Synthesis of Graphenes on Ni Foils by Chemical Vapor Deposition of Alcohol with IR-Lamp Heating

Naoki Kishi[1*], Akiji Fukaya[1], Ryo Sugita[1], Takuya Kado[1], Tetsuo Soga[1], Takashi Jimbo[2]

[1]*Department of Frontier Materials, Nagoya Institute of Technology,*

Nagoya 466-8555, Japan

[2]*Research Center for Nano Device and System, Nagoya Institute of Technology,*

Nagoya 466-8555, Japan

*Corresponding Author; kishi.naoki@nitech.ac.jp

Abstract

We report the synthesis of single-layer graphenes on polycrystalline Ni foils by alcohol-based chemical vapor deposition (CVD) with IR-lamp heating. Heating with an IR lamp allows fast cooling and a reduction in the overall CVD time because of the rapid thermal processes in the heating and cooling stages. Spatially resolved Raman spectroscopy shows that single-layer graphenes are synthesized by CVD of alcohol with IR-lamp heating. The effects of the reaction temperature and alcohol type on the number of layers and graphene quality are investigated.

1. Introduction

Graphenes, which are novel nanocarbon materials, have attracted much interest in recent years. Some potential applications of graphenes have been proposed, such as field effect transistors [1] and transparent conductive films [2]. These applications have accelerated research activities on the syntheses of graphenes in the past few years.

Chemical vapor deposition (CVD) is expected to be a simple and low-cost method for the industrial synthesis of graphenes. Large-area graphenes have been grown by CVD on transition-metal substrates such as Ni [2-9], Co [10], and Cu [11-13]. In the case of Ni, a mechanism of graphene synthesis consisting of carbon precipitation from Ni during cooling after the reaction has been proposed [2-4], and a deposition mechanism that is similar to growth on Cu has recently been proposed [5]. In growth by carbon precipitation from Ni, the number of layers and graphene quality depend on the cooling rate. Yu *et al.* reported that few-layer graphenes were obtained on Ni foils by methane CVD with a cooling rate of 10 °C/s [3]. The rapid cooling process was carried out by mechanically pushing the sample holder to a lower-temperature zone after the reaction. Lee *et al.* reported the large-area synthesis of few-layer graphenes on Ni using a cold-wall CVD system with methane as the carbon source [6]. Their CVD system with a local Joule heater achieves faster cooling than that obtained with a conventional hot-wall CVD system. Recently, graphene growth using acetylene with a photothermal CVD system was reported [7]. Fast cooling, at a rate of 100 °C/min, was achieved in the CVD process.

Typical CVDs of graphenes use hydrocarbon gases such as methane [2-6,10,11] and acetylene [7,8] as the carbon source. Recently, CVD growth of graphenes using liquid carbon sources has been demonstrated and is expected to be a milestone in graphene synthesis because liquid precursors are inexpensive and easy to use [9,12-13]. Srivastava *et al.* reported the synthesis of single- and few-layer graphenes on Cu foils using hexane [12]. The synthesis of single-layer graphenes from ethanol on Ni foils using flash cooling by extracting the substrate from the electric furnace after the reaction has been reported [9]. However, further studies on CVD of graphenes using liquid precursors are required for facile graphene synthesis.

Here we report the synthesis of single-layer graphenes on Ni foils by alcohol-based CVD with IR-lamp heating. Heating with an IR lamp allows rapid cooling and a reduction in the overall CVD time because of the fast thermal processes in the heating and cooling stages. The obtained graphene materials were

characterized by Raman spectroscopy, which revealed that single-layer graphenes were synthesized by alcohol CVD with IR-lamp heating. We have investigated the effects of the reaction temperature and alcohol type on the number of layers and the graphene quality.

2. Experimental Details

Graphenes were synthesized on polycrystalline Ni foil (thickness 10 μm and area 1 cm × 1 cm) by CVD using ethanol or 2-propanol as the carbon source. An IR heating system with a SiC-coated graphite susceptor was used as the CVD reactor. The temperature of the CVD reactor was controlled using a thermocouple mounted in the susceptor. The CVD process was carried out at atmospheric pressure. Ni foil was loaded in the reactor, and the temperature was raised to the reaction temperature at a heating rate of 17 °C/s under a N_2 flow of 1000 mL/min, followed by annealing at the reaction temperature for 10 min. After annealing, the reaction was carried out by introducing alcohol into the reactor for 5 min. The alcohol vapor concentration in the CVD reactor was controlled to 1% by bubbling N_2 gas at a rate of 56 mL/min through temperature-controlled liquid ethanol and a 1000 mL/min dilution N_2 flow. After the reaction, the alcohol bubbling was stopped and the reactor was cooled to room temperature under N_2 flow. The temperature profile of the synthesis at 1000 °C, measured by a thermocouple mounted on the surface of the sample during the cooling process, is shown in Fig. 1. The temperature measured by this thermocouple is about 20 °C higher than that measured by the thermocouple mounted in the susceptor. The obtained graphene materials were characterized by spatially resolved Raman spectroscopy (JASCO; NRS-3300) with a ×50 objective lens. The Raman mappings were measured over 30 μm×30μm area with 3μm steps. The excitation wavelength of the Raman measurements was 532 nm. Transmission electron microscopy (TEM) observation was carried out on a JEOL JEM-z2500.

3. Results and Discussion

Fig. 2(a) shows a TEM image of graphenes synthesized using ethanol at 1000°C. The presence of graphenes was confirmed by TEM observation. Raman measurements were carried out to determine the number of layers and the graphene quality. The full width at half maximum (FWHM) of the 2D-band peak at around 2700 cm^{-1} and the intensity ratio of the G peak at around 1580 cm^{-1} to the 2D peak (I_G/I_{2D}) provide

information on the number of graphene layers [11,14-16]. Fig. 2 (b) shows the Raman mapping results for the FWHMs of the 2D peaks of graphene materials synthesized using ethanol at 1000 °C. It can be seen that several regions clearly show narrow FWHMs, colored in red. Fig. 2 (c) shows the map of I_G/I_{2D} in the same area. Comparisons between the 2D-FWHM and I_G/I_{2D} maps reveal that narrower 2D-FWHM regions are almost consistent with smaller I_G/I_{2D} regions. Fig. 2 (d) shows the Raman spectra obtained at the points A, B, and C marked in Fig. 2 (b). At A, there are a narrow 2D peak with an FWHM of 27 cm^{-1} and a small I_G/I_{2D} of 0.29; this indicates formation of single-layer graphenes. The 2D-FWHM and I_G/I_{2D} at B are 60 cm^{-1} and 1.31, respectively. This indicates that few-layer graphenes are formed at point B. The Raman spectrum at C has a large FWHM (76 cm^{-1}) and I_G/I_{2D} (1.89), indicating thicker-layer graphenes. The D-band peak at around 1350 cm^{-1} is negligible in these spectra, indicating high-quality graphene materials.

The distribution of the numbers of layers was estimated using the 2D-FWHM statistics. Fig 2 (e) shows the histogram of the FWHM of the 2D-band obtained from the Raman mapping. The histogram has a bimodal distribution. The peak positions of the distribution were evaluated to be 34 cm^{-1} and 63 cm^{-1} by Gaussian fitting; these correspond to single- and double-layer, and multi-layer graphenes, respectively. Furthermore, the cumulative counts plotted in Fig. 2 (f) indicate that about 33% of the FWHM values are less than 40 cm^{-1}.

The effects of synthesis temperature on the number of layers and the graphene quality were investigated systematically. Fig. 3(a)-(c) show Raman mappings of the 2D-FWHMs of samples synthesized using ethanol at 700 °C, 800 °C, and 900 °C. The samples synthesized at 700 °C and 800 °C show broader FWHMs of the 2D peak. Compared with the samples synthesized at 700 °C and 800 °C, there were smaller 2D-FWHM regions, colored in green, in the mapping of the sample synthesized at 900 °C. However, narrow FWHMs, less than 35 cm^{-1}, are not observed in the 900 °C sample. Fig. 3(d) shows Raman spectra taken from point A in Fig. 2 (b) and Fig. 3(a)-(c). As the growth temperature increased from 700 °C to 1000 °C, the intensity of the D-band peak decreased. This indicates that increasing the growth temperature increases the graphene crystal domain size [17] and improves the graphene quality.

We also tried to synthesize graphenes using 2-propanol as another alcohol carbon source. Fig.4(a) and (b) show a Raman map and the histogram of 2D-FWHM of the sample synthesized at 1000°C using 2-propanol, respectively. As shown in Fig.4(a), the Raman map shows narrow FWHM region, colored in red.

However, narrow FWHM region decreases in the mapping of the 2-propanol sample compared with that using ethanol as shown in Fig. 4(b). Therefore ethanol is better than 2-propanol for synthesis of single-layer graphenes in the present CVD process.

