Proceedings of the 24th CANCAM
Saskatoon, Saskatchewan, Canada, June 2-5, 2013

Paper MS25

Synthesis of Graphene on Copper by Hot Filament Chemical Vapor Deposition

S. K. Behura[1], I. Mukhopadhyay[2] and O. Jani[1]
[1]Solar Energy Research Wing and [2]School of Solar Energy
[1]GERMI-RIIC and [2]PDPU
Gandhinagar-382 007, Gujarat, India
E-Mail: sanjay.b@germi.res.in

Q. Yang[3] and A. Hirose[4]
[3]Dept. of Mechanical and [4]Dept. of Physics
University of Saskatchewan
Saskatoon, SK S7N 5A9, Canada
E-Mail: qiaoqin.yang@usask.ca

ABSTRACT

We report on the synthesis of large-domain graphene films on Cu metal substrates using hot-filament chemical vapor deposition (CVD). The intensity ratio between G and 2D-band is ~ 0.7 and the full-width at half maximum of 2D-band is 55 cm^{-1}, indicating the formation of few-layer graphene films on Cu surface. The importance of this study is the use of vertical mass flow CVD system for the graphene synthesis, which has a great potential for commercialization.

Keywords: graphene, chemical vapor deposition, Raman spectra, copper.

INTRODUCTION

The discovery of two-dimensional carbon nanomaterial, Graphene, brought intense interest among the scientific community due to its unique properties [1]. It has many potential applications including field effect transistor, solar cell, fuel cell and field emission. In graphene, the carbon atoms are arranged periodically in a honeycomb lattice. Mechanical exfoliation of graphene has enabled many basic studies of this novel material. While most exfoliated samples are of high quality, the lateral dimensions are at most tens of micrometers, limiting the fabrication of consistent, wafer-scale graphene structures. To that end, techniques have been developed for the fabrication of large-area graphene samples by epitaxy on SiC and by chemical vapor deposition (CVD) on catalytic metals like Ni or Cu.

Graphene grown by CVD on Cu foils has generated interest due to the low cost and the prospect of large-area monolayer coverage [2]. Synthesis of graphene by CVD on Cu is generally attributed to the surface diffusion of carbon atoms on Cu. Graphene growth is a catalytic process, involving hydrocarbon decomposition and surface diffusion, which includes: (i) absorption and de-absorption of hydrocarbon molecules on Cu, (ii) decomposition of hydrocarbon to form carbon atoms, (iii) aggregation of carbon atoms on Cu surface to form graphene nucleation centers, (iv) diffusion and attachment of carbon atoms to nucleation centers to form graphene film. On the other hand, the lower decomposition rate of methane on Cu, due to its low carbon solubility (i.e., 0.0001 wt %), allows the possibility of controlling the number of graphene layers.

Most of the researches on the synthesis of CVD graphene are based on the horizontal flow of precursor gases [3]. Till today, limited research has been done on the fabrication of graphene using vertical flow of precursor gases. In the present work, we report on the graphene fabrication by vertical flow of gases using hot-filament CVD (HFCVD).

EXPERIMENTAL

In this study, graphene was grown on polycrystalline Cu foils (Alfa Aesar, metal basis=99.8%) of thickness 25 μm using a custom designed HFCVD reactor [4]. Usually as-supplied foils contain surface oxides such as Cu_2O and CuO, which has to be removed before the growth of graphene. The foils were cut into 1.5X1.5 cm^2 area and pre-treated following the method proposed by W. Liu et al. [5], which is the ultrasonication in acetone for 30 minutes. The CH_4 and H_2 gases were used as the precursors and a temperature of approximately 1000 °C was maintained for the growth of graphene.

The detailed growth process is as follows: the chamber was first evacuated to 0.1 mTorr, then the Cu substrate was heated to 1000 °C (substrate holder temperature) with a flow of hydrogen at 10 sccm and held for 20 minutes for the annealing and subsequently grain growth of the Cu film. After that, the temperature was maintained at 1000 °C with a gas mixture of CH_4:H_2=1:50 sccm flowing into the reaction chamber, and maintaining a pressure of 320 mTorr for

growth of graphene films. After 10 minutes of growth, the chamber was cooled at 25 ^{o}C/min under the flow of hydrogen at 10 sccm.

