A simple alcohol-chemical vapor deposition synthesis of single-layer graphenes using flash cooling

Yasumitsu Miyata,[1] Keiichi Kamon,[1] Kazunori Ohashi,[1] Ryo Kitaura,[1] Masamichi Yoshimura,[2] and Hisanori Shinohara[1,a]

[1]*Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*
[2]*Toyota Technological Institute, Tempaku-ku, Nagoya 468-8511, Japan*

We report the synthesis of single-layer graphenes from ethanol using, what we call, "flash cooling" just after chemical vapor deposition. The single-layer graphenes synthesized are high-quality and several micrometers in grain size as revealed by Raman spectroscopy. Detailed comparison of the cooling processes suggests that the single-layer graphene growth does not occur during the carbon precipitation but rather stems from surface diffusions of carbon on a nickel substrate. Because of the present simple and easiness for the large-scale synthesis under an inert gas atmosphere and at atmospheric pressure, the present method can easily be applied for the future large-scale and low-cost graphene production. © *2010 American Institute of Physics*. [doi:10.1063/1.3458797]

Graphenes have attracted much attention as components of future electronic devices such as field effect transistors and transparent electrodes/conducting films because of their excellent electron transport properties.[1,2] To realize these potential applications, it is essential to synthesize high-quality and large-area graphene films. To date, such graphenes have been synthesized by several methods such as the thermal decomposition of SiC,[3] the carbon precipitation on Ru(0001),[4] and the chemical vapor deposition (CVD) on various metal substrates.[5–10] In particular, the CVD method provides a promising way for device applications since the large-area graphene films synthesized can be easily separated from the metal substrate and transferred to other desired substrates.[6,11,12]

One of the major challenges in CVD synthesis is the development of facile synthesis that should be essential in their industrial production. However, the previous methods require vacuum and explosive gases such as methane and hydrogen,[5–8] which entails a high cost of instrumentation together with a high degree of safety precautions. Thus, it is highly desirable to develop a facile synthesis method of high-quality graphenes.

Here, we report the facile synthesis of high quality single-layer graphenes from ethanol using "flash cooling" right after CVD growth. The graphenes are synthesized on nickel (Ni) foils under argon atmosphere at atmospheric pressure. The single-layer graphenes so synthesized are high-quality and several micrometers in grain size as revealed by Raman spectroscopy. Interestingly, the graphenes have never been observed for naturally cooled substrates in the present synthesis condition. This indicates that the graphenes synthesized were decomposed during the natural cooling process and that the flash cooling does not lead to this decomposition. This situation is quite different from the graphene growth on Ni substrates through the conventional precipitation process. We, therefore, conclude that carbon absorption on the Ni surface consists mainly of the following two different processes: (i) the carbon dissolution into the Ni substrate and (ii) the direct formation of graphenes on the surface.

Graphenes were synthesized through the reaction of a Ni substrate with ethanol at a temperature of 900 °C. First, a quart tube (3 cm in diameter, 100 cm in length) was filled with Ar gas with a flow rate of 300 cm^3/min. This gas flow continues throughout the graphene synthesis and cooling. Commercial Ni substrate (foil with a thickness of 5 μm, nilaco) was inserted into a preheated quart tube at 600 °C. When the temperature reaches at 900 °C, ethanol was introduced through the bubbling of liquid ethanol using Ar gas at 200 cm^3/min. After the reaction for 5 min, the bubbling was stopped. The substrate was then cooled at different cooling rates as shown in Fig. 1(a). In the flash cooling, the substrate was immediately extracted from the quart tube and then the temperature was decreased from 900 to 560 °C for around 10 s. In the natural cooling, the temperature was decreased from 900 to 560 °C for around 20 min. Graphenes synthesized were transferred from Ni onto a SiO$_2$/Si wafer using HNO$_3$ as reported by Yu *et al.*[9]

Raman spectra were measured in the back-scattering geometry using a single monochromator with a microscope (HR-800, Horiba Jobin Yvon) equipped with a charge-coupled device detector and a notch filter. The sample was excited by a He–Ne laser at 633 nm. Raman imaging of graphenes was performed with a micro-Raman spectrometer (inVia, Renishaw, Inc.) in the backscattering geometry using a 100 objective lens. The excitation wavelength was at 532 nm from a Nd–YAG laser.

