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Influence of Nickel Catalyst Film Thickness and Cooling Condition for Synthesis of Monolayer Graphene by Thermal Chemical Vapor Deposition at 800 °C

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Abstract: Graphene has shown great potential for high speed devise and transparent electrode in recent years. Thermal CVD (Chemical vapor deposition) with methane gas is the most popular method for graphene synthesis. However, a high temperature of 900 °C and higher is necessary for synthesizing high-quality graphene. In this study, monolayer graphene with fewer defects was synthesized using acetylene gas at 800 °C. In addition, an optimal CVD condition for monolayer graphene with fewer defects was investigated by changing the nickel catalyst film thickness, hydrogen concentration, and cooling condition. The results showed that the number of the graphene layers decreased with an increase of the nickel film thickness. Furthermore, although a small amount of hydrogen reduced the amount of the defect, a lot of hydrogen etched the graphene. The fastest cooling rate in pure nitrogen was effective for synthesis of graphene with high crystallinity and with almost no defect. We succeeded in the monolayer graphene synthesis with a low density of defects on nickel catalyst film by a thermal CVD at 800 °C using acetylene gas.

Key words: Graphene, thermal CVD (Chemical vapor deposition).

1. Introduction

Graphene is a planar material which is composed of the six-membered ring of carbon atoms in the shape of a sheet. The graphene specificities are a high carrier mobility of 100 times higher than silicon, a high transmittivity and a high mechanically flexibility [1-3]. In 2004, Geim and Novoselov succeeded in extracting a graphene lamina by exfoliating HOPG (Highly oriented pyrolytic graphite) surface using an adhesive tape [4]. Researches of a high-speed transistor and a transparent electrode have actively been studied for their applications in parallel to a lot of the basic researches because of the high carrier mobility of graphene. Although graphene and CNT (Carbon nanotube) are commonly treated as a carbon nanomaterial, the graphene transistor can be operated at higher speed than the CNT transistor owing to the higher carrier mobility of graphene than that of CNT. Therefore, graphene attracts attention as a next-generation material.

CVD (Chemical vapor deposition) is one of the methods to synthesize graphene. By the contribution of a lot of reports concerning CVD of graphene, it is now easy to synthesize graphene on a copper foil using the mixed gas of methane and hydrogen [5, 6]. The synthesis of graphene using nickel catalyst was also reported in recent years [7-9]. Methane and ethanol are commonly used as a source gas for graphene synthesis because they are safe gases. One carbon atom and four hydrogen atoms are bonded strongly by sigma-bonding in methane molecule. Therefore, a high temperature of about 1,000 °C is needed for decomposing into carbon and hydrogen on

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Ni catalyst [10]. The synthesis temperature strongly influences on the graphene property. Raman spectroscopic analysis is often used and the ratio of the D-band intensity to the G-band one (I_D/I_G) is correlated with the amount of defects on graphene. Although I_D/I_G of the synthesized graphene by using methane at 900 °C is almost 0, I_D/I_G became 0.6 at 850 °C, respectively. It is difficult to synthesize a high quality graphene at a temperature less than 900 °C.

On the other hand, decomposition of acetylene molecule is easy owing to the unsaturated hydrocarbon. In CNT synthesis, because the decomposition activity of acetylene molecule is higher than that of methane molecules, CNT synthesis with a high number density by using acetylene gas was reported [11]. Based on this result, it is possible to synthesize graphene by using acetylene gas at a lower temperature than by using methane gas. In this study, acetylene gas was used as a source gas for graphene synthesis. We investigated the influence of the hydrogen concentration, the nickel film thickness and the cooling rate on the properties of graphene. The number of layers of the graphene and its domain size were evaluated by Raman spectroscopic analysis and the surface of the graphene was observed using an optical microscope.

2. Experimental Setup

Process flow diagram of graphene is shown in Fig. 1. After RCA cleaning of a thermally oxidized (100 nm thickness) Si wafer, a nickel layer with a thickness of 200-800 nm was deposited on the Si wafer by magnetron sputtering. This substrate was sent to the center of the quartz tube. While the mixed gas of nitrogen and hydrogen was flown at a total flow rate of 450 sccm, the quartz tube was heated from room temperature at 800 °C for 35 min. At a temperature of 800 °C, 50 sccm of acetylene gas was added to the nitrogen/hydrogen mixed gas flow, the gas flow of these three gases was maintained for 5 min at 50 Pa. Note that all the graphene samples in this study were synthesized in acetylene/nitrogen/hydrogen gas mixture. After this step, the flow of acetylene gas was cut off and the tube was rapidly cooled to 100 °C for 10 min to 100 min while the gas flow of nitrogen and hydrogen gas mixture was continued at 450 sccm. The ratio of the flow rate of hydrogen gas to that of nitrogen gas was varied between 0 and 20 %, while the total gas flow rate was kept constant at 450 sccm. The graphene samples were synthesized on the different nickel film thicknesses and using the different hydrogen concentrations. We investigated the dependence of the film thicknesses and the hydrogen concentration on the property of grown graphene. The crystallinity and the defect in the graphene samples were measured by a Raman spectroscope and the surface condition was evaluated using an optical microscope (NFS-230HKG, JASCO, Tokyo, Japan). The excitation wavelength was 532 nm.

