band (I_D), G-band (I_G), and 2D-band (I_{2D}) were obtained from the spectra and the I_{2D}/I_G and I_G/I_D peak intensity ratios were calculated using the intensities. The ratio of I_{2D}/I_G is the measure of the layer number of the graphene as mentioned before. On the other hand, it is known that the domain size of the graphene can be estimated from the following formula;

$$L_a = 2.4 \times 10^{-10} \lambda_{\text{laser}}^4 \left(\frac{I_G}{I_D} \right), \quad (1)$$

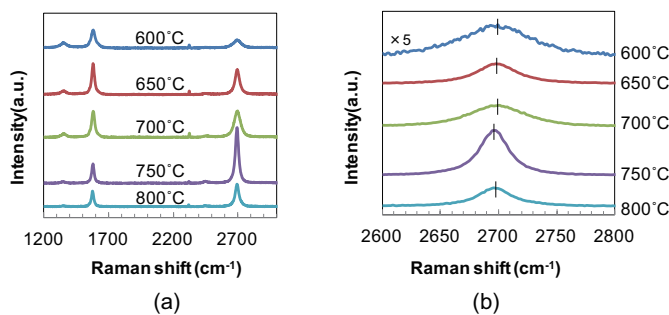


FIG. 3. (a) Representative Raman spectra and (b) enlarged 2D spectra of samples processed at each CVD temperature.

TABLE I. Peak positions and FWHMs of 2D spectra graphene films grown at each CVD temperature.

CVD temperature (°C)	Peak position (cm^{-1})	FWHM (cm^{-1})
600	2700 ± 2	59 ± 9
650	2699 ± 3	47 ± 7
700	2700 ± 3	45 ± 11
750	2697 ± 3	32 ± 6
800	2699 ± 4	51 ± 20

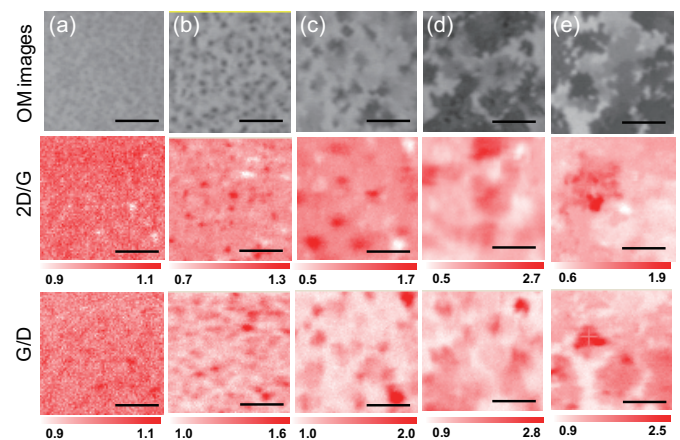


FIG. 4. OM images and the corresponding Raman mapping images of I_{2D}/I_G and I_G/I_D for each CVD temperature. The CVD temperatures are (a) 600 °C, (b) 650°C, (c) 700°C, (d) 750°C and (e) 800°C. The scale bars are 5 μm .

where L_a is domain size of graphene and λ_{laser} is the wavelength of the laser for excitation. Thus, the domain size of the graphene can be estimated from the intensity ratio I_G/I_D . The values of I_{2D}/I_G and L_a for the each CVD temperatures are plotted on Figs. 5. The both values increases as the CVD temperature rises. The value of I_{2D}/I_G reaches the maximum value at 750°C, and then decreases at 800°C. These changes correspond to that of the peak positions and the FWHMs of 2D spectra shown in Table 1, and also indicate that the number of the graphene layer decreased at 750°C. In these graphs, steep increases are seen at the temperature between 700°C and 750°C, indicating that a drastic change occurred in the growth mode of the graphene.