Raman spectroscopy has been used to characterize the number of layers and grain size of graphenes synthesized as previously reported.[13,14] Raman spectra of a Ni surface after the CVD process show the G-band at 1580 cm^{-1} and symmetric two-dimensional (2D)-band with a narrow full width of half maximum (FWHM) of 33 cm^{-1} [Fig. 1(b)]. This corresponds to the well-known feature of single-layer graphenes.[13] The relatively low intensity of D peak suggests that synthesized graphenes is in high quality. The high G/D ratio (typically more than 20) suggests that grain size of graphenes is larger than 500 nm.[14]

---

a)Author to whom correspondence should be addressed. Electronic mail: noris@nagoya-u.jp.
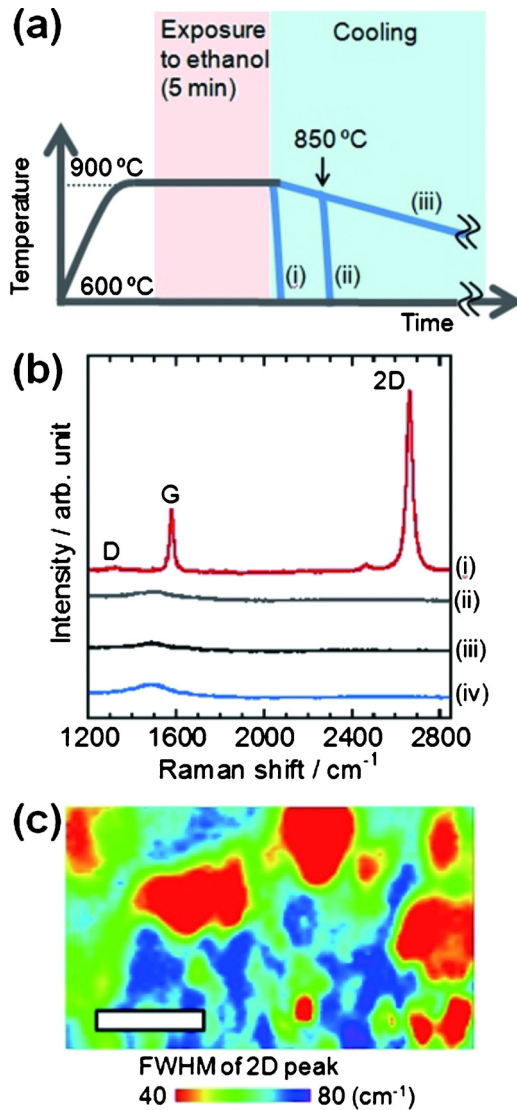
96, 263105-1

FIG. 1. (Color online) (a) Illustration of the present CVD process and the three different cooling processes after the reaction. The temperature of substrates was changes (i) from 900 to 600 °C within 10 s (flash cooling), (ii) from 900 to 850 °C around 70 s (natural cooling) and then to 600 within 10 s (flash cooling), and (iii) from 900 to 600 °C around 15 min (natural cooling). (b) Raman spectra of the surface of Ni substrates after [(i)–(iii)] each cooling processes and (iv) reannealing of graphenes on Ni at 900 °C for 5 min under Ar atmosphere (same to CVD condition except no ethanol flow). (c) Raman maps of the FWHM of 2D (around 2700 cm^{-1}) band on a nickel substrate. Scale bar is 10 μm.

The grain size of single-layer graphene was also evaluated by using Raman mapping. Figure 1(c) shows the mapping result of FWHM of 2D peak of graphenes on a Ni substrate. It can be seen that the several spots clearly show the narrow FWHM (around 40 cm^{-1} colored in red) of single-layer graphenes. From this mapping result, the grain size is estimated to be ranging from 1 to 10 μm. This is almost the same as the typical size of mechanically cleaved single-layer graphenes.[15] It is noted that the mapping of both the 2D peak position and the intensity ratio of 2D to G peaks are consistent with the result of the 2D FWHM. This indicates all of these Raman features can be used for the evaluation of grain size. In the same substrate, 2D peaks with broader FWHM (40–60 cm^{-1}) were also observed. These 2D peaks are similar to that of double-layer graphenes which were obtained from mechanically cleaved graphite[13] and also have grain sizes from 1 to 10 μm.
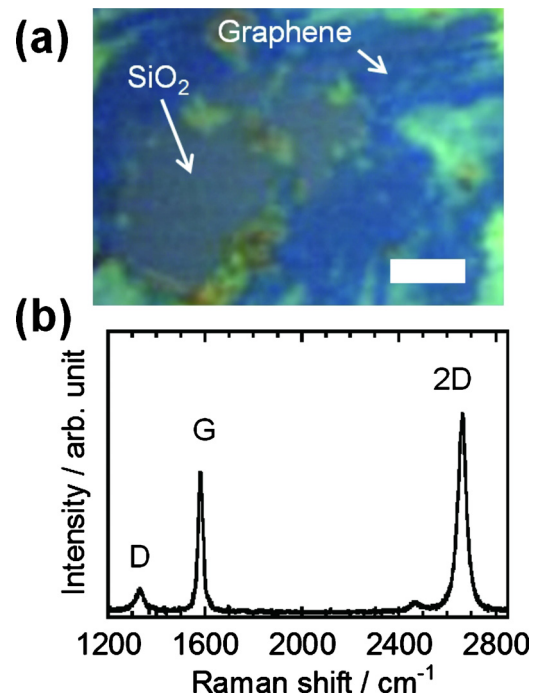