3. Experimental Results

3.1 Dependence of Nickel Catalyst Film Thickness

The graphene samples were synthesized at 800 °C using the flow rate ratio of hydrogen gas to hydrogen/nitrogen gas mixture of 3% and the nickel film thicknesses of 200, 400, 600 and 800 nm. The acetylene gas flow rate was kept at 50 sccm. $I_G/I_{2D,}$

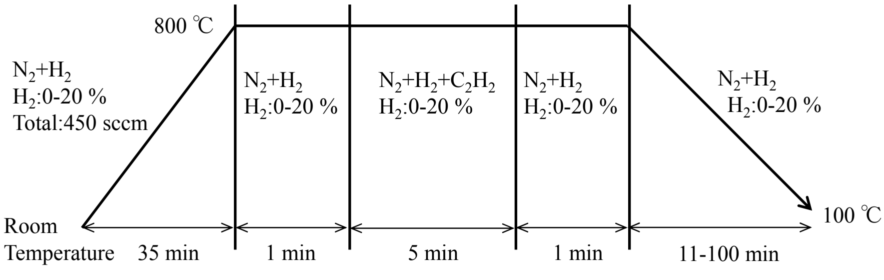


Fig. 1 Process flow diagram of grapheme.

I_D/I_G and the domain size (La) of graphene were shown in Table 1. From the intensity ratio of the G band to the 2D band, which appeared close to 2,685 cm^{-1} (I_G/I_{2D}), the number of layers of the synthesized graphene was evaluated. I_G/I_{2D} of the graphene samples on the 200 nm, 400, 600 and 800nm thick nickel films were 2.2, 1.0, 0.8 and 0.7, respectively. It was reported that I_G/I_{2D} is strongly correlated with the graphene layers. $I_G/I_{2D} < 0.7$ for monolayer graphene, $0.7 < I_G/I_{2D} < 1.0$ for bilayer graphene and $1.0 < I_G/I_{2D}$ for multilayer graphene [12]. Therefore, on the nickel film thicknesses of 200 nm graphene of multilayers were synthesized. In the cases of 400 nm and 600 nm, bilayers were synthesized. Moreover, in the cases of 800 nm, monolayer graphene was synthesized. It was found that the number of the graphene layers decreased with an increase of the nickel film thickness. These results suggest that the amount of segregating carbon atoms from the nickel increased with a decrease of the nickel film thickness because the distance from the bottom of the nickel film to the surface decreased.

I_D/I_G of the graphene samples on the 200, 400, 600, and 800 nm thick nickel films were 0.30, 0.22, 0.23, and 0.20, respectively. This results indicate that the graphene synthesized on the 800 nm nickel film had higher crystallinity than the other graphene samples. From this result, the nickel film thickness required to synthesize monolayer graphene with high crystallinity was determined to be 800 nm.

La of the graphene samples on the different nickel film thicknesses were calculated from the I_D/I_G relation by the following Eq. (1) [13].

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

where, λ is the excitation wavelength in the Raman measurement. La of the graphene samples on the 200, 400, 600, and 800 nm thick nickel films were 64, 88, 85, and 97 nm, respectively. The largest La was obtained using the 800 nm nickel film thickness. From these results, the 800 nm nickel film was used as the catalyst in the following experiments.

3.2 Dependence of Hydrogen Concentration

The gas flow rate ratio of hydrogen to acetylene was changed from 0 to 20% while the gas flow rate of acetylene was kept at 50 sccm, and that of hydrogen/nitrogen gas mixture was kept at 450 sccm. I_G/I_{2D}, I_D/I_G and La of the graphene samples were shown in Table 2.The graphene obtained with all the hydrogen ratio except for 20%, I_G/I_{2D} of the graphene using the hydrogen were smaller than or equal to 0.7. Therefore, monolayer graphene was synthesized at all the hydrogen ratios below 20%. This result suggest that although a small amount of hydrogen reduced the amount of the defect on graphene, the supply of too much hydrogen etched the graphene. Moreover, La obtained at 6% was about two times larger than that at

Table 1 Relationship between nickel film thickness and graphene properties.

Nickel film thickness (nm)	I_G/I_{2D}	Number of layers	I_D/I_G	Domain size (nm)
200	2.2	Multilayer	0.30	64
400	1.0	Bilayer	0.22	88
600	0.8	Bilayer	0.23	85
800	0.7	Monolayer	0.20	97

Table 2 Relationship between hydrogen concentration and graphene properties.

Hydrogen gas flow ratio (%)	I_G/I_{2D}	Number of layers	I_D/I_G	Domain size (L_a) (nm)
0	0.4	Monolayer	0.28	68
3	0.7	Monolayer	0.20	96
6	0.7	Monolayer	0.18	107
10	0.5	Monolayer	0.39	50
20	-	-	-	-

0%. From these results, an optimum hydrogen concentration for the synthesis of graphene with high crystallinity was 6% because *La* was the largest. From these results, the hydrogen concentration was set to 6% in the following experiments.

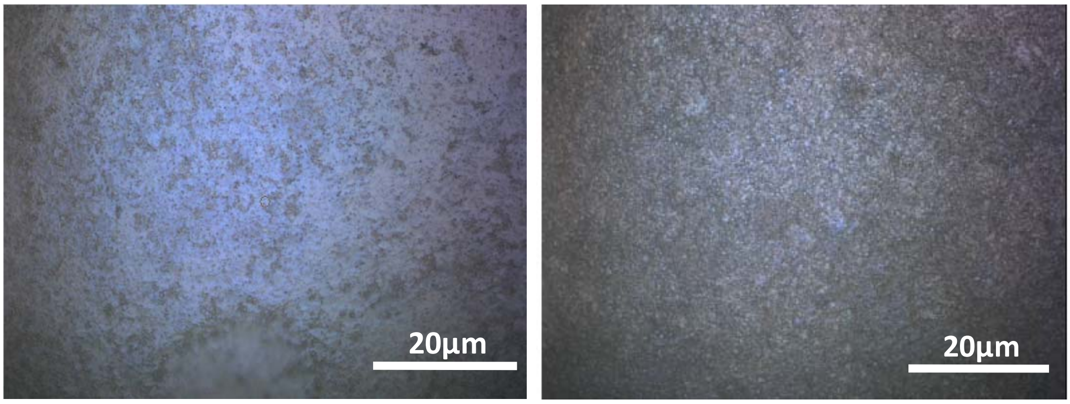
3.3 Dependence of Gas Atmosphere and Cooling Rate

The influence of hydrogen gas during the cooling in CVD process on the graphene property was investigated because too high ratio hydrogen gas flow ratio was found to etch the graphene in the previous section. The graphene synthesized with the hydrogen/nitrogen gas mixture or nitrogen gas during cooling. Multilayer graphene was synthesized because I_G/I_{2D} of the graphene using the nitrogen gas was 1.8, which was thinker than that using hydrogen/nitrogen gas mixture. Moreover, I_D/I_G of the graphene using nitrogen gas was 0.16, which was lower than that using the all concentrations of hydrogen/nitrogen gas mixture in Table 2, indicating the presence of low defects on graphene. This result suggests that the graphene was etched by hydrogen during the cooling. We have found that the graphene with low density of defect was synthesized when it cooled in pure nitrogen gas atmosphere.

Then, in order to obtain monolayer graphene, the influence of the cooling rate was investigated by changing the cooling period from 11 to 100 min. The cooling period was defined by the time from the initiation of cooling to that at which the furnace temperature became 100 °C. I_G/I_{2D}, I_D/I_G and *La* of the graphene samples were shown in Table 3 and the optical microscope images was shown in Fig. 2. The shortest cooling period of 11 min in this study resulted in the growth of monolayer graphene with high crystallinity and almost no defect. In an optical microscope image of the graphene samples with the cooling period of 100 min, the dark region extended in the whole surface. This result indicates that the number of the graphene layers and density of defects increased with an increase of the cooling period due to too much carbon segregated from the nickel films as the cooling period increased. These results suggest that the fastest cooling period of 11 min in pure nitrogen atmosphere was effective for the synthesis of graphene with high crystallinity and with almost no defects.

Table 3 Relationship between cooling time and graphene properties.