These results can be explained by the behavior of the carbon on/in the Fe film. It is considered that the formation of the graphene film on the transition metals with higher carbon solubility limit, such as Fe, Ni, and Co, occurs by the solution of the carbon atoms into the metals and the precipitation of the carbon on the surface of the metals [13,14,15]. In this study, the carbon atoms are produced by the decomposition of the ethanol on the Fe films. Those carbon atoms solve into the Fe film during heating at the CVD temperature and precipitate again on the surface during the cooling process. In this process, the decomposition and the solution of carbon atoms are more promoted at higher temperature. Thus the higher CVD temperatures are preferable. Based on the phase diagram of Fe-C system, austenite phase (γ -Fe) changes into a mixed phase of ferrite (α -Fe) and cementite (Fe_3C)

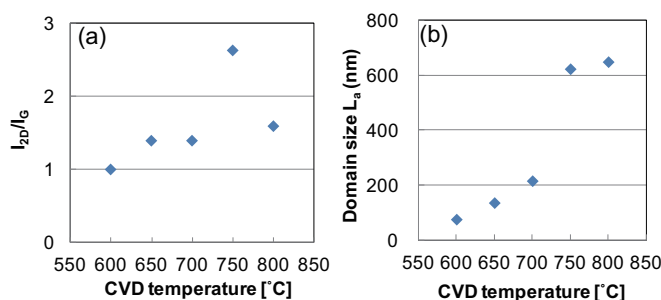


FIG. 5. The values of (a) I_{2D}/I_G ratios and (b) graphene domain sizes (L_a) plotted as a function of the CVD temperature. These values were obtained from the Raman spectra shown in Fig. 3.

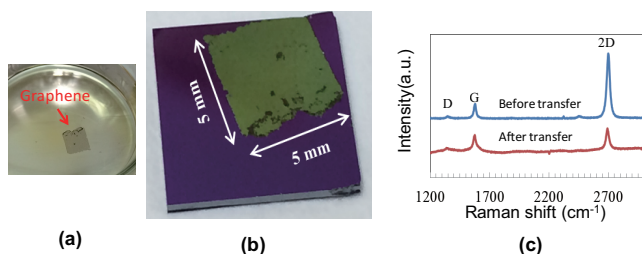


FIG. 6. (a) Graphene exfoliated from the substrate and floating on the water. (b) Graphene transferred on the $\text{SiO}_2/\text{Si}(100)$ substrate. (c) The Raman spectra of the graphene before and after the transfer.

phases at 723°C [16]. The drastic changes of I_{2D}/I_G and L_a seen at the temperature between 700°C and 750°C are probably due to this phase transformation.

An austenite phase can contain much carbon atoms than ferrite phase. Thus the austenite phase precipitates more carbon atoms than the ferrite phase on surface because few solution of carbon, resulting in promotion of graphene growth. Therefore, growth temperature $\geq 750^\circ\text{C}$ gives larger domain size. The I_{2D}/I_G ratio also showed the maximum value at 750°C, that is, the number of the graphene layers became minimum at 750°C. This is probably due to the enlargement of the domain size of the graphene at this temperature. At this condition, the carbon atoms were consumed for the formation of the thin and large graphene layer because of the higher catalyst activity and the active solution/precipitation of the Fe film at the higher temperature. As a result, the thin graphene was uniformly formed on the Fe films. In the case of the lower CVD temperature, the active solution/precipitation behavior occurred at the limited small area on the Fe film. This resulted in the formation of thicker graphene with the small domain size.

Finally, we demonstrated exfoliation of the graphene film from the substrate and transfer it to the $\text{SiO}_2/\text{Si}(100)$ substrate. The graphene film grown at 750°C was used for the exfoliation process. The exfoliation was carried out by immersing the substrate after the graphene growth in FeCl_3 aqueous solution (1 M/l) for 24 hours. The graphene exfoliated and floating on the water is shown in Fig. 6 (a). The graphene film was then scooped up on the $\text{SiO}_2/\text{Si}(100)$ substrate [Fig. 6 (b)]. Figure 6 (c) is Raman spectra of the graphene films before and after the exfoliation. It can be confirmed that the decrease of the I_{2D}/I_G ratio and increase of the D-band after the transfer. These indicate that the crystallinity of the graphene degraded after the transfer.

IV. CONCLUSIONS

We have examined growth characteristics of graphene by means of a low-pressure alcohol catalytic CVD (LP-ACCVD) method using the adopted nozzle injection of ethanol gas to supply carbon source gas to a substrate. The dependences of the growths of the graphene on the CVD temperature showed that the optimum CVD temperature existed. In this study, the CVD temperature of 750°C gave the thinner and more uniform graphene with the largest domain size. The exfoliation of the graphene film from the Fe film and its transfer to the $\text{SiO}_2/\text{Si}(100)$ substrate were successfully demonstrated.

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