4. Summary

We have presented the synthesis of single-layer graphenes on polycrystalline Ni foils by alcohol CVD with IR-lamp heating. Spatially resolved Raman measurements show that about 33% of the 2D-FWHM values are less than 40 cm^{-1} for the graphene materials synthesized using ethanol at 1000 °C. We believe that these results will play an important role in developing facile syntheses of graphenes on Ni using liquid precursors.

References

[1] Meric I, Han M Y, Young A F, Ozilmaz B, Kim P, Shepard K L, Nature Nanotech 2008; 3: 654-9.

[2] Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M, Kim K S, Ahn J H, Kim P, Choi J Y, Hong B H, Nature 2009; 457: 706-10.

[3] Yu Q, Lian J, Siriponglert S, Li H, Chen Y P, Pei S S, Appl Phys Lett 2008; 93: 113103 1-3.

[4] Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S, Kong J, Nano Lett 2009; 9: 30–5.

[5] Juang Z Y, Wu C Y, Lu A Y, Su C Y, Leou K C, Chen F R, Tsai C H, Carbon 2010; 48: 3169-74

[6] Lee J M, Jeoung H Y, Park W I, J Electron Mater 2010; 39: 2190-5.

[7] Tan Y Y, Jayawardena K D G I, Adikaari A A D T, Tan L W, Anguita J V, Henley S J, Stolojan V, Carey J D, Silva S R P, Carbon 2012; 50: 668-73

[8] Nandamuri G, Roumimov S, Solanki R, Nanotech 2010; 21: 145604 1-4.

[9] Miyata Y, Kamon K, Ohashi K, Kitaura R, Yoshimura M, Shinohara H, Appl Phys Lett 2010; 96: 263105 1-3.

[10] Ago H, Ito Y, Mizuta N, Yoshida K, Hu B, Orofeo C M, Tsuji M, Ikeda K, Mizuno S, ACS Nano 2010; 4: 7407-14.

[11] Li X, Cai W, An J, Kim S, Nah J, Yang D, Piner R, Velamakanni A, Jung I, Tutuc E, Banerjee S K, Colombo L, Ruoff R S, Science 2009; 324:1312-4.

[12] Srivastava A, Galande C, Ci L, Song L, Rai C, Jariwala D, Kelly K F, Ajayan P M, Chem Mater 2010; 22: 3457-61.

[13] Guermoune A, Chari T, Popescu E, Sabri S S, Guillemette J, Skulason H S , Szkopek T, Siaj M, Carbon 2011; 49: 4204-10.

[14] Ferrari A C, Meyer J C, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov K S, Roth S, Geim A K, Phys Rev Lett 2006; 97: 187401 1-4.

[15] Hao Y, Wang Y, Wang L, Ni Z, Wang Z, Wang R, Koo C K, Shen Z, Thong J T L, Small 2010; 6: 195-200.

[16] Malard L M, Pimenta M A, Dresselhaus G, Dresselhaus M S, Phys Rep 2009; 473: 51-87

[17] Pimenta M A, Dresselhaus G, Dresselhaus M S, Cancado L G, Jorio A, Saito R, Phys Chem Chem Phys 2007; 9: 1276-91.

Figure captions

Fig. 1 Temperature profiles under cooling process, measured using a thermocouple mounted on the sample surfaces.

Fig. 2 (a) A TEM image of grahpenes synthesized using ethanol at 1000 °C. The scale bar is 0.2 μm. (b)-(f) The results of spatially resolved Raman spectroscopy of graphene materials synthesized using ethanol at 1000 °C. Raman mappings of (b) FWHMs of 2D-band and (c) I_G/I_{2D} values. (d) Raman spectra obtained at the points A, B, and C marked in (b). (e) Histogram of 2D-FWHM (gray bars) taken from the Raman mapping. The dotted lines denote fitting curves with Gaussian functions. The solid line indicates the sum of the fitting curves. (f) Cumulative count plot of FWHMs of 2D-band.

Fig. 3 Raman mappings of FWHMs of 2D-bands in samples synthesized using ethanol at (a) 700 °C, (b) 800 °C, and (c) 900 °C. (d) Raman spectra obtained at point A in Fig. 2 (b) and Fig. 3(a)-(c).