Cooling time (min)	I_G/I_{2D}	Number of layers	I_D/I_G	Domain size (L_a) (nm)
11	0.7	Monolayer	0.08	240
30	1.3	Multilayer	0.18	107
60	1.8	Multilayer	0.16	120
100	1.8	Multilayer	0.28	69



(a) (b)

Fig. 2 Optical microscope images of the graphene synthesized with various cooling periods: (a) 11 min and (b) 100 min.

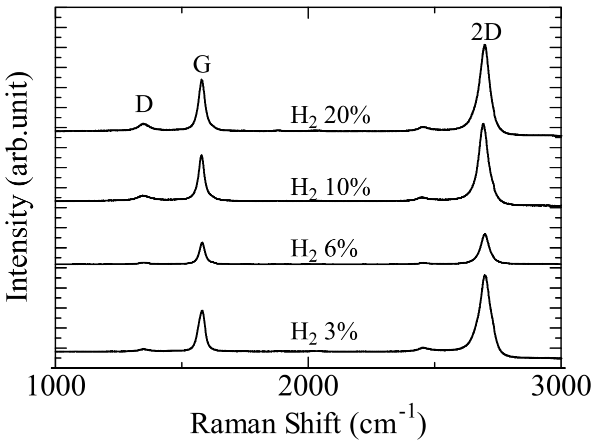


Fig. 3 Raman spectra of graphene synthesized with the different gas flow rate ratios of hydrogen to acetylene.

Table 4 Relationship between hydrogen concentration and graphene properties.

Hydrogen gas flow ratio (%)	I_G/I_{2D}	Number of layers	I_D/I_G	Domain size (L_a) (nm)
3	0.6	Monolayer	0.11	192
6	0.7	Monolayer	0.08	240
10	0.6	Monolayer	0.19	96
20	0.6	Monolayer	0.20	94

3.4 Dependence of Hydrogen Concentration Again

The influence of the hydrogen gas flow rate ratio during the cooling on the graphene property was again investigated because the fastest cooling rate in pure nitrogen atmosphere was shown to be effective in previous section. The gas flow rate ratio of hydrogen to hydrogen/nitrogen gas mixture was changed from 3% to 20%. The Raman spectra of the graphene samples were shown in Fig. 3. Although all the peaks disappeared when the cooling was performed at the hydrogen ratio of 20% as shown in Table 2, all the peaks appeared at the same hydrogen ratio of 20% when the cooling was performed without hydrogen. It was found, hydrogen etched graphene, especially during the cooling.

I_G/I_{2D}, I_D/I_G and *La* of the graphene samples were shown in Table 3. I_G/I_{2D} of the graphene using the hydrogen ratios of 3%, 6%, 10% and 20% were 0.6, 0.7, 0.6 and 0.6, respectively. The monolayer graphene obtained with all the hydrogen ratio. Moreover, I_D/I_G and *La* of the graphene with the hydrogen ratios of 3%, 6%, 10% and 20% were 0.11, 0.08, 0.19 and 0.20, and 192, 240, 96 and 94 nm, respectively. An optimum hydrogen gas flow ratio for the synthesis of a high quality monolayer graphene was 6% because of the largest *La* and the smallest I_D/I_G. Moreover, *La* and I_D/I_G of this sample respectively were double and half compared with those using nitrogen/hydrogen gas mixture during the cooling hydrogen gas flow ratio of 6% in Table 2. These results suggest that the synthesis of monolayer graphene with high crystallinity and with almost no defects was achieved using the hydrogen ratios of 6% during the synthesis period and the fastest cooling rate in pure nitrogen atmosphere.

4. Conclusions

In conclusion, we investigated the CVD conditions for synthesis of monolayer graphene by using acetylene gas on nickel catalytic substrate.

We found that the optimal nickel film thickness was 800 nm. The amount of segregating carbon atoms from the nickel increased with a decrease of the nickel film thickness because the distance from the bottom of the nickel film to the surface decreased.

An optimum hydrogen concentration for the synthesis of monolayer graphene with high crystallinity was 6% because of the largest *La* and the small amount of defects. Although a small amount of hydrogen reduced the amount of the defect, too much hydrogen etched the graphene. The cooling condition was the most important factor for the number of the layers and the quality of the graphene. The defect and quality of graphene were improved by rapid cooling in pure nitrogen.

Based on the results above, when the hydrogen gas flow ratio were 3% and 20%, monolayer graphene could be grown by rapid cooling in pure nitrogen. It is possible to synthesize monolayer graphene with high quality of 800 °C by using acetylene gas with an optimal hydrogen gas flow ratio and nickel catalyst thickness. The number of the graphene layers was decreased with increasing the cooling rate. Therefore, fastest cooling period in pure nitrogen was effective for synthesis of graphene with high crystallinity and with almost no defects.

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