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Effect of Acetic Acid Pre-Treatment on the Growth Temperature of Graphene on Copper by Thermal Chemical Vapor Deposition

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Abstract. Graphene is a flat monolayer of carbon atoms arranged in a honeycomb lattice. Graphene has many outstanding properties such as high electron mobility, superb strength, transparency and great flexibility. These exotic properties make graphene a promising candidate for solar cell, fuel cell, battery, supercapacitor and so on. In this report, we have studied the effect of acetic acid pre-treatment on the growth temperature of graphene on copper by thermal chemical vapor deposition (CVD). In case of graphene growth without acetic acid pre-treatment, the high temperature of 1000 °C is needed for the growth of graphene by CVD. In contrast, the growth temperature can be decreased to 800 °C for graphene growth with acetic acid pre-treatment. We found that acetic acid pre-treatment can eliminate copper oxide from the sample surface resulting in the growth temperature of graphene decreases.

1. Introduction

Graphene is a flat monolayer of carbon atoms arranged in a honeycomb lattice. Graphene has many outstanding properties such as high electron mobility [1], superb strength [2], transparency [3] and great flexibility [4]. These exotic properties make graphene a promising candidate for solar cell [5], fuel cell [6], battery [7], supercapacitor [8] and so on. Graphene can be fabricated in many methods such as mechanical exfoliation of graphite [9], annealing SiC substrates [10-13] and chemical vapor deposition (CVD) of hydrocarbon gas on metal surface [14-15]. The growth of graphene on copper by CVD has been attracted attention since the high-quality monolayer graphene can be grown on copper due to its low carbon solubility [16]. However, the growth of high-quality and large-area monolayer graphene is still challenging because the conditions of CVD and copper surface have to be controlled intensively.

Pre-treatment of copper surface is a necessary process for the growth of graphene on commercial copper by CVD because it can remove the impurity and copper oxide from the copper surface.

Chemical etching is a popular procedure for etching of copper surface [17]. Nevertheless it cannot treat the extreme-thin copper because the chemical etching reduces the thickness of copper. Boiling copper in acetic acid is a pre-treatment for eliminating oxide layer from the copper surface without etching. Therefore, the acetic acid pre-treatment becomes a suitable method for cleaning the copper surface. In this report, the effect of acetic acid pre-treatment on the growth of graphene on copper by CVD is studied. The presence of copper oxide is confirmed using Raman spectroscopy and energy dispersive X-ray spectroscopy (EDX).

2. Experiment

Copper plates with the thickness of 0.18 mm were cut to dimension of 40 mm×30 mm followed by boiling in acetic acid at 100 °C for 20 minutes. After that, the copper plates were cleaned by ultrasonic cleaner in acetone for 5 minutes. After the acetone evaporated, a copper plate was put in a quartz tube of CVD furnace. The air was evacuated from the quartz tube until the base pressure reached ~10^{-3} torr and then heated to 800-1000 °C with an average heating rate of 15 °C per minute. At the growth temperature, acetylene gas with flow rate of 200 sccm was introduced into the quartz tube. The copper plate was annealed for 30 minutes under a pressure of 1 torr. After that the acetylene gas was stopped and the sample was cooled down rapidly to room temperature.

The presence of graphene and copper oxide on the copper plate was confirmed by Raman measurements carried out at room temperature using a Renishaw spectrometer with a 100x objective and a 532 nm laser. The laser beam size is 1 μm in diameter. Surface morphology and element analysis were measured using field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive analysis of X-rays (EDX) facility (Jeol) at incident beam of 15 keV.

3. Results and discussion

Figure 1 shows Raman spectra of the samples annealed at 800-1000 °C with/without acetic pre-treatment. In the case of samples annealed at 800 °C and 900 °C without acetic pre-treatment, the Raman peaks at 280, 330 and 612 cm^{-1} are clearly appeared. The presence of these Raman peaks reveals that the surfaces of these samples are covered by CuO [18]. The absence of G peak (~1584 cm^{-1}) and 2D (~2700 cm^{-1}) confirms that there is no graphene on these samples. For the sample annealed at 1000 °C without acetic pre-treatment and the sample annealed at 800 °C and 900 °C with acetic pre-treatment, the Raman spectra show D, G and 2D peaks at ~1350 cm^{-1}, ~1584 cm^{-1} and ~2700 cm^{-1}, respectively. The presence of G and 2D peaks of these samples confirms the presence of graphene on the sample surfaces. Figure 2 shows SEM images of the sample annealed at 800 °C and 900 °C with/without acetic pre-treatment. The presence of oxide on the surfaces is also confirmed by EDX as shown in Table 1. However, the Raman spectroscopy and EDX are measured at different position therefore the appearance of little weight% of oxygen in the sample annealed at 800 °C with acetic pre-treatment is possible.

The results of Raman spectroscopy and EDX reveal that the presence of CuO on the sample surface obstructs the formation of graphene therefore the elimination of CuO before the growth of graphene on Cu is needed. The sample annealed at 1000 °C shows that the CuO can be removed from the surface at annealing temperature of 1000 °C. In addition, the acetic pre-treatment can eliminate CuO by reacting with CuO to form cupric acetate by the following reactions [19]

$$CuO + 2CH_3COOH \rightarrow Cu(CH_3COO)_2 + H_2O$$

The cupric acetate can be eliminated from the surface at low temperature (~240 °C) therefore the acetic acid pre-treatment can lower the growth temperature of graphene on copper.

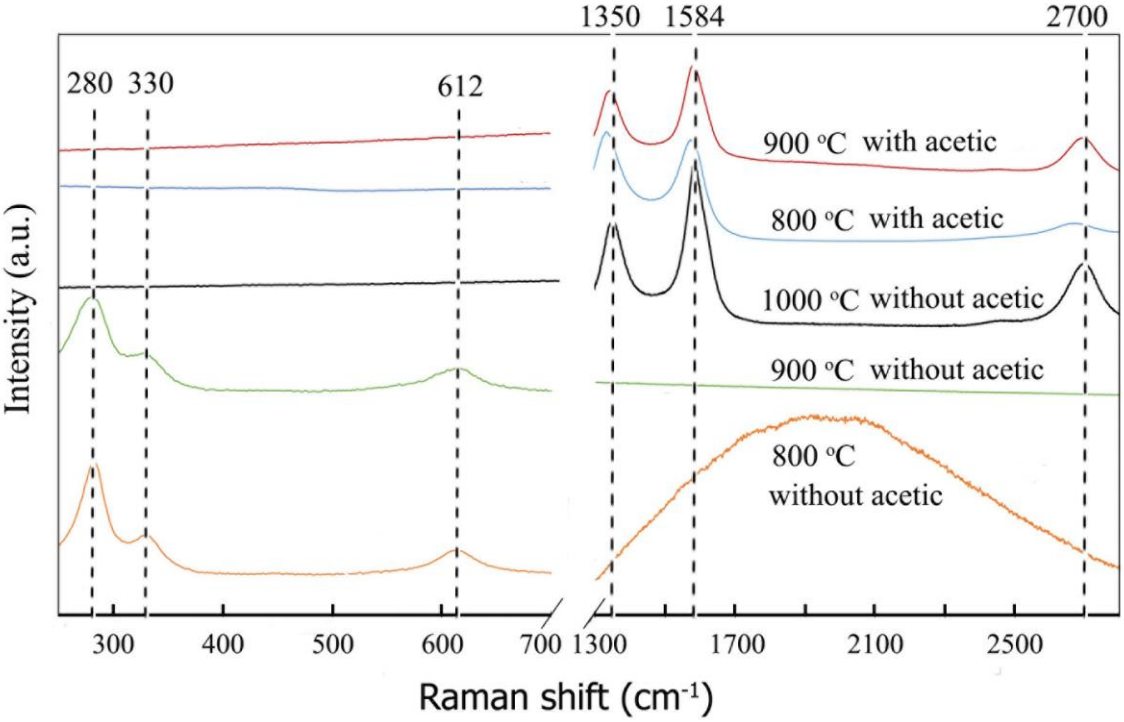

Figure 1. Raman spectra of as prepared copper with/without acetic pre-treatment at growth temperature from 800°C to 1000°C.

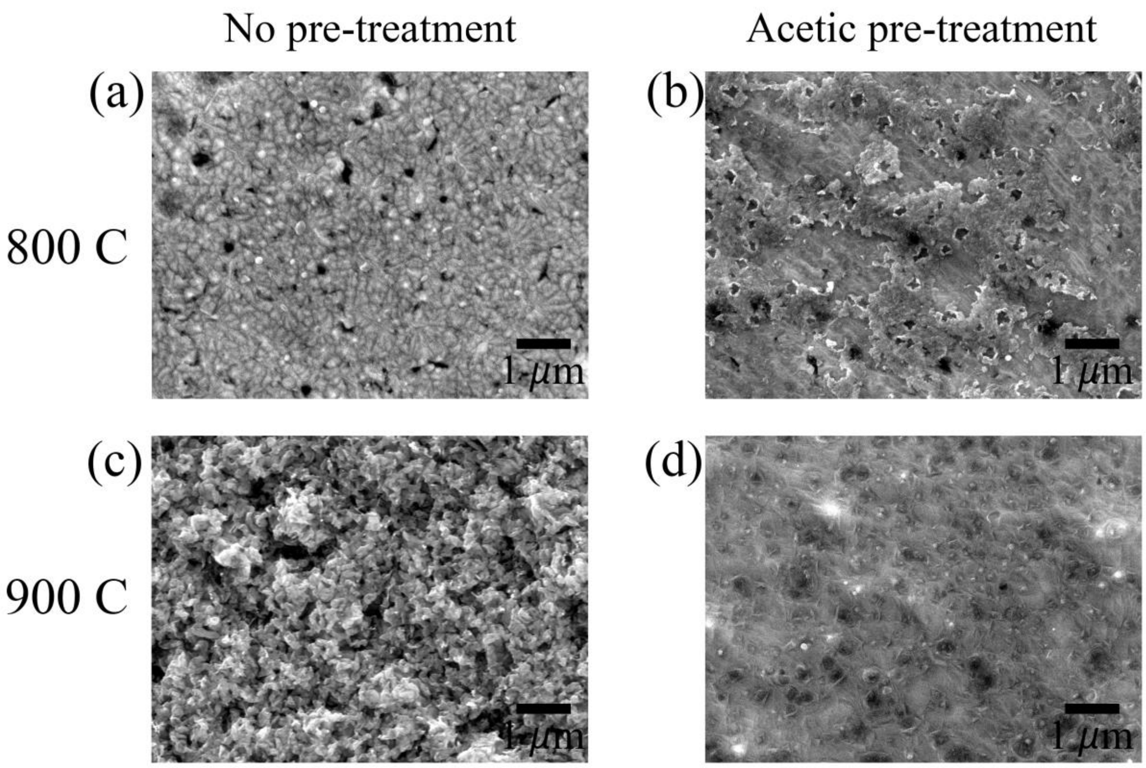

Figure 2. SEM images measured on the as prepared copper with/without acetic pre-treatment at annealing temperature of 800°C and 900°C.

Table 1. EDX analysis of as prepared copper with/without acetic pre-treatment at annealing temperature from 800°C to 1000°C.

Acetic pre-treatment	Growth temperature	Weight%			Atomic%		
		C	O	Cu	C	O	Cu
No	800	10.99	1.12	87.88	38.64	2.97	58.40
	900	4.00	19.35	76.65	12.12	44.00	43.88
	1000	63.52	-	36.48	90.21	-	9.79
Yes	800	18.97	0.66	80.37	54.73	1.43	43.83
	900	10.82	-	89.18	39.10	-	60.90

4. Conclusion

In this report, the effect of acetic acid pre-treatment on the growth of graphene on copper by CVD is studied. The acetic acid pre-treatment can eliminate copper oxide from the copper surface resulting in reduction of the growth temperature of graphene on copper.

5. References

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