Journal of Ceramic Processing Research. Vol. 15, No. 4, pp. 269~272 (2014)

JOURNAL OF
Ceramic Processing Research

Synthesis of graphene on various copper foils by chemical vapor deposition

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Recently, mono-layer and few layer graphene films grown by chemical vapor deposition (CVD) using metal substrate as a catalyst have attracted tremendous attention for the last few years. Copper (Cu) has been extensively used as a growth catalytic substrate due to its very low carbon solubility, which is thought to be responsible for the self-limiting precipitation growth and surface decomposition of carbon-containing molecules. Graphene films were synthesized on two types of catalytic substrates, electro-plating and rolling Cu foil, by chemical vapor deposition. Graphene film grown on various Cu foils was analyzed by Raman spectroscopy and scanning electron microscopy (SEM), with the aim of assessing their characteristics and finding the optimum catalyst conditions.

Key words: Graphene, CVD (chemical vapor deposition), Cu catalyst, electrolyte Cu foil, rolled Cu foil.

Introduction

Graphene is a 2-dimentional structure obtained from graphite that was found in 2004 by a group in Manchester [1]. Graphene is defined as massless a Dirac fermion, and it shows electron mobility that is 20 time higher than that of silicon [2], a Young's modulus 5 times more than that of Fe [3], a thermal conductivity 20 times higher than Cu [4]. In the case of monolayer graphene, it absorbs 2.3% of the incident light and shows high transmittance [5]. Graphene has attracted attention because of these superior characteristics.

In 2009, using CVD with the decomposition of methane (equation 1) [6], a thin Cu film was used as a catalyst to produce graphene. After it was found out that the production of graphene with CVD with a metal catalyst was very efficient, research using CVD received attention.

$$CH_4 \underset{Cu}{\Leftrightarrow} C+2H_2 \tag{1}$$

The catalytic metal Cu used in the synthesis of graphene has low solubility in carbon, so the growth is controlled by the surface of catalytic substrate to make monolayer graphene.[7]

Among the various things that influence the growth of graphene by CVD, the catalyst copper is the most important element. In this work, graphene was synthesized on various Cu catalysts using CVD, and the characteristics of graphene were analyzed by Raman spectra, sheet resistance, SEM, and optical microscopy.

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Experimental

The four kinds of Cu foils (99.8%) used are electroless, electrolytic (Iljin materials (No.ICS)), and two rolled foils (Alfa Aesar (No.13382) and Nippon Mining & Metals Corporation (No. BHZ-Z-T)). The Cu foils were cleaned in Acetone for 30 min, washed with DI water, and dried in an oven.

The Cu foil was annealed for 1 hr under H_2 (10 sccm) to remove impurities on the Cu surface and to grow the Cu grain size at 1000 ºC. The graphene growth was performed under a mixture of H_2 (10 sccm) and CH_4 (15 sccm) gas at 1000 ºC for 25 min. After graphene growth, the H_2 was turned off at 1000C and cooled down at a cooling rate of 10 ºC/sec until 600 ºC. CH_4 was turned off at 600 ºC and the gas was exchanged with Ar (30 sccm) until room temperature [8]. The graphene on Cu foil was spin-coated with PMMA (polymethylmethacrylate) and baked for 1 min at 180 ºC.

The graphene underneath the Cu foil was etched away by O_2 plasma, and the PMMA/graphene/Cu was floated in $(NH_4)_4S_2O_8$ solution to etch the Cu away. After Cu etching, PMMA/graphene film was transferred onto PET and SiO_2 (300 nm)/Si substrates [8].

PMMA/graphene/substrates were immersed in acetone

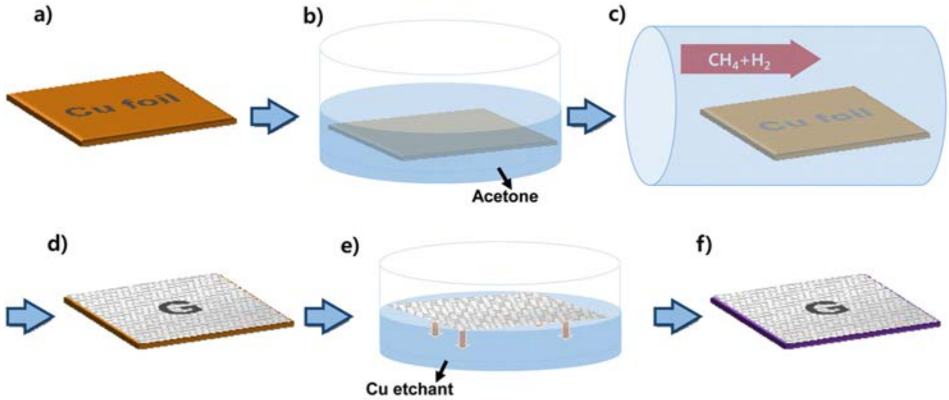

Fig. 1. Synthesis, etching and transfer processes diagram; (a) 4 types of Cu foil preparation, (b) Cu foil pretreatment in acetone, (c) Graphene growth in CVD system, (d) Graphene grown on Cu foil, (e) Cu foil etching using Ammonium per sulfate, (f) Transfer of graphene.

and then in IPA (isopropanol) to remove the PMMA layer, followed by annealing in a dry oven at 70 ºC for 1 hr (Fig. 1).