FIG. 2. (Color online) (a) An optical microscope image and (b) Raman spectrum of the transferred graphene on a SiO$_2$/Si wafer. Scale bar is 5 μm.

Similar Raman spectra of single-layer graphene were observed for transferred graphenes on Si/SiO$_2$ wafers and glass substrates [Fig. 2(b)]. The contrast of graphenes (against that of SiO$_2$ substrate) in Fig. 2(a) is higher than that of mechanically cleaved single-layer graphenes as shown in the Ref. 16. This is probably due to the presence of some surface impurities and/or the unique rotational stacking of the graphene films which causes adjacent graphene layers to be electronically decoupled.[17] The presence of single-layer graphenes was also supported by high-resolution transmission electron microscopy observations which clearly show their edge structures (Fig. S1 in Ref. 18).

In the present study, we found that the flash cooling (immediately after the CVD process) is necessary to obtain high quality single-layer graphenes. Although the flash cooling can provide the single-layer graphenes, such graphenes have never been observed for the surface of naturally cooled substrate (Fig. 1). A similar result was obtained for the substrate with flash cooling just after the natural cooling from 900 to 850 °C (within 70 s). This indicates that the decomposition of graphenes start rapidly just after the stop of the supply of carbon source. The graphenes decomposition on the high-temperature Ni was also confirmed by a reannealing experiment. Before the reannealing, the presence of graphenes was confirmed from Raman spectra at room temperature. The reannealed sample also does not show any D- and G-band Raman peaks, indicating the decomposition of graphenes. A similar result was reported previously for graphenes on Ni (111),[19] where graphenes start to decompose above 650 °C although they are stable at temperatures below 650 °C. Based on these results, we think that the flash cooling does not lead to this decomposition as illustrated in Fig. 3.

This situation is different from the graphene growth on Ni substrates through precipitation processes as described in previous reports. It is known that the CVD growth of graphenes occurs through two different growth processes: (i)
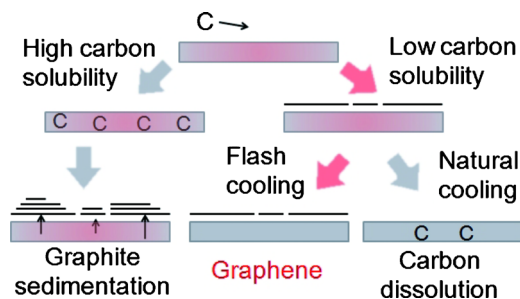
FIG. 3. (Color online) Schematic illustration of graphene and graphite synthesis processes on a nickel substrate.

carbon dissolution into metals and the concomitant precipitation, and (ii) surface diffusion of carbon on metal surface. The former process has often been observed for a high-temperature Ni substrate which has high carbon solubility around 1000 °C.[6,11] This precipitation process can produce both single layer and multilayer graphenes depending upon the cooling rate. In this process, single-layer graphenes were preferentially produced by controlling the cooling rate of substrate at typically 10 °C/s (Refs. 6 and 9) and 4–25 °C/min.[7] Furthermore, this graphene formation has quenched at an extremely fast cooling rate.[9] Importantly, this quenching has never been observed in the present experimental conditions.

The latter has been seen for copper (Cu) around 1000 °C and led to high-quality, uniform single-layer graphenes.[12] In this process, the low carbon solubility and surface catalytic activity jointly result in graphene growth through surface diffusion. Although the bulk Ni usually has high carbon solubility, it usually forms oxides on the surface. Because the surface oxide may reduce the carbon solubility, we attribute the presence of surface oxides to one of the main reasons for graphene growth through not only the carbon dissolution but also the surface diffusion.

