Low-temperature synthesis of graphene on nickel foil by microwave plasma chemical vapor deposition

Y. Kim,¹ W. Song,¹ S. Y. Lee,¹ C. Jeon,¹ W. Jung,¹ M. Kim,¹ and C.-Y. Park^{1,2,a)}

¹BK21 Physics Research Division, Sungkyunkwan University, Suwon 440-746, Korea

²Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea

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Microwave plasma chemical vapor deposition (MPCVD) was employed to synthesize high quality centimeter scale graphene film at low temperatures. Monolayer graphene was obtained by varying the gas mixing ratio of hydrogen and methane to 80:1. Using advantages of MPCVD, the synthesis temperature was decreased from 750 °C down to 450 °C. Optical microscopy and Raman mapping images exhibited that a large area monolayer graphene was synthesized regardless of the temperatures. Since the overall transparency of 89% and low sheet resistances ranging from 590 to 1855 Ω/sq of graphene films were achieved at considerably low synthesis temperatures, MPCVD can be adopted in manufacturing future large-area electronic devices based on graphene film. © 2011 American Institute of Physics. [doi:10.1063/1.3605560]

Graphene, with its unique physical and structural properties, has recently become a proving ground for various physical phenomena,^{1–3} and it is a promising candidate for a variety of electronic devices and flexible display applications.^{4–7} Nevertheless, a major challenge in achieving the practical potential of graphene is the lack of a reasonable synthesis method for large-scale graphene films with tunable thickness, compatible with established large-scale semiconductor technologies. Various methods have been reported for the synthesis of graphene, one of which is mechanical exfoliation from highly oriented pyrolytic graphite.⁸ This method suffers from low throughput and produces graphene with limited area. Another method is chemical exfoliation from bulk graphite.⁹ In this case, oxidized graphite was cleaved via rapid thermal expansion or ultrasonic dispersion, and the graphene oxide sheets were subsequently reduced to graphene. A serious drawback of this method is that the oxidation process induces various defects that would degrade the electronic properties of graphene. A final method is the thermal decomposition of SiC.¹⁰ Even though the epitaxial graphene on SiC showed a good quality, the expensive SiC substrate limited its applications. Recently, thermal chemical vapor deposition (TCVD) synthesis on transition metal substrates has been emerged as a promising method for obtaining large-area and uniform graphene film. This method has been conducted at high temperatures around 1000 °C with a dependency on the source gases.^{7,11} However, a low temperature process for graphene synthesis would be indispensable for applications of graphene in electronic devices. Therefore, there is still a need to develop a reliable and reproducible method for low temperature synthesis of high-quality graphene that is suitable for the full exploitation of graphene properties and application potentials.

Microwave plasma CVD (MPCVD) has been shown to be successful in synthesizing carbon nanotubes (CNTs),^{12,13} nanowalls,¹⁴ nanosheets,¹⁵ and diamond films.¹⁶ MPCVD is thus envisioned to be also capable of synthesizing graphene

films. Recently, two works using surface wave plasma (SWP)-CVD (Ref. 17) and remote plasma assisted CVD (Ref. 18) exhibited a capacity to synthesize graphene at low temperatures. But, the former method showed a difficulty in synthesis of monolayer graphene, and graphene was synthesized at a relatively higher temperature of 650 °C in the latter method.

In this study, we demonstrated the capability of MPCVD in terms of a low temperature synthesis of monolayer graphene. High quality monolayer graphene films were synthesized on polycrystalline nickel foil by varying the mixing ratio of hydrogen (H₂) and methane (CH₄). The synthesis temperature was decreased down to 450 °C, resulting in graphene with a high transparency of 89% and a good sheet resistance of 1855 Ω/sq.

Graphene films were synthesized on polycrystalline nickel foil (Nilaco, 50 μm) using a cold-wall type MPCVD system (Woosin Cryovac, Korea) with a heating stage. The parameters for graphene synthesis included a substrate temperature of 450 to 750 °C and a total pressure of 20 Torr under various mixing ratios of H₂ and CH₄. During synthesis, a 2.45 GHz microwave with a power of 1400 W was used to generate the plasma. After synthesis, the foil was cooled to room temperature at a cooling rate of 3 °C/s. The synthesized graphene films were transferred onto SiO₂ (300 nm)/Si or polyethylene terephthalate (PET) using an aqueous FeCl₃ solution (1 mol/L) as previously reported.^{7,19} Raman spectroscopy (Renishaw, RM1000-Invia) with an excitation wavelength of 514 nm was used to measure crystallinity and the number of layers in the graphene films. Raman mapping was conducted using a confocal Raman spectrometer (WiTec, CRM200) with an excitation wavelength of 532 nm. High-resolution transmission electron microscopy (HR-TEM, JEOL, JEM2100F) was used to investigate the number of layers in the graphene films.

As mentioned above, we expected that MPCVD would allow for graphene synthesis at a lower temperature than TCVD synthesis. The synthesis of graphene films was started at 750 °C, and Raman spectra were recorded on the graphene

^{a)}Electronic mail: cypark@skku.edu.