Results and Discussion

Fig. 2 shows the Cu grain size after graphene growth. The grain growth aspect of the Cu surface could be verified for facilitating the growth of graphene. The grain size was the smallest in the electroless Cu foil, but the size of all grains looked uniform. In the case of electrolytic Cu foil, the grains did not seem homogenous. The rolled Cu foil had the largest grain size among them.

Raman spectroscopy has been used to investigate the structural and electronic characteristics of graphite materials. Useful information is obtained from the D

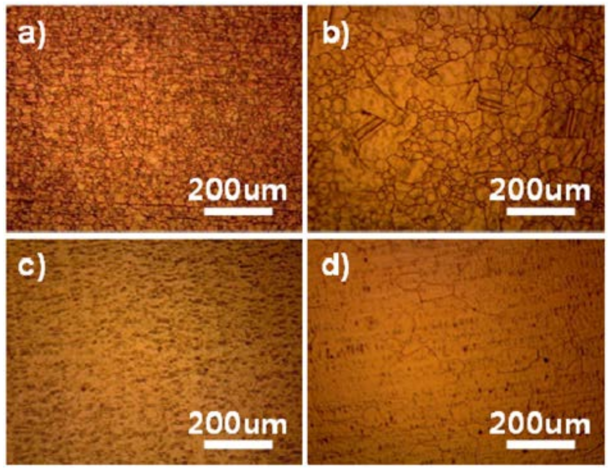

Fig. 2. Grown Cu grain of (a) electroless (b) electrolytic (c) rolled (A. Co.) (d) rolled (N. Co) method.

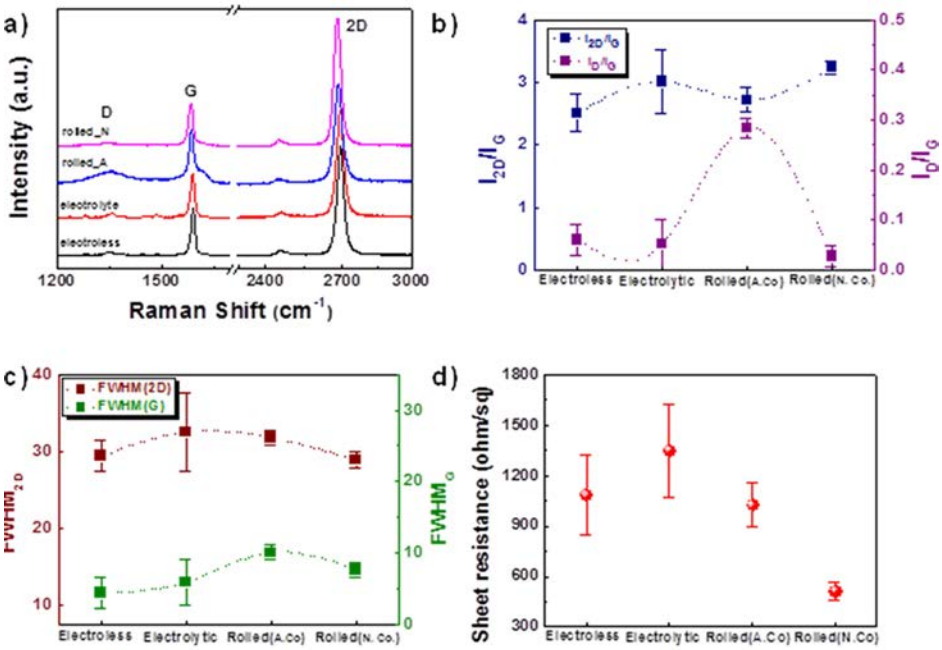

Fig. 3. (a) Raman spectra of graphene grown on different Cu catalysts (b) I_{2D}/I_G and I_D/I_G of (a), (c) FWHM of 2D and G peak (d) The sheet resistance of grapheme.

band regarding the defects, from the G band regarding the sp^2 carbon atom vibration, and from the 2D band regarding the stacking order information. [9, 10]

Fig. 3(a) shows Raman spectra of the graphene grown on different Cu catalysts, which from bottom to top correspond to the electroless, electrolyte, and the two rolled Cu foils (A. Co. and N. Co.). The intensity ratios of the 2D peak to the G peak are 2.5, 3.1, 2.7, and 3.3, respectively, and the FWHMs of the 2D peak after a single Lorenz fitting are 29.3, 32.5, 31.7, and 28.9, respectively, as shown from left to right in Figs. 3(b) and 3(c). The range of I_D/I_G is from 0.02 to 0.2. All graphene grown on various Cu foils were monolayer [11], and the quality of the graphene differed somewhat depending on the Cu type.