If there were such different growth processes, one can expect that the graphene formation depends on various reaction conditions such as reaction time and CVD buffer gases. In fact, in the case of reaction for 30 min, most of the surface was covered with multilayer graphenes. This is reasonable because excess carbon dissolution should accelerate the segregation of multilayer graphenes. This multigrowth process can explain the presence of not only single-layer graphenes but also multilayer graphenes as shown in Fig. 1(c). For the buffer gases, we found that introduction of hydrogen gas as a carrier gas also caused the preferential growth of multilayer graphenes in the present synthesis (Fig. S2 in Ref. 18). This suggests that the hydrogen etching removes surface oxide on Ni and promotes the dissolution process of carbon in Ni. These results indicate that the suppression of the carbon dissolution is a key factor for single-layer graphene growth in the present condition and the presence of two different growth processes on the Ni substrate as summarize in Fig. 3. The suppressed carbon dissolution can explain why the slow cooling do not lead to the graphene formation through carbon precipitation in the present study, in contrast to the previous studies where sufficient carbon atoms could be dissolved in chemically etched Ni substrates.[6–9]

[1] A. K. Geim and K. S. Novoselov, Nature Mater. **6**, 183 (2007).
[2] K. I. Bolotin, K. J. Sikes, J. Hone, H. L. Stormer, and P. Kim, Phys. Rev. Lett. **101**, 096802 (2008).
[3] K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Rohrl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, and T. Seyller, Nature Mater. **8**, 203 (2009).
[4] P. W. Sutter, J. I. Flege, and E. A. Sutter, Nature Mater. **7**, 406 (2008).
[5] X. S. Li, W. W. Cai, J. H. An, S. Kim, J. Nah, D. X. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, Science **324**, 1312 (2009).
[6] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, J. H. Ahn, P. Kim, J. Y. Choi, and B. H. Hong, Nature (London) **457**, 706 (2009).
[7] A. Reina, S. Thiele, X. T. Jia, S. Bhaviripudi, M. S. Dresselhaus, J. A. Schaefer, and J. Kong, Nano Res. **2**, 509 (2009).
[8] S. J. Chae, F. Gunes, K. K. Kim, E. S. Kim, G. H. Han, S. M. Kim, H. J. Shin, S. M. Yoon, J. Y. Choi, M. H. Park, C. W. Yang, D. Pribat, and Y. H. Lee, Adv. Mater. **21**, 2328 (2009).
[9] Q. K. Yu, J. Lian, S. Siriponglert, H. Li, Y. P. Chen, and S. S. Pei, Appl. Phys. Lett. **93**, 113103 (2008).
[10] D. Kondo, S. Sato, K. Yagi, N. Harada, M. Sato, M. Nihei, and N. Yokoyama, Appl. Phys. Express **3**, 025102 (2010).
[11] Y. Lee, S. Bae, H. Jang, S. Jang, S. E. Zhu, S. H. Sim, Y. I. Song, B. H. Hong, and J. H. Ahn, Nano Lett. **10**, 490 (2010).
[12] X. S. Li, Y. W. Zhu, W. W. Cai, M. Borysiak, B. Y. Han, D. Chen, R. D. Piner, L. Colombo, and R. S. Ruoff, Nano Lett. **9**, 4359 (2009).
[13] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, Phys. Rev. Lett. **97**, 187401 (2006).
[14] M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cancado, A. Jorio, and R. Saito, Phys. Chem. Chem. Phys. **9**, 1276 (2007).
[15] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proc. Natl. Acad. Sci. U.S.A. **102**, 10451 (2005).
[16] Z. H. Ni, H. M. Wang, J. Kasim, H. M. Fan, T. Yu, Y. H. Wu, Y. P. Feng, and Z. X. Shen, Nano Lett. **7**, 2758 (2007).
[17] M. Sprinkle, D. Siegel, Y. Hu, J. Hicks, A. Tejeda, A. Taleb-Ibrahimi, P. Le Fevre, F. Bertran, S. Vizzini, H. Enriquez, S. Chiang, P. Soukiassian, C. Berger, W. A. de Heer, A. Lanzara, and E. H. Conrad, Phys. Rev. Lett. **103**, 226803 (2009).
[18] See supplementary material at http://dx.doi.org/10.1063/1.3458797 for the TEM images (Fig. S1) and the Raman results (Fig. S2).
[19] A. Grüneis, K. Kummer, and D. V. Vyalikh, New J. Phys. **11**, 073050 (2009).