# Comparison Characteristic of Large Area Graphene Films Grown by Chemical Vapor Deposition with Nano-Graphite Structures

Oybek Tursunkulov, Bunyod Allabergenov, Amir Abidov, Sang-Yeop Kim, Heung-Woo Jeon, Soon-Wook Jeong, and Sungjin Kim

Abstract—The unique properties of graphene are making it an attractive material for a wide variety of applications in nano-electronic. Various techniques have been developed to produce graphene to realize its potential applications. Chemical vapor deposition (CVD) of graphene films on Cu substrate is a primary technique for high quality graphene synthesis. In this work we demonstrate the growth of large area graphene lavers by chemical vapor deposition (CVD) on copper substrates. Graphene growth was achieved by the flow of methane and hydrogen gasses over a copper thin film acting as catalyst at ambient pressure. Optimal growth conditions were found by varying the different parameters. A transfer process was carried out through treatment with a nickel etchant solution to isolate the graphene with using polymer bond for placement on an oxidized silicon substrate. Transfer methods are essential for effective optical contrast and SEM microscopy measurements. Characterization was performed with optical microscopy, Raman spectroscopy, XRD, SEM and other to determine the quality of layers.

*Index Terms*—Graphene, graphite, chemical vapor deposition, transferring, Raman spectroscopy.

# I. INTRODUCTION

Grapnene is one of the most interesting and promising novel materials in nanotechnology. Recently A.K Geim and K.S. Novoselov used a mechanical technique to peel graphene from graphite [1]. The great interest has developed in using graphene as nanoelectronic application due to its excellent physical and electrical properties such as tunable band gap, high thermal conductivity, and mechanical strength [2], [3]. It has exceptional carrier transport properties which makes it a promising material for future nanoelectronics [4]. Besides graphene's high optical transmittance and conductivity it is also being considered as transparent electrode for flexible transparent displays and printable electronics [5]-[7]. To realize these potential applications, it is essential to synthesize high-quality and

Manuscript received January 20, 2013, revised March 18, 2013. This paper was supported by Research Fund, Kumoh National Institute of Technology.

Sungjin Kim is the corresponding author.

Bunyod Allabergenov, Oybek Tursunkulov, Amir Abidov, Sang-Yeop Kim, Soon-Wook Jeong, and Sungjin Kim are with the Department of Advanced Materials Engineering, Kumoh National Institute of Technology, Deahak-Ro 61, Gumi, Gyeongbuk 730-701, Korea (e-mail: bunyod\_kit@yahoo.com, oybtm09@gmail.com, abidov\_kit@yahoo.com, saintkim1213@naver.com, swjeong@kumoh.ac.kr, sjghim@nate.com).

Heung-Woo Jeon is with the Department of Electronic Engineering, Kumoh National Institute of Technology, Daehak-Ro 61, Gumi, Gyeongbuk 730-701, Korea (e-mail: hwjeon@kumoh.ac.kr). large-area graphene films. Chemical vapor deposition (CVD) of graphene films on Cu substrate is a primary technique for high quality graphene synthesis [8]-[10]. The metal substrate such as copper is put in to CVD furnace and heated under low vacuum to ~1000 0C for fabrication of graphene. Annealing carried out in hydrogen gas environment. Then methane and hydrogen gases are flowed in to quartz furnace. The hydrogen catalyzes a reaction between methane and surface of the metal surface causing carbone atoms from the methane gas to be deposited on to surface of copper through chemical absorption [11]. After process of deposition the furnance is quickly cooled to keep deposited carbon layer from agregating into bulk, which formed into continuous or nonecontinuous graphene layers Fig. 1 a) and b). Different recipes have been proposed to obtain high quality graphene.



a)

Fig. 1. a) Schematic image of process of graphene growth on copper. b) Copper surface after CVD treatment

There are many reports related to application of CVD grown graphene. In particular graphene growth has been demonstrated on to transition metal substrate SiC [12], Ni [13]. After grown process graphene was transferred to arbitrary substrate using a polymer bonder or different organic solutions.

## II. EXPERIMENTAL PROCEDURE

In this work we demonstrate the growth of large graphene layers by thermal chemical vapor deposition on copper substrates. In experiments polycrystalline Cu foil (Alpha Aesar, 99,9999% metal basis) with thickness of 500  $\mu$ m is used as a substrate. Then CH4 (20-40 sccm) as precursor gas is carried by H2 (20sccm:30 sccm) pressure is less than 5mTorr; and the graphene formation time is 20-40 min at ~1000 °C. After graphene formation, samples are cooled down by mechanically opening CVD box to decrease temperature in Ar (20sccm:40 sccm) atmosphere. Cooling rates are measured by a thermal couple on the sample holder. After graphene formation, samples are cooled down by mechanically opening CVD box to decrease temperature in Ar atmosphere Fig. 2 a). It is highly desirable to describe the underlying growing processes to optimize graphene growth conditions.





Fig. 2. The growth of graphene layers by thermal chemical vapor deposition on copper substrates: a) photo of CVD heater during cooling process (CVD box open), on the top of photo is image of quartz tube during annealing process; b) schematic image of optimal CVD condition for fabrication large area graphene thin films.

Cooling rates are measured by a thermal couple inside of the quartz tube. For transferring graphene to Si/SiO2 substrates, as-synthesized samples are coated by PMMA using a spinner. The spinning speeds are in range between 300 to 3000 rpm depending on the size of samples. After coating PMMA, samples are placed on an aqueous solution of Nickel Etchant for etching off the Cu substrate. Afterwards, graphene/PMMA films are scooped out from the solution, rinsed several times by DI water and placed on the Si/SiO2 substrates. At last, PMMA is removed by acetone.





Fig. 2. a) schematic process of transferring graphene/PMMA to SiO substrate; a) optical images of graphene/PMMA to SiO substrate; c) graphene on SiO after removing PMMA

After the film was transferred to SiO substrate, it was characterized by optical microscopoy, Raman spectroscopy, and SEM. Besides we used carbon based structure like graphite oxide, graphene oxide and Highly Ordered Pyrolytic Graphite(HOPG) for comprising of Raman Spectra Optimal growth of graphene films were found by varying the different CVD conditions such as annealing temperature and gas flow rate. It was found that relatively uniform graphene formed at low gas pressure and fast cooling time for high purity Cu foils.

## A. Characterization

The crystal structure and the chemical composition of obtained powders were analyzed by X-ray diffraction (Model D5005, Bruker, Karlsruhe, Germany) equipped with a primary graphite monochromatic selecting the Co Ka radiation. The voltage was 40 kV, and the current was 30 mA. The diffraction angle  $2\Theta$  was chosen to be 30-90°. The scanning speed was 0.020 per 0.8 seconds. The microstructure of the specimens was investigated by FESEM (JSM-6500F, Japan) and the chemical content of iron and titanium of the specimens was evaluated by EDX. The effect of heat treatment on the mechanical properties of the composites was studied by measuring the hardness of the specimens before and after annealing. The hardness values of polished specimens were measured 10 times by Vickers's hardness test method, and average value was obtained for each sample [13]. Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The corrosion resistance of the sintered STS: TiC<sub>x</sub>N<sub>y</sub> specimens were evaluated by analyzing of the polarization curves. The testing electrolyte was  $0.5M H_2SO_4$  aqueous solution at 80 °C. The measurements were conducted using a measuring system Gamry-DC 105. The reference electrode was a saturated calomel electrode with carbon electrode as a support electrode. The measuring of potentiodynamic polarization current with a scan rate 1 mV/s was performed [13], [14].

### III. RESULT AND DISCUSSION

The deposition technique of graphene should essentially provide precise control growing condition. In particular we suppose that deposition must terminated right after the several layers of graphene are formed on Cu substrate and then start fast cooling process for providing thin film uniformity. In other words in the chemical reaction is controlled process, like the reaction rate of graphene deposition can be optimized by reaction temperature and concentration of the reactants. Hence it is helpful to reduce deposition temperature, increase cooling rate and decrease partial pressure during deposition on catalyst surface. However, temperature affects not only reaction process, but also to the microstructure of the substrate of the deposited film. The process of formation of grains with different size on copper surface after thermal annealing is shown in Fig. 3 a) and b). According this figure, before thermal annealing Cu surface have surface grooves caused by extrusion process Fig. 3 a) and grooves are disappeared after 1000 <sup>0</sup>C of thermal annealing. Instead of grooves on copper surface is formed different size of grains Fig. 3 b). We suppose that these grains have different growing plane of indexes [14]. That is why graphene was deposited in selective area of copper surface. Besides the key advantage to CVD growth is the ability to transfer the graphene to an arbitrary substrate. Ones graphene/copper foil cooled up to room temperature, after CVD treatment, a polymer material, such as polymethyl methacerylate (PMMA) can be coated on to graphene, then the copper removed using etchant, and PMMA can be removed in acetone. However in the SEM image of Fig. 3 it is shown that acetone cannot be totally removed from surface even after long time (~2 hours) of oxide treatment. The small fraction of polymer is left after acetone treatment, although it's invisible in optical images Fig. 2 d). Therefore it is necessary to optimize of transferring processes or use direct transfer without polymer bonder.



Fig. 3. SEM images of Cu surface before annealing (a) and graphene on copper foil after CVD treatment (b). Surface image of PMMA/graphene/SiO after acetone cleaning SEM image (c) and (d) optical microscope image. It is visible PMMA flecks on SiO surface.

Raman spectroscopy technique is optimal and most reliable method of determine the presence of graphene [15]. Graphene produced two strong optical peaks in Raman spectra: the G peak and the D peak. The G peak is due to individual bonds stretching and compressing, while D peak is due to formation modes of the hexagonal structures of carbon atoms. They occurs around 1300-1380 and 1550-1600 cm<sup>-1</sup>, respectively. In particular, the different peak position of

graphite oxide compared to graphene oxide and HOPG is shown in Fig. 4. Raman spectra shown in Fig. 4 a) display the G line at about 1570 cm<sup>-1</sup> and D line at 1340 cm<sup>-1</sup>, respectively. The smaller peaks intensity ratio is assigned to graphitized structure and local defects particularly located subsurface areas. Raman spectra of highly oriented pyrolytic graphite Fig. 4 b) and CVD graphene films Fig. 4 c) transferred to SiO2 are very similar to each other. The peaks around ~1580 cm<sup>-1</sup> are the G band which is inherent in graphite lattice; the peaks around ~ 2720 cm<sup>-1</sup> are attributed to the main 2D band in the subsurface region. The large surface area of grahene is thick and small defective because the D peak is appeared and the G peak is lower than 2D peak. According to the Raman spectra in most areas of surface graphene is multilayer [16].



Fig. 4. Optical microscopic image and Raman spectra of (a) graphite oxide; (b) highly oriented pyrolytic graphite; and graphene obtained by CVD transfered to SiO2

#### IV. CONCLUSIONS

In this study large area graphene layers were grown by chemical vapor deposition on copper substrates. It was observed the process of formation of grains with different size on copper surface after thermal annealing. It is shown that that acetone cannot be totally removed from surface even after long time treatment. Probably it is necessary to use direct transfer of graphene on arbitrary substrate without using organic polymers. It was carrie out comprision characteristic of Raman spectra of graphene, HOPG and graphite oxide. It is shown that Raman spectra of highly oriented pyrolytic graphite and CVD graphene films transferred to SiO2 are very similar to each other. The peaks around ~1580 cm-1 are the G band which is inherent in graphite lattice; the peaks around ~ 2720 cm-1 are attributed to the main 2D band in the subsurface region.

## ACKNOWLEDGMENT

This work was supported by Research Fund of Kumoh National Institute of Technology. We thank Dr. Seok-Hwang Chung and Byeongdae Choi (Division of Nano & Bio Technology, Daegu Gyeongbuk Institute of Science and Technology) for the help of discussion of results and providing of HOPG samples.

#### References

- [1] A. K. Geim and K. S. Novoselov, "The rise of grapheme," *Nature Mater.* vol. 6, no. 18, 2007.
- [2] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The electronic properties of graphene," *Reviews of Modern Physics*, vol. 81, no. 1, pp. 109–162, 2009.
- [3] P. Avouris, "Graphene: electronic and photonic properties and devices," *Nano Letters*, vol. 10, no. 11, pp. 4285–4294, 2010.
- [4] F. Giannazzo, V. Raineri, and E. Rimini, "Transport properties of graphene with nanoscale lateral resolution," *Scanning Probe Microscopy in Nanoscience and Nanotechnology*, vol. 2, pp. 247–258, 2011.
- [5] K. S. Kim, Y. Zhao, and H. Jang *et al.*, "Large-scale pattern growth of graphene films for stretchable transparent electrodes," *Nature*, vol. 457, no. 7230, pp. 706–710, 2009.
- [6] F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," *Nature Photonics*, vol. 4, no. 9, pp. 611–622, 2010.
- [7] L. Gomez De Arco, Y. Zhang, C. W. Schlenker, K. Ryu, M. E. Thompson, and C. Zhou, "Continuous, highly flexible, and transparent graphene films by chemical vapor deposition for organic photovoltaics," ACS Nano, vol. 4, no. 5, pp. 2865–2873, 2010.
- [8] W. Choi, I. Lahiri, R. Seelaboyina, and Y. S. Kang, "Synthesis of graphene and its applications: a review," *Critical Reviews in Solid State* and Materials Sciences, vol. 35, no. 1, pp. 52–71, 2010
- [9] S. Lee, K. Lee, and Z. Zhong, "Wafer scale homogeneous bilayer graphene films by chemical vapor deposition," *Nano Letters*, vol. 10, no. 11, pp. 4702–4707, 2010.
- [10] H. J. Park, J. Meyer, S. Roth, and V. Sk'akalov'a, "Growth and properties of few-layer graphene prepared by chemical vapor deposition," *Carbon*, vol. 48, no. 4, pp. 1088–1094, 2010.
- [11] Physics and Applications of Graphene Experiments, Edited by Sergey Mikhailov, Published by InTech. pp. 540, 2011
- [12] K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Röhrl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, and Th. Seyller, "Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide," *Nature Mater.*, vol. 8, pp. 203- 207, 2009.
- [13] S. J. Chae, F. Gu nes, K. K. Kim, E. S. Kim, G. H. Han et al., "Synthesis of Large-Area Graphene Layers on Poly-Nickel Substrate by Chemical Vapor Deposition: Wrinkle Formation," Advanced Materials, vol. 21, pp. 2328–2333, 2009
- [14] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. Banerjee, L. Colombo, and R. Ruoff, "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils," *Science*, vol. 324, no. 5932, 1312–1314, 2009
- [15] Z. H. Ni, Y. Y. Wang, T. Yu, and Z. X. Shen, "Raman spectroscopy and imaging of graphene," *Nano Research*, vol. 1, no. 4, pp. 273–291, 2008.
- [16] S. Chen, A. L. Moore, and W. Cai *et al.*, "Raman measurements of thermal transport in suspended monolayer graphene of variable sizes in vacuum and gaseous environments," *ACS Nano*, vol. 5, no. 1, pp. 321–328, 2011.



**Oybek Tursunkulov** received his Master Degree in Semiconductor and Dielectric Material department of National University of Uzbekistan and Ph.D. in Physics of Semiconductors and Dielectrics of Physical-Technical Institute "Physics-Sun". He is currently postdoctoral fellow Prof. Sungjin Kim at Kumoh National Institute of Technology. His research mainly focused Nanotechnology and Material Science, Photovoltaic

Materials. All collected data related to reseach and experimental results can be use the development of novel technology and creation effective photovoltaic nanomaterials and photosensitive nanostructures.



**Bunyod Allabergenov** received his Master's degree he received from Material Science, Department of Mechanical Engineering, Tashkent State Technical University, Tashkent city, Uzbekistan in 2010 and currently he is pursuing his Ph.D. under the supervision of Prof. Sungjin Kim at School of Advanced Materials and Engineering, Kumoh National Institute of Technology, Gumi city, South KoreaHis research

interests mainly focus on porous and nonporous composites and ceramic materials, currently his research devoted to study of photoluminescence properties of thin film materials for light emitting diodes.



Amir Abidov is a doctorate student at the Department of Advanced Materials and Engineering, Kumoh National Institute of Technology (Gumi, South Korea). He received his bachelor's degree at Tashkent Automobile and Roads Construction Institute (Tashkent, Uzbekistan) in 2005, and master's degree in Materials science at Kumoh National Institute of Technology (Gumi, South Korea) in 2012. Current research interests: Silicon solar cells, Dye-sensitized solar cells, TiO2

photocatalyst and nanostructures, Graphene, composite porous materials by Spark plasma sintering, organic-inorganic solar cells, hybