Optimization of multi-layer graphene/PMMA synthesized by low-pressure chemical vapor deposition from acetylene precursor

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Abstract. High quality and large-scale graphene are required for large-scale applications, especially flexible transparent conductive touch-screen panels. Chemical vapor deposition is so far the best method for the synthesis of high-quality graphene on the large scale. In this work, we synthesized multi-layer graphene on copper foils by low-pressure chemical vapor deposition from acetylene precursor at the flow rate of 20-40 mL/min and with reaction times from 10-30 minutes. Graphene on copper foils was then coated with PMMA and transferred by a wet chemical etching method. The transmittance and electrical properties of graphene on polymer were investigated. The Raman spectra of graphene synthesized with the acetylene flow rate of 30 mL/min for 10 minutes showed the characteristics of bi-layer graphene (I_{2D}/I_G = 1.6) with the lowest sheet resistance values (2.05 kΩ/sq) and the best transmittance (73 %).

1. Introduction

Graphene is sp^2 carbon atom arranged in hexagonal lattice structure in a two-dimensional structure. It has fantastic electronic properties [1] which are small band gap and light weight. The applications of graphene are flexible transparent conductive electrodes, barrier films, touch-screen panels etc. For high quality and large-scale graphene, graphene from CVD on copper [2,3] is the best method which gives high-quality graphene and large area. The graphene from CVD commonly used methane as a precursor. By using low-pressure CVD (LPCVD) with methane gas, the exposure times were more than 1 hour and the reaction temperature was ~1000°C [4]. Due to the high dissociation energy of methane, higher processing temperature and longer processing times are required which can induce copper sublimation. Thus, acetylene is a competitive choice of hydrocarbon gases to use in graphene CVD that has lower dissociation energy and higher adsorption energy on copper surface than methane. Qi et al. reported the synthesis of graphene on copper foils using the atmospheric pressure chemical vapor deposition (APCVD) with acetylene [5] and studied the effect of hydrogen concentration on graphene growth. Mueller et al. succeeded to produce monolayer graphene on copper foil by ultrahigh vacuum CVD (UHVCVD) using acetylene [6]. The exposure times of acetylene process was up to 1 hour in the UHCVD process. Yang et al. used LPCVD to synthesize graphene on Cu foil using acetylene precursor

[7]. The acetylene flow rate and duration time in CVD process showed significant effects on the quality of graphene, copper sublimation and cost per round. Therefore, in this work, we synthesized graphene by LPCVD using acetylene precursor. We optimized the flow rate and the exposure time of acetylene gas in the CVD process. These parameters affected the quality of graphene, especially the I_{2D}/I_G, sheet resistance and transmittance of the synthesized specimens.

2. Experiments

In our experiment, commercial copper foil (99%, 500 μm thick) was used as the substrate. Copper foils were dipped into 5% aqueous solution of nitric acid for 120 s and washed by deionized water to remove the impurity on copper. Then, the copper foils were placed in a cylindrical quartz tube reactor (outer diameter 50 mm). The reactor was heated up to 880°C under Ar ambient with the flow rate of 90 mL/min. In the pre-heating process, the mixture gas of Ar:H_2 (95%:5%) with the flow rate of 80 mL/min has been fed into the chamber for 20 min. Then, acetylene gas with different flow rates from 20, 30 and 40 mL/min was introduced into the reactor with different reaction times from 10, 20 and 30 minutes. The total pressure in this state was 6.5 mbar. After the reaction process, the specimens were cooled down to room temperature in Ar ambient. Our experiment generated 9 samples. The label capital G stands for the graphene sample. The number from left to right indicates the acetylene flow rate in mL/min and the last number represents the exposure time in minutes.

The as-grown graphene/copper foils were coated with Poly(methyl methacrylate) (PMMA) as supported films during the copper etching process. Then, copper foils were soaked in Iron (III) nitrate aqueous solution (1 M) for overnight to remove copper layer and leave graphene on top of the solution. Graphene was rinsed with deionized water 10 times to get rid of Iron (III) nitrate solutions. Polyethylene terephthalate (PET) film was used to pick up graphene/PMMA. It was then dried by heating on a hotplate at 80°C for 5 minutes. After that, Raman spectrometer, UV-Vis spectrometer and 4-point probe measurements were used to observe the number layer of graphene, disorder structure, transparency and sheet resistance, respectively. Field emission scanning electron microscope was used to characterize defects and wrinkles of graphene/PMMA.

3. Results and Discussion

Figure 1 shows the Raman spectra of graphene/PMMA at the excited wavelength of 532 nm from graphene synthesized with the acetylene flow rate of 30 mL/min and the exposure time of 10 minutes (figure 1a) and 30 minutes (figure 1b). The spectra show three main peaks of sp^2 carbon D, G and 2D peak at ~1347, ~1581 and ~2690 cm^{-1}, respectively. Other peaks besides D, G and 2D peak in figure 1 are the Raman signal from PMMA and PET film beneath the graphene layer.

The relative ratio of I_D/I_G represents defects in graphite structure, while the ratio of I_{2D}/I_G represents fingerprint graphene layer. The I_D/I_G only 0.2 with the highest I_{2D}/I_G of 1.6 was obtained from the graphene synthesized from the acetylene flow rate of 30 mL/min for 10 minutes (figure 1a). This indicated that bi-layer graphene formed in this condition [8,9]. While, in other samples, the Raman spectra represent the I_D/I_G was ~0.6-0.9 and the I_{2D}/I_G was ~0.2-0.5. This indicated that the multilayer graphene formed. The example of multilayer graphene from G-30-30 was shown in figure 1b.

From SEM images, shown in figure 2a and 2b, the surface morphology of graphene on PMMA of sample G-30-10 showed smooth surface than that of the sample G-30-30. While, many wrinkles appeared in sample G-30-30 because the multilayer graphene formed. The white particle seen in both figures were contaminated silicon particles possibly from fused quartz during the CVD process [10].

The Raman spectra of all conditions were summarized in table 1. As seen from the table, as the exposure times increased, the I_{2D}/I_G showed the decreasing trend. However, the increase of acetylene flow rate did not affect the I_{2D}/I_G. This ratio varied between 0.2 and 0.5. Except in the sample G-30-10, the highest I_{2D}/I_G of 1.6 was obtained. This condition confirmed the formation of bi-layer graphene.

Qi et al. and Yang et al. achieved bi-layer graphene with the acetylene flow rate of 1 mL/min for 10 and 4 minutes, respectively. Moreover, Qi et al. reported when increasing additional H_2 concentration to acetylene gas, new graphene layers continue to form on top of graphene [5]. The selection of acetylene

flow rate might be different depending on dissociation temperature, pressure, H_2 concentration in the reaction and the size of CVD chamber. These affected the kinetic growth of graphene.

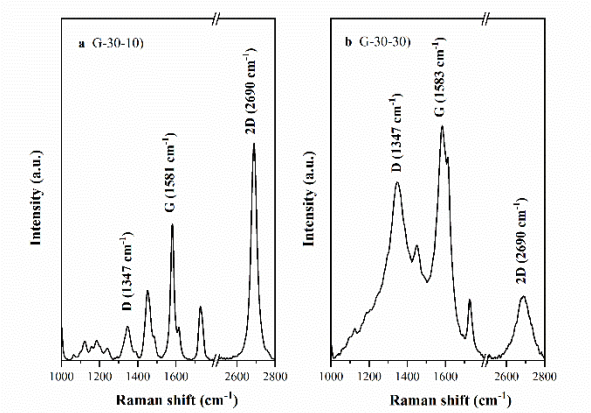

Figure 1. Raman spectrum of graphene/PMMA using acetylene flow rate of 30 sccm for (a) 10 minutes and (b) 30 minutes.

Table 1. Summary of peak position, the ratio of I_D/I_G and I_{2D}/I_G, sheet resistance and transmittance of synthesized graphene.

Sample	Peak center (cm^{-1})			I(D)/I(G)	I(2D)/I(G)	Sheet Resistance (kΩ/sq)	%T
	D Band	G Band	2D Band				
G-20-10	NA	1581	2687	NA	0.5	843	83
G-20-20	1349	1586	2699	0.9	0.4	20.1	71
G-20-30	1347	1581	2685	0.7	0.2	2.77	55
G-30-10	1347	1581	2690	0.2	1.6	2.05	73
G-30-20	1342	1583	2673	0.8	0.4	3.32	63
G-30-30	1347	1583	2690	0.8	0.3	3.15	58
G-40-10	NA	1585	2615	NA	0.5	109	83
G-40-20	1342	1586	2687	0.6	0.4	9.94	61
G-40-30	1347	1580	2687	0.7	0.3	3.79	50

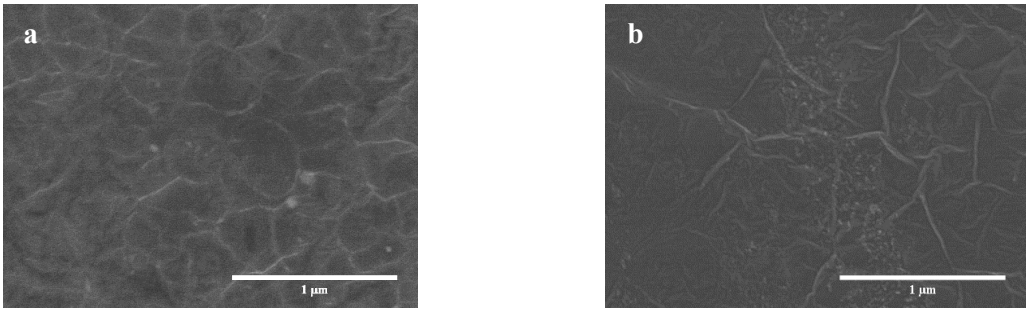

Figure 2. SEM images of graphene on PMMA using acetylene flow rate 30 mL/min for (a) 10 minutes and (b) 30 minutes

The 4-point probe measurement and UV-Vis spectrometer were used to investigate the sheet resistance and the transmittance at 550 nm of graphene/PMMA. The obtained data were also shown in table 1. The lowest sheet resistance was 2.05 kΩ/sq with the transmittance of 73 were observed from the sample G-30-10. The sheet resistance obtained from others sample are varied from ~ 2768 to 1M Ω/sq. Cai et al. reported that graphene on copper by LPCVD using methane had the sheet resistance of ~2kΩ/sq with transmittance values of ~90%. While, Yang et al. reported the sheet resistance was ~1.1-1.3 kΩ/sq without the transmittance data. Our best sheet resistance from sample G-30-10 was similar to those of Cai et al. [2] and Muller et al. [6] but higher than that of Yang et al.

4. Conclusion

The best graphene synthesized by LPCVD was obtained with the acetylene flow rate of 20 mL/min and the exposure time of 10 minutes. This highly uniform bi-layer graphene had the sheet resistance of 2.05 kΩ/sq and the corresponding transmittance of 73%. For the application of flexible transparent conductive films, the sheet resistance and transmittance of graphene CVD should be improved.

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