FIG. 1. (Color online) (a) Raman spectra taken at an excitation wavelength of 514 nm for the graphene films synthesized at various gas mixing ratio (synthesis time: 1 min, temperature: 750 °C). HR-TEM images of the graphene films synthesized at various gases mixing ratio: (b) 80:1 (H_2 : CH_4), (c) 40:1, and (d) 10:1.

films synthesized by varying gas mixing ratio of hydrogen and methane, as shown in Figure 1(a). Raman spectroscopy is a powerful, yet relatively specimen-specific measurement to characterize the crystalline quality and number of graphene layers. Several criteria have been used to measure the number of graphene layers, such as the full width at half maximum (FWHM), the position of the 2D peak, and the intensity ratio of the 2D to G peak (I_{2D}/I_G).²⁰ When graphene was synthesized at a gas mixing ratio of 80 (H_2):1 (CH_4), a very strong 2D peak at 2700 cm^{-1} and a G peak at 1580 cm^{-1} appeared on the Raman spectra, and the D peak at 1350 cm^{-1} was very weak. The I_{2D}/I_G was around 3.7, 2.9, 2.3, and 0.6, corresponding to the gas mixing ratio of 80:1, 40:1, 20:1, and 10:1, respectively. The HR-TEM image in Figure 1(b) revealed that a perfect single layer graphene was formed on the nickel foil and agrees well with the Raman results at a ratio of 80:1. Decreasing the ratio of H_2 to CH_4 from 80:1 to 10:1 caused the 2D peak to decrease sharply and the D peak to rise gradually. The HR-TEM results agreed well with the Raman results and clearly showed that the number of graphene layers increased when decreasing the ratio. As shown in Figure 1(d), at 10:1 of H_2 to CH_4 , a graphene film was synthesized with 6 layers. Introducing more CH_4 gas, the 2D peak drastically decreased and the D peak was stronger. Moreover, at a ratio higher than 80:1, graphene of similar high quality was synthesized. These results show that 80:1 is the optimized gas mixing ratio to synthesize a monolayer graphene over a large-area with high quality and without defects.

FIG. 2. (Color online) (a) Raman spectra taken at an excitation energy of 2.41 eV for the graphene synthesized at several synthesis temperatures (gas mixing ratio (H_2 : CH_4): 80:1, synthesis time: 1 min). (b) FWHM of the 2D peak and the intensity ratio of the 2D peak compared to the G peak as a function of synthesis the temperature.

The dependence of graphene synthesis using MPCVD on temperature was investigated in a temperature range from 450 to 750 °C. When the synthesis temperature decreased, the 2D peak decreased slowly and the D peak gradually increased, as shown in Figure 2(a). At a temperature lower than 500 °C, the D peak increased, but there was no significant change in the G peak. Surprisingly, the I_{2D}/I_G over a large area at 450 °C was 2.1-2.9 (Figure 2(a)), which means that a monolayer graphene was synthesized with some defects. The shoulder on the right side of the G peak (D' peak) is due to defect-induced Raman features, and thus, this peak cannot be seen for a high crystalline graphene.²¹ The 2D peaks at all synthesis temperatures showed a nearly single Lorentzian line-shape. Nevertheless, the FWHM of the 2D peak gently increased with decreasing temperature, as shown in Figure 2(b), which indicates that defects in the graphene layer were formed locally. On the other hand, at less than 450 °C, a very poor graphene layer with abundant defects was synthesized.

The uniformity of graphene films synthesized at 750 and 450 °C were examined by (a, c) optical microscopy and (b, d) Raman mapping, as shown in Figure 3. The results show that overall coverage of monolayer is $\sim 80\%$ regardless of the temperatures. The coverage of monolayer was also confirmed by measuring transmittance of the graphene films, resulting in $\sim 89\%$ at a 550 nm wavelength regardless of the synthesis temperatures (not shown here). The sheet resistances of the graphene films synthesized at 750, 700, 600, 500, and 450 °C were examined for practical applications after being transferred onto the PET substrate, as shown in Figure 3(e). Each sheet resistance was measured using the four-point probe

FIG. 3. (Color online) (a) and (c) Optical microscopy and (b) and (d) Raman mapping images of graphene films on SiO₂/Si substrate synthesized at 450 and 750 °C, respectively. (e) Plot of sheet resistance as a function of the synthesis temperature. The inset shows a photograph of the graphene film transferred onto the PET substrate.

method and was found to be 1855, 1660, 1430, 690, and 590 Ω/sq at 450, 500, 600, 700, and 750 °C, respectively. These results strongly suggest that the graphene films synthesized with decreasing the temperature are all monolayer with some defects. The best sheet resistance, 590 Ω/sq, was obtained from the graphene film synthesized at 750 °C, a finding that is comparable to those of other reported graphene films. The rapid increase in sheet resistance at a temperature lower than 500 °C indicated that considerable defects at the atomic level were generated in the graphene layer during the synthesis.

In summary, we demonstrated a low-temperature synthesis of centimeter scale monolayer graphene on nickel foil using MPCVD. Monolayer graphene films were synthesized at temperatures ranging from 450 to 750 °C with a gas mixing ratio of 80 (H₂):1 (CH₄). The transmittance of graphene films was ~89% at 550 nm regardless of the temperatures,

and the good sheet resistances ranging from 590 to 1855 Ω/sq were obtained. These results prove that the MPCVD method can generate high quality graphene at significantly lower temperatures (450-750 °C) than that in conventional TCVD processes. We believe that MPCVD is potentially useful for the synthesis of graphene films for electronic device applications because a low temperature process in electronic device manufacturing is imperative.

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