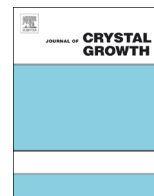




ELSEVIER

Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

## Journal of Crystal Growth

journal homepage: [www.elsevier.com/locate/jcrysgr](http://www.elsevier.com/locate/jcrysgr)

## Graphene films grown at low substrate temperature and the growth model by using MBE technique

Meng-Yu Lin<sup>a,b</sup>, Wei-Ching Guo<sup>c</sup>, Meng-Hsun Wu<sup>d</sup>, Pro-Yao Wang<sup>c</sup>, Si-Chen Lee<sup>a</sup>, Shih-Yen Lin<sup>b,\*</sup><sup>a</sup> Institute of Electronics, National Taiwan University, Taipei, Taiwan<sup>b</sup> Research Center for Applied Sciences, Academia Sinica, 128 Sec. 2, Academia Road, Nankang, Taipei 11529 Taiwan<sup>c</sup> Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, Taiwan<sup>d</sup> College of Photonics, National Chiao-Tung University, Tainan, Taiwan

## ARTICLE INFO

Available online 4 January 2013

## Keywords:

A1. Crystal structure  
A1. Growth models  
A3. Molecular beam epitaxy  
B1. Elemental solids

## ABSTRACT

By depositing atomic C atoms on the grained Cu foil by using molecular beam epitaxy technique (MBE), high-quality graphene is obtained at low substrate temperature 300 °C. A model of initial graphene flake formation as crystal seeds and following lateral graphene growth is established to explain the growth mechanisms. After atomic C atom deposition, no significant difference is observed before and after MBE growth. The results suggest that the deposition of atomic C atoms will not improve the crystalline quality of pre-formed C films. The low substrate temperature required would be advantageous for the practical application of graphene.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

With the huge number of papers published in the last few years, the research on graphene has become one of the most fast-growing topics in the world [1–8]. With its unique characteristics, graphene has revealed its potential in the applications of semiconductor, biosensor and material industries. To obtain this material, different approaches are developed such as exfoliation from highly ordered pyrolytic graphite (HOPG) [1–3], SiC sublimation at high temperature [4–6] and chemical vapor deposition (CVD) on metal templates [7,8]. To obtain large-area graphene films for practical applications, SiC sublimation and CVD growth is the most common approaches adopted since HOPG exfoliation can only obtain graphene flakes. However, for the former approach of SiC sublimation, it would take place at a temperature ~1400 °C and leave the carbon (C) atoms on the surface for graphitization. Although this method does provide large-area graphene films, the high price of SiC substrates and the only substrate choice would limit the practical application of this approach. Compared with the previous approach, CVD grown graphene on metal templates has provided a cheaper and layer-number-controllable approach to obtain large-area graphene films. In CVD growth method, Ni and Cu templates are commonly used for film growth. With different growth mechanisms of the metals, different growth temperatures are required. When graphene is grown on Ni template, the dissolution and precipitation process of the C atoms only happens at 900–1000 °C to obtain high quality

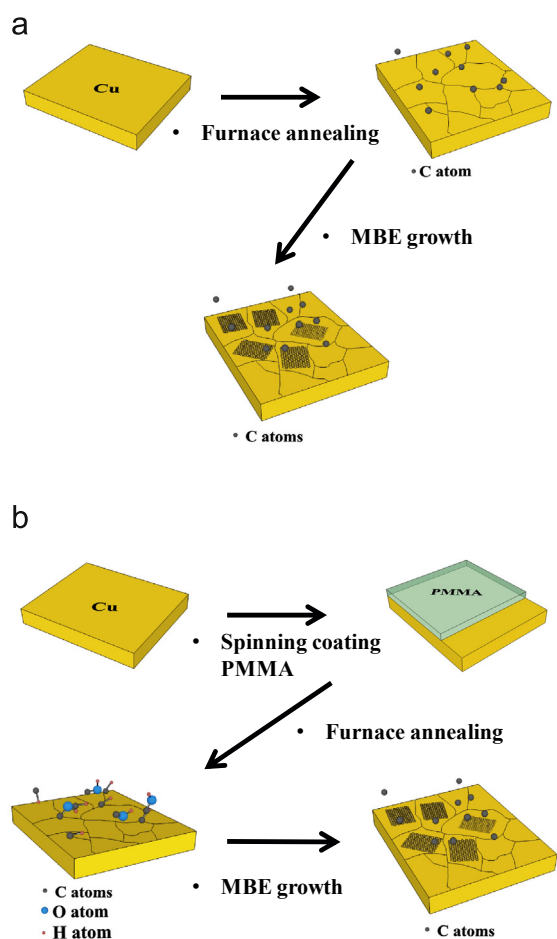
graphene film [8]. For the graphene grown on Cu foil, self-limited process of the C atoms would result in only few layers of graphene growth on Cu surface. And the growth temperature can be reduced to 600–900 °C [9,10]. However, the still high substrate temperature required for this approach would become a major drawback of applications for graphene.