In the case of using rolled foil (N. Co.), the graphene had a sharp, high 2D peak, roughly over three times more intense than the G peak, with the narrowest FWHM of the 2D peak. The coverage rate, $v_{coverage}$, with increases of the graphene coverage (graphene area, A_{gr}, divided by the total Cu area, A_{Cu}) within unit time (t) is represented as [12];

$$v_{coverage} = dA_{gr}/\ A_{Cu}\ dt = n\ v_{domain} \quad (2)$$

Equation 2 is used for copper foil to determine the growth of the grain size and the surface roughness, which affects the graphene.

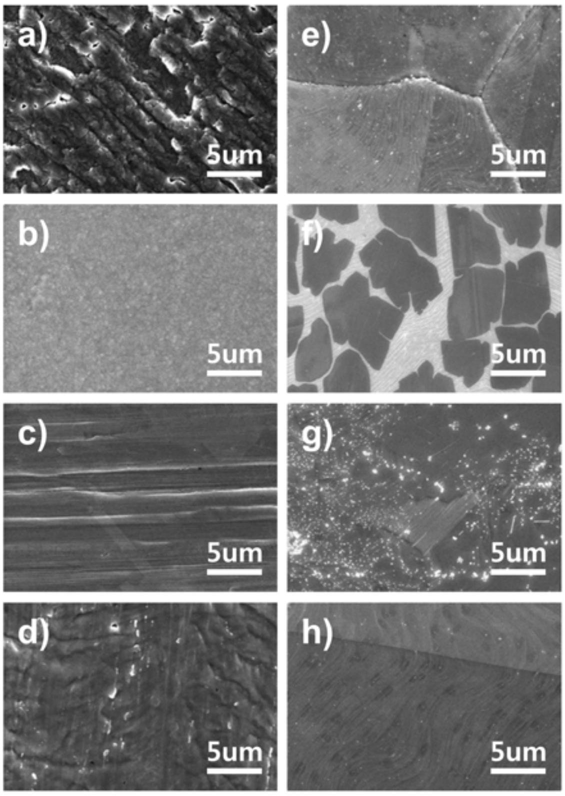

Fig. 4. The SEM image of (a) electroless, (b) electrolyte, (c) rolled (A.Co.), (d) rolled (N. Co) bare Cu foil surface and graphene grown on, (e) electroless, (f) electrolyte, (g) rolled (A.Co.), (h) rolled (N.Co) Cu foil.

Rolled Cu foil shows parallel lines to the foil plane, as shown in Fig. 4. The electrolyte Cu foil has micro-scale features on its surface, because crystals tend to grow perpendicular to the foil plane during electrolyte deposition, even though they can be formed at various orientations with chloride (Cl^-) and gelatin as the additives and with controlling the stirring rate [13].

The growth rate of graphene domains, v_{domain}, was too slow to cover the entire surface under the graphene growth conditions of Figs. 4(f-h) show that uniform graphene film fully covered the entire Cu surface. The graphene grown on electroless Cu foil was torn after transferring onto SiO_2/Si.

The sheet resistance was taken as the average of measurements from seven different points. Fig. 3(d) shows that the sheet resistances of graphene using different types of Cu are 1.080 kΩ/cm, 1.350 kΩ/cm, 1.020 kΩ/cm, and 438 Ω/cm, respectively.

The sheet resistances of the two kinds of rolled Cu foils were different, even though they were manufactured by the same method. This was due to the impurities of the Cu foil. This means that the elimination of Cu foil impurities is very important to ensure high-quality CVD graphene synthesis because native copper oxide, additives, and other metal components of Cu reduce its catalytic activity [14].

Conclusions

Graphene was synthesized on various Cu foils using a CVD system. Under the conditions used, the largest uniform graphene had sufficient coverage, and the lowest sheet resistance appeared in the graphene grown on rolled Cu foils. The electrolyte and electroless Cu foils were not suitable for graphene synthesis, because large-area uniform graphene films could not be obtained in these cases. Impurities and surface treatment after manufacturing affected the graphene quality, so the methods used for cleaning to eliminate the impurities on the Cu surface are very important.

Acknowledgments

This work was supported by Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) (No. 2012T1002 01723) funded by the Korea government Ministry of Knowledge Economy, the Technology Innovation Program (No. 10044410, Commercialization of flexible touch panels based on 900 × 1600 mm^2 large, less than 1-nm thick graphene film synthesis technique).

This research was supported by Basic Science Research Program through the National\Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2013R1A2A 2A01010027).

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