Fig. 4 (a) Raman mapping of 2D-FWHMs in the sample synthesized using 2-propanol at 1000 °C. (b) Histogram of 2D-FWHMs (gray bars) taken from the Raman mapping. The dotted lines denote fitting curves

with Gaussian functions. The solid line indicates the sum of the fitting curves.
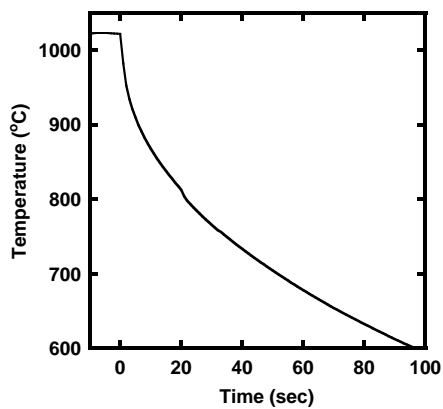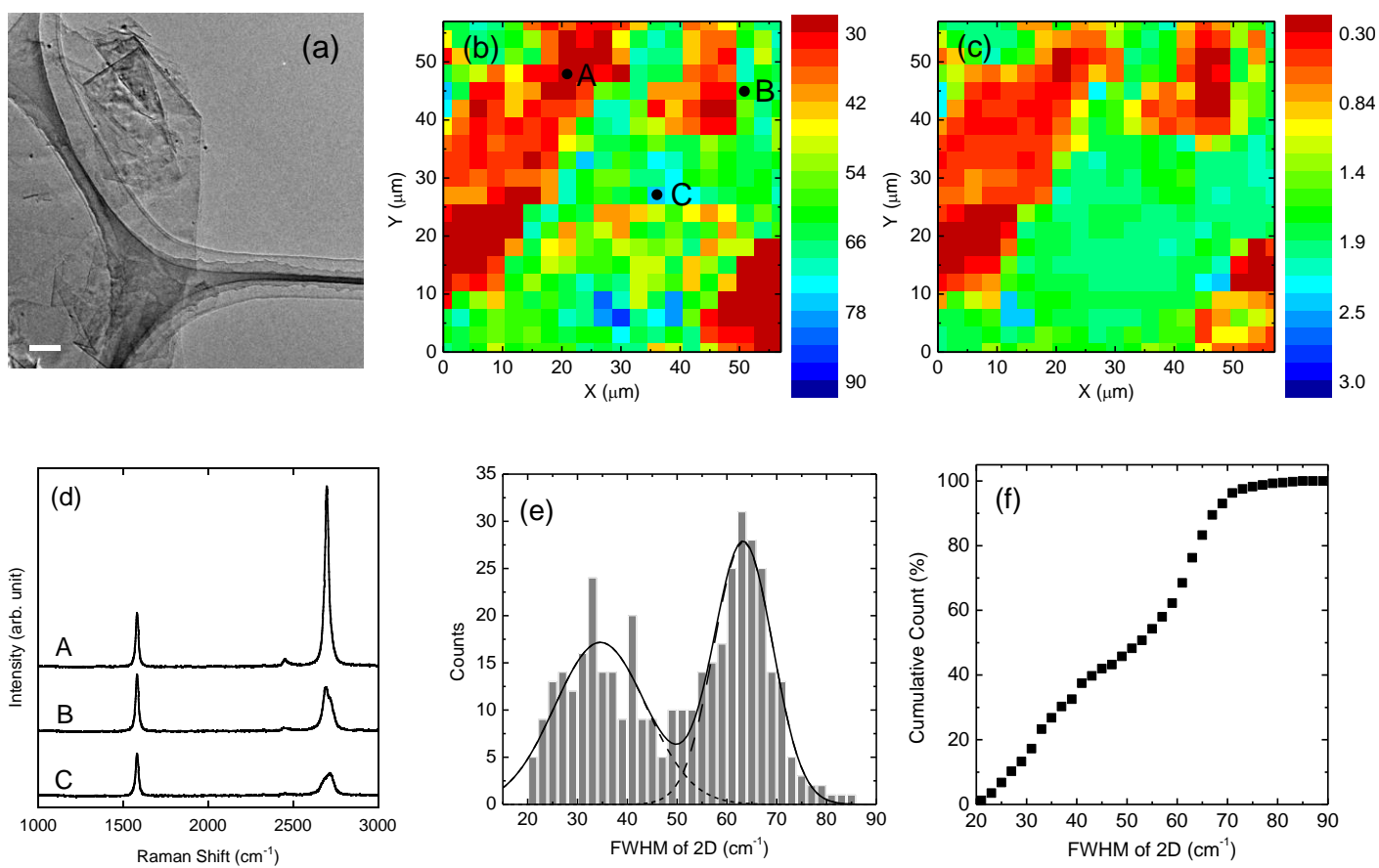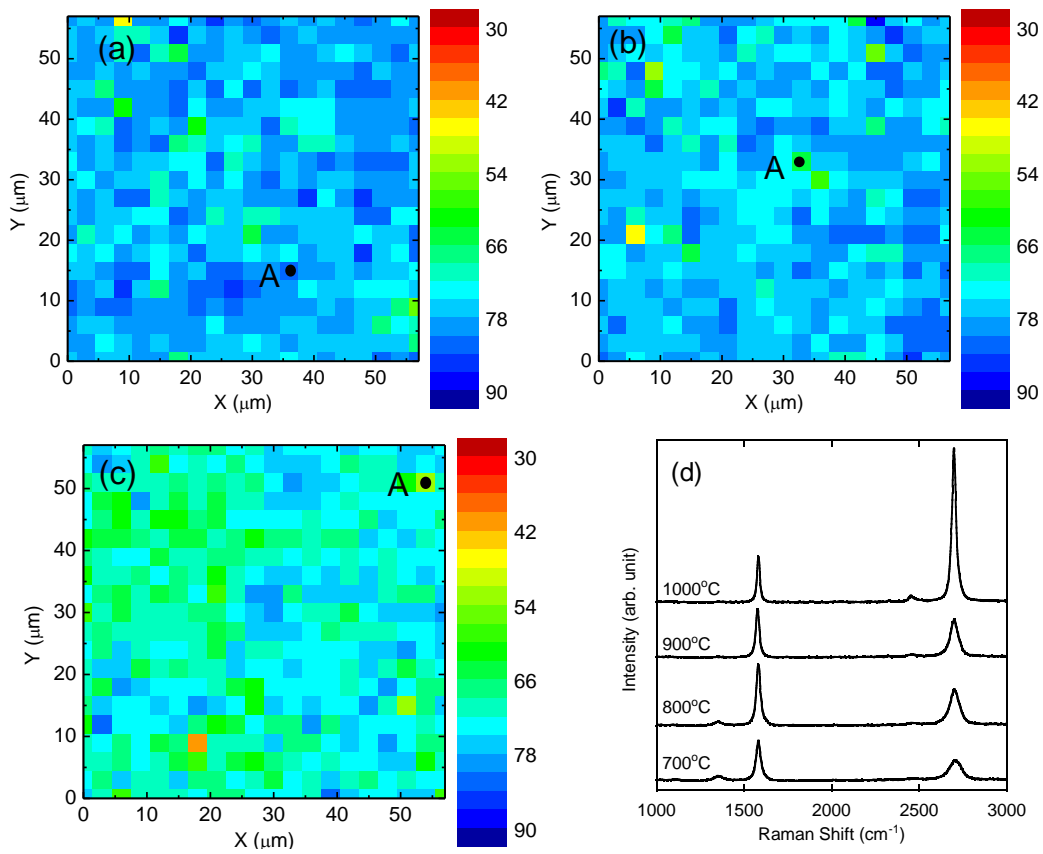
Fig. 1 N. Kishi *et al.*