As-grown graphene films were characterized by scanning electron microscopy (JEOL, JSM-6010LV) and Raman spectroscopy (Renishaw InVia Spectrometer 2000). For Raman measurement, the Ar^{+} laser of wavelength, λ=514 nm was used as the excitation source at an incident power of 3.6 mW. The laser beam was focused onto sample by a 5X microscope objective lens and the scattered light was collected and collimated by the same objective. The scattered signal was detected by a liquid-nitrogen-cooled master charge-coupled-device (CCD) camera detector.

RESULTS AND DISCUSSION

As we know, the original surface state of the metal is very important for the uniform growth of large-area graphene, thus, we observed the Cu surface using scanning electron microscopy and field-emission scanning electron microscopy. The typical images are displayed in figures 1 and 2, respectively. Rolling striations are a governing feature of the as received Cu foils for which FESEM (figure 2) shows Cu grain sizes ≥ 2 μm with diverse surface orientations. We find the detailed deformation texture of the used commercial cold-rolled Cu foils. It should be noted here that, we do not use any additional Cu surface treatment procedure, such as electropolishing.

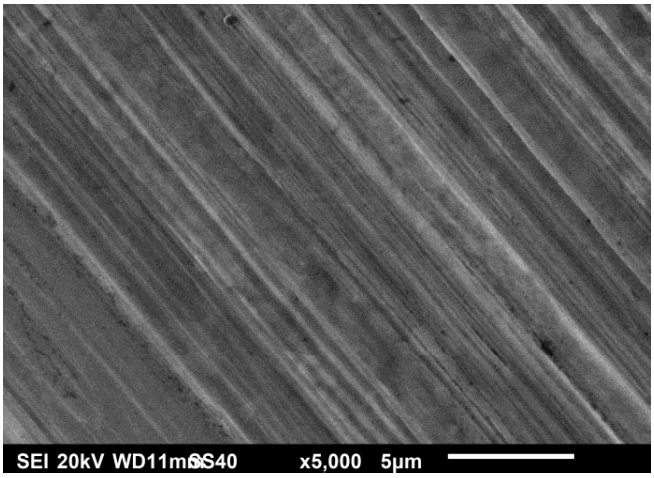

Figure 1: SEM micrograph of bare Cu surface.

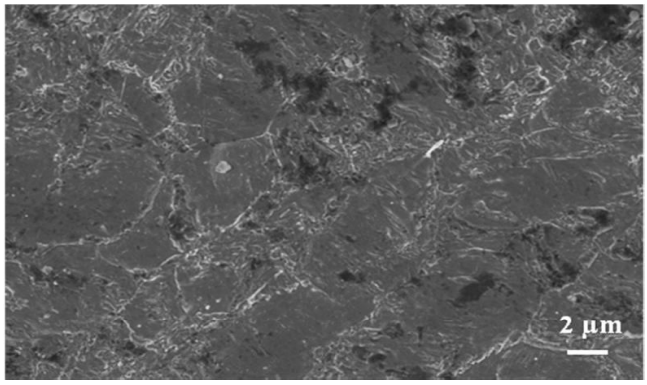

Figure 2: FESEM micrograph of bare Cu surface.

Considering the fact that, annealing of the Cu substrate is an important parameter, which governs the graphene growth, therefore, the post-annealing Cu surface microstructure was observed by SEM and presented in figure 3. It can be seen that after high temperature processing, the Cu surface contains different structures, including polycrystalline facets, grain boundaries, annealing twins and wrinkles with increase in grain size ≈ 50 μm for low-pressure CVD conditions.

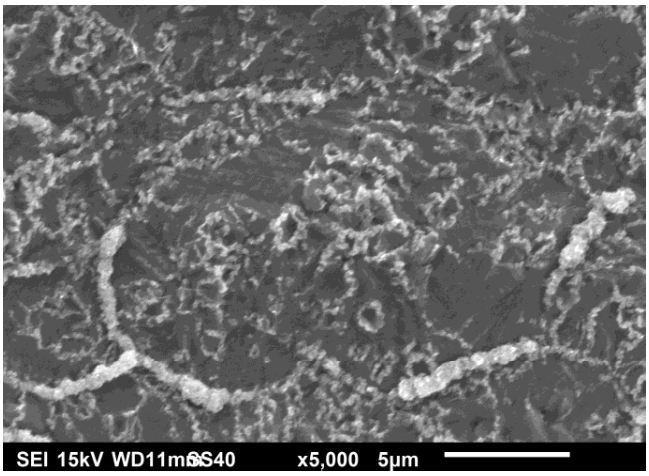

Figure 3: SEM micrograph of annealed Cu surface.