In this work, by using an effusion cell equipped with a high purity pyrolytic graphite (PG) filament to supply C atoms, large-area and high quality graphene is fabricated on a 100 μm grained Cu foil by using molecular beam epitaxy (MBE) technique. Before growth, no significant Raman signal is observed on the grained Cu foil, which is fabricated after high temperature annealing in the furnace. After MBE growth at 300 °C substrate temperature, complete hexagonal structure and low defect signal is observed on the sample with Scanning tunneling microscope (STM) and Raman measurements. The same MBE growth procedure is also applied on another sample covered with amorphous C film. The same amorphous carbon signal is observed before and after MBE growth. This result suggests that although high-quality graphene can be obtained on grained Cu foils at 300 °C, the atomic C source cannot improve the crystalline quality of amorphous C films. The reason may lie on the possible growth mechanism of seeding and then lateral growth by using atomic C source, while such mechanism cannot take place on complete amorphous C films.

## 2. Experiment

Two samples with different fabrication procedures are discussed in this report. The flow charts of the fabrication procedures

\* Corresponding author. Tel.: +886 3 5744364; fax: +886 3 5745233.  
E-mail address: shihyen@gate.sinica.edu.tw (S.-Y. Lin).

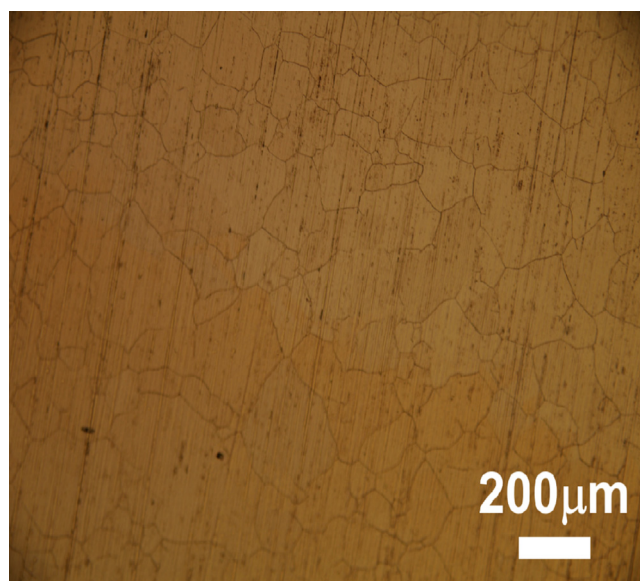


**Fig. 1.** Flow charts of graphene film fabrication of (a) Cu foil high temperature annealing in furnace following by MBE growth at substrate temperature 300 °C and (b) Cu foil coated with PMMA before high-temperature annealing following by MBE growth at substrate temperature 300 °C. The two samples are referred as samples A and B, respectively.

of the two samples are shown in Fig. 1(a) and (b), respectively. In Fig. 1(a), 100  $\mu\text{m}$  Cu foil is annealing in a 1000 °C furnace with Ar/H<sub>2</sub> mixture gas for 10 min. The pressure is kept at 7 Torr and the flow rate of Ar and H<sub>2</sub> are set at 150 and 500 sccm, respectively. For the MBE growth procedure, the samples are transferred into a home-made MBE system equipped with Ribar PG filament cell in less than 30 s. To deposit the C atoms, the cell temperature is set at 2173 °C. After 30 min of growth, the sample is transferred out of the chamber, which is referred as sample A. In Fig. 1 (b), similar procedure is performed on the other Cu foil except a 100 nm polymethylmethacrylate (PMMA) film is spin on the sample surface before being sent into the furnace for high temperature annealing. The sample is referred as Sample B. The PMMA applied in this experiment is A5 from Microchem. And the Raman measurements are performed by using a HORIBA Jobin-Yvon HR800UV spectrum system. The STM image is taken by using a RHK-SRM 100 system under ambient circumstances.

### 3. Result and discussion

Following the similar mechanism of graphene growth on Cu foil by CVD method, Cu foil after high temperature annealing procedure shows a grain like structure on the Cu surface. The image of grained Cu foil is shown in Fig. 2. With the annealing procedure, removing of the Cu oxide is a key issue to grow



**Fig. 2.** Picture of Cu foil taken under an optical microscopy after high temperature annealing.

high-quality graphene and this approach has been widely applied in CVD-grown graphene. Although the Cu foil may expose to the air when transferring into the MBE system for growth, we believe that only minimum amount of CuO, Cu<sub>2</sub>O and Cu(OH)<sub>2</sub> is formed on the Cu surface in less than 30 s of transferring [11]. Fig. 3(a) and (b) shows the Raman spectra of sample A before and after MBE growth. The wavelength of the excitation laser is 638.2 nm. The Raman spectrum of Fig. 3(b) is measured after film transferring to a 600 nm SiO<sub>2</sub>/Si substrate to avoid the influence of Cu foil on the measurement results. The measurement in Fig. 3(a) is done directly on Cu foil since no film is observed after the transferring procedure. As shown in the figure, no significant carbon-related signal is obtained before MBE growth. And after 30 min of C atoms deposition in the MBE system, low D/G intensity ratio ( $\sim 0.1$ ) and high 2D/G ratio ( $\sim 0.8$ ) of Raman spectrum is observed, which indicate low defect and few layers of graphene is formed. To confirm the formation of graphene films, a  $4.2 \times 4.2 \text{ nm}^2$  STM images of sample A before film transferring is shown in Fig. 3(c). In the STM image, well-arranged C atoms can be observed on the sample surface in hexagonal structure. Therefore, these results suggest that C atoms form successive and good quality graphene when deposited on the grained Cu foil at low substrate temperature 300 °C.

For CVD grown graphene on Cu foil, the widely accepted growth model is the high-temperature decomposition of hydrocarbon gas following by adatom segregation and then graphitization [9]. However, for MBE-grown graphene, since atomic C atoms are already provided, high-temperature hydrocarbon gas decomposition is no longer required. In this case, low-temperature growth will become one important advantage of MBE-grown graphene. However, considering the low substrate temperature 300 °C as the case of sample A, C adatom migration on the surface should not be as free as the case at higher temperatures. Therefore, a growth model is proposed for low-temperature grown graphene. The schematic diagrams showing the graphene growth evolution is depicted in Fig. 4. In the initial step, although the substrate temperature is low, the high-temperature C atoms accelerated by the PG filament should have sufficient energy to form graphene flakes on the surface. With the graphene flakes as the crystal seeds, lateral growth of graphene with following C atom supply would gradually form a complete graphene film on

the surface. However, due to lack of sufficient C adatom migration, possible crystal defects may appear on the boundaries connecting neighboring graphene flakes. This is the main reason why D-peak is still observed in the Raman spectrum. To overcome this disadvantage, growth condition optimization is still required in the future.

Similar growth model of graphene nucleation and following expansion has also been discussed in literature [12]. At the nucleation state, the carbon concentration needs to be few times higher than the concentration when expanding. Since the C flux

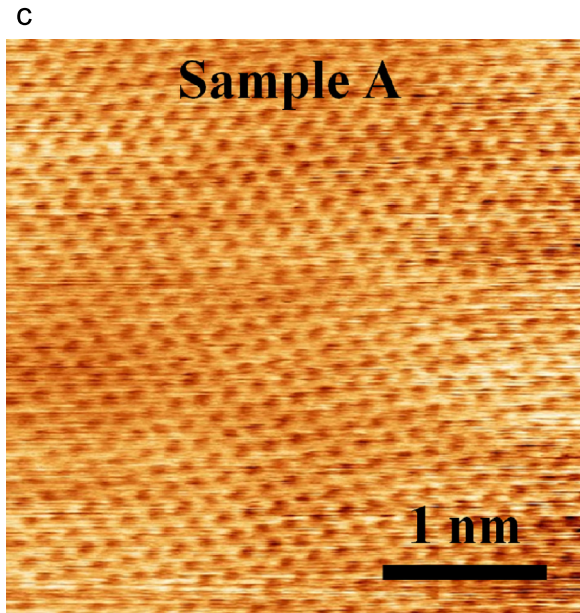
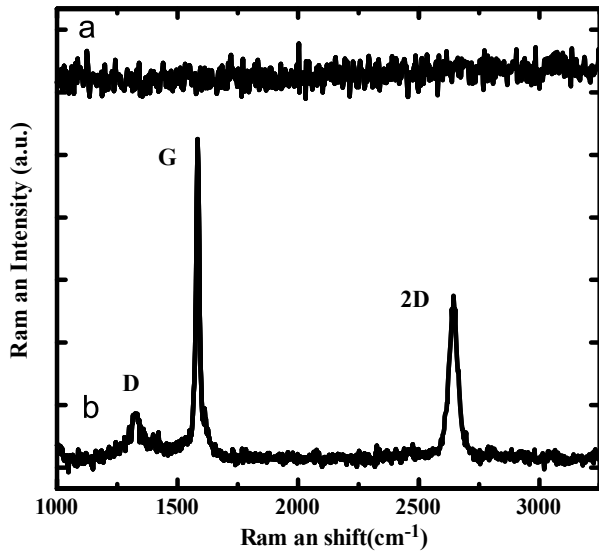


Fig. 3. Raman spectra of (a) grained Cu foil and (b) sample A. (c) The  $4.2 \times 4.2 \text{ nm}^2$  STM image of sample A.

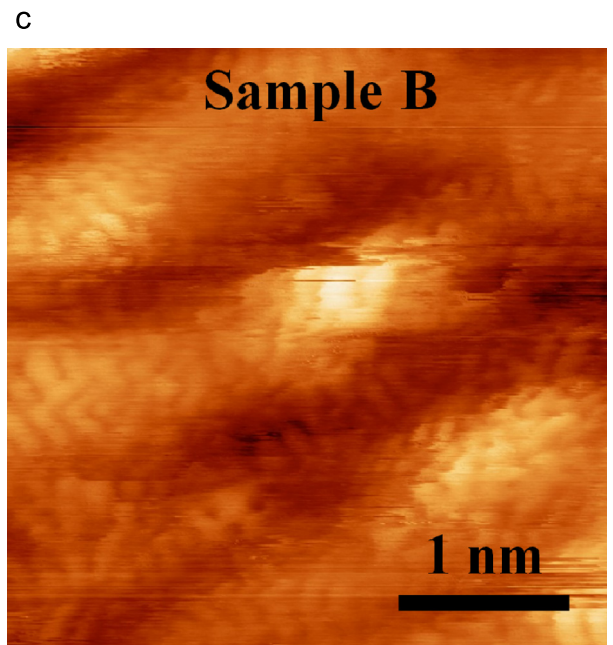
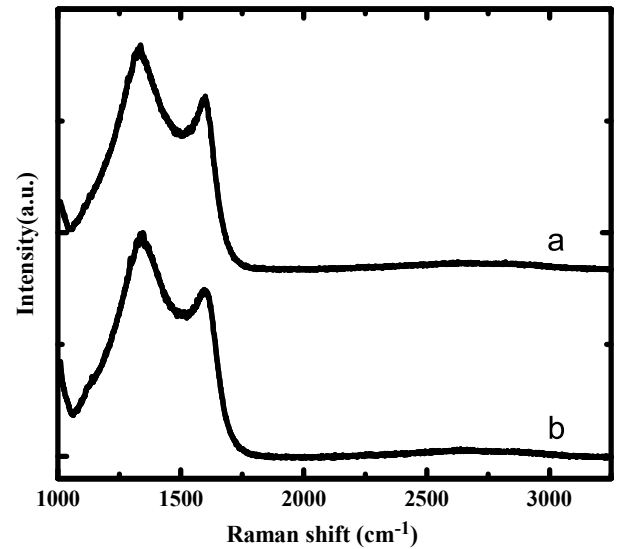


Fig. 5. The Raman spectra of sample B (a) before and (b) after MBE growth and (c) the  $4.2 \times 4.2 \text{ nm}^2$  STM image of sample B after MBE growth.

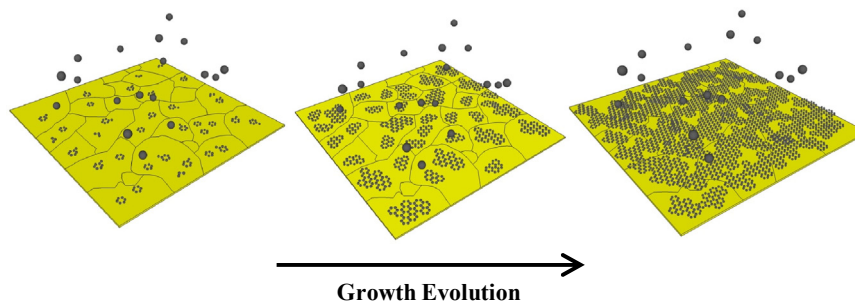


Fig. 4. Schematic diagrams showing the graphene growth evolution.

provided by the C source we adopted in the MBE chamber should be relatively low than the CVD method, there is possibility that the C concentration may not be enough by using the PG filament C source. As indicated in the literature, with decreasing growth temperatures, the required C concentrations in both nucleation and expansion stages become less [12]. Therefore, we believe that there are two major issues, which make possible the high-quality graphene films grown by using MBE at 300 °C. They are (a) lower substrate temperature to meet minimum C concentration required for the nucleation stage and (b) the assist of Cu surface for C adatom migration.

Since low-temperature graphene is achieved by using the atomic C source, it would be interesting to see if they can improve the crystalline quality of amorphous C films and transfer them into graphene films. Following the procedure described in Fig. 1(b), sample B is prepared for investigation. The Raman spectrums of the sample before and after MBE growth are shown in Fig. 5(a) and (b), respectively. As shown in the figure, no significant difference is observed before and after MBE growth. The film appears to be flakes of graphene embedded in the amorphous C film since G- and D- peaks are still observed in the spectra. The  $4.2 \times 4.2 \text{ nm}^2$  STM image of the film after MBE growth is shown in Fig. 5 (c). No hexagonal structure formation is observed on the sample surface. This result can be explained because when depositing C atoms on the pre-formed amorphous carbon film, the surface atomic structure is not grained Cu foil but amorphous carbon. Therefore, the physically deposited C atoms cannot undergo graphitization. The results would be the similar film crystalline quality before and after MBE growth.

#### 4. Conclusion

In conclusion, by using the carbon filament cell to deposit C atoms on the grained Cu foil surface, graphene is observed on the sample surface at low substrate temperature 300 °C. A model is established to explain the growth mechanisms of MBE-prepared

graphene films. By using PMMA as the carbon source, amorphous carbon film is observed on the Cu foil surface after high-temperature furnace annealing. Similar MBE growth condition is applied on the amorphous carbon film. No significant improvement on the film quality is observed. The low substrate temperature is the major advantage for graphene growth by using MBE, which is helpful for the practical application of graphene.

#### Acknowledgment

This work was supported in part by the National Science Council, Taiwan under the grant number NSC NSC 101-2628-E-001-001 and the Nano-project granted by Academia Sinica.

#### References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* 306 (2004) 666.
- [2] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A.K. Geim, *Proceedings of the National Academy Sciences, USA* 102 (2005) 10451.
- [3] F. Xia, T. Mueller, R. Golizadeh-Mojarad, M. Freitag, Y.M. Lin, J. Tsang, V. Perebeinos, P. Avouris, *Nano Letters* 9 (2009) 1039.
- [4] C. Riedl, A.A. Zakharov, U. Starke, *Applied Physics Letter* 93 (2008) 033106.
- [5] N. Camara, G. Rius, J.-R. Huntzinger, A. Tiberj, L. Magaud, N. Mestres, P. Godignon, J. Camassel, *Applied Physics Letter* 93 (2008) 263102.
- [6] N. Camara, G. Rius, J.-R. Huntzinger, A. Tiberj, N. Mestres, P. Godignon, J. Camassel, *Applied Physics Letter* 93 (2008) 123503.
- [7] X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R.D. Piner, L. Colombo, R.S. Ruoff, *Nano Letter* 9 (2009) 4359.
- [8] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M.S. Dresselhaus, J. Kong, *Nano Letter* 9 (2009) 30.
- [9] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo, R.S. Ruoff, *Science* 324 (2009) 1312.
- [10] B. Zhang, W.H. Lee, R. Piner, I. Kholmanov, Y. Wu, H. Li, H. Ji, R.S. Ruoff, *ACS Nano* 6 (2012) 2471.
- [11] K.L. Chavez, D.W. Hess, *Journal of Electrochemical Society* 148 (2001) G640.
- [12] E. Loginova, N.C. Bartelt, P.J. Feibelman, K.F. McCarty, *New Journal of Physics* 11 (2009) 063046.