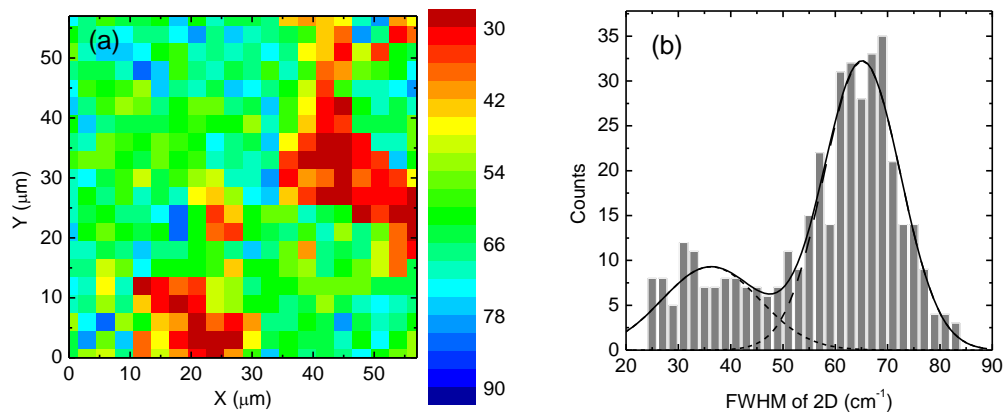**Fig.2 N. Kishi** *et al.*

Fig.3 N. Kishi *et al.*

Fig. 4 N. Kishi *et al.*