The SEM image of the surface after graphene growth is shown in figure 4. The formation of graphene films can be clearly seen. Domains of graphene films with several tens of micrometers in the side length were observed, as shown with the red dashed lines. An optical image of the graphene film on Cu foil is also presented in the inset of figure 4.

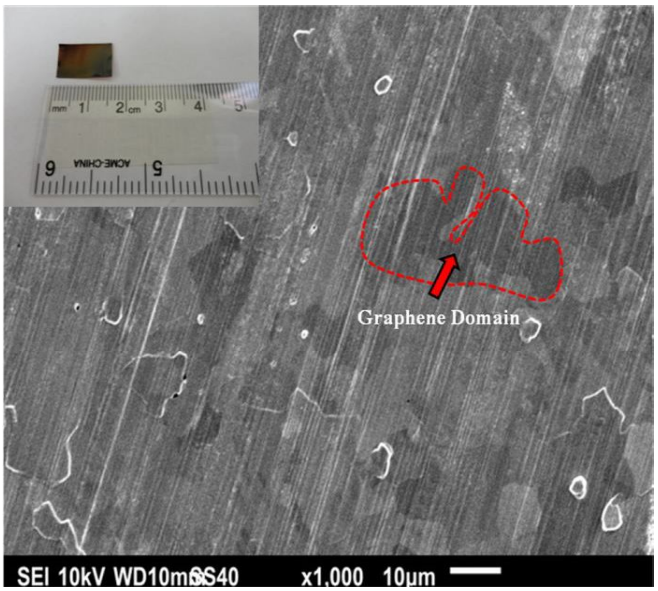

Figure 4: SEM micrograph of graphene films on Cu surface with optical photograph shown in the inset.

The structural defects and number of layers of the as-formed graphene films can be determined by the Raman spectroscopy. Figure 5 shows a typical Raman spectrum of as-grown graphene film and a Raman spectrum of graphite is presented in figure 6 for comparison. The presence of two intense peaks, G and 2D-band at 1583.6 cm^{-1} and 2702.6 cm^{-1}, respectively, indicate the formation of graphene films [6]. The G-band originates from the Stokes Raman scattering with one phonon (E_{2g}) emission and its intensity increases almost linearly with the increasing number of layers [6, 7]. The 2D-band is due to the Stokes-Stokes double resonant Raman scattering with two phonon emissions [6, 7]. The broadening and the blue-shift of the 2D-band are the signature of increasing number of graphene layers [6]. The D-band at 1346.7 cm^{-1} corresponds to the defects in the synthesized film, because the D-band originates from the backscattering of phonon by disorder sites (such as edges and defects) [6]. The intensity ratio between G and 2D-band (i.e., I_G/I_{2D}) is ~ 0.7 and the full width at half maximum (FWHM) of the 2D peak is ~ 55 cm^{-1}, indicating that the formation of few-layer graphene (FLG) [3, 8, 9]. The large intensity of D-band indicates the presence of high amount of defects in the film. On the other hand, graphite (figure 6) shows much larger I_G/I_{2D} intensity ratio of >2 and much lower D-band intensity.

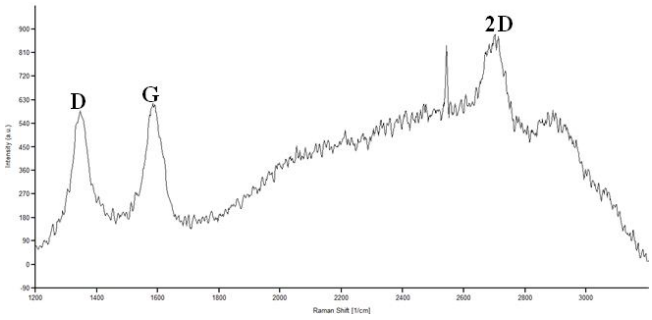

Figure 5: Raman spectrum of graphene film on Cu surface.

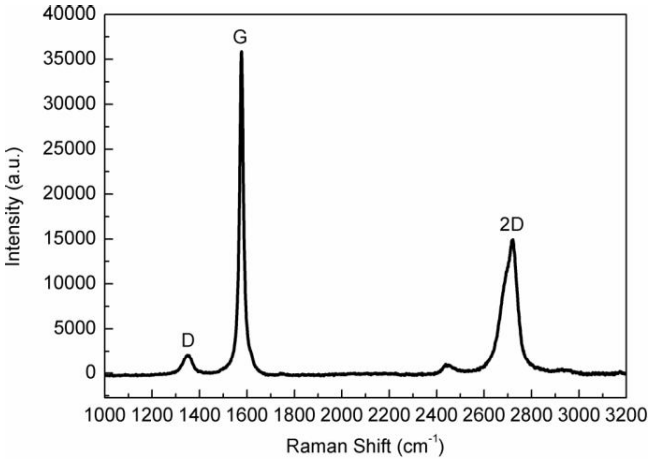

Figure 6: Raman spectrum of highly-ordered pyrolytic graphite.

The results presented show that FLG films were successfully synthesized on Cu surface by a vertical mass flow based HFCVD system.

CONCLUSIONS

Growth of FLG films on Cu foil was investigated using HFCVD system, which relies on vertical mass flow with respect to the substrate. The results obtained have demonstrated that, FLGs can be synthesized on polycrystalline Cu foil using HFCVD and has a great potential for commercialization compared to the horizontal mass flow, where the size of the graphene film is limited by the tube diameter.

ACKNOWLEDGMENTS

This work is supported by Foreign Affairs and International Trade Canada (DFAIT) under Commonwealth Graduate Student Exchange Program Scholarship (2011-12). Q.Y. and A.H acknowledge support from NSERC and Canada Research Chair Program. S.K.B. and Q.Y. acknowledge the support of Dave McColl, PPL, Rob Peace, Department of Mechanical Engineering and Jason Maley, SSSC, University of Saskatchewan, Canada.

REFERENCES

1. Geim, A. K., and Novoselov, K. S. 2007, "The rise of graphene", *Nature Mater.*, 6, pp. 183-191.
2. Kim, K. S., Zhao, Y., Jang, H., Lee, S. Y., and Kim, J. M. 2009, "Large-scale pattern growth of graphene films for stretchable transparent electrodes", *Nature*, 457, pp. 706-710.
3. Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., Bulovic, V., et al. 2009, "Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition", *Nano Lett.*, 9 (1), pp. 30-35.
4. Yang, Q., Xiao, C. Chen, W. Singh, A. K., Asai T., and Hirose, A. 2003, "Growth mechanism and orientation control of well-aligned carbon nanotubes", *Dia. and Rel. Mater.*, 12 (9), pp. 1482-1487.
5. Liu, W., Li, H., Xu, C., Khatami, Y., and Banerjee, K., 2011 "Synthesis of high-quality monolayer and bi-layer graphene on copper using chemical vapor deposition," *Carbon*, 49, pp. 4122-4130.
6. Yoon, D., Moon, H., Son, Y. W., Choi, J. S. Park, B. H., Cha, Y. H., Kim, Y. D., and Cheong, H. 2009, "Interference effect on Raman spectrum of graphene on SiO_2/Si", *Phys. Rev. B*, 80 (12), pp. 125422.
7. Pimenta, M. A., Dresselhaus, G., Dresselhaus, M. S., Cancado, L. G., Joriao, A., and Saitoe, R. 2007, "Studying disorder in graphite-based systems by Raman spectroscopy", *Phys. Chem. Chem. Phys.*, 9, pp. 1276-1291.
8. Lee, H., Lee, S., Hong, J., Lee, S. G., Lee, J. H., and Lee, T. 2012, "Graphene converted from the photoresist material on polycrystalline nickel substrate", *Jpn. J. Appl. Phys.*, 51, pp. 06fd17.
9. Ni, Z. H., Wang, H. M., Kasim, J., Fan, H. M., Yu, T., Wu, Y. H., Feng, Y. P., and Shen, Z. X. 2007, "Graphene thickness determination using reflection and contrast spectroscopy", *Nano Lett.* 7 (9), pp. 2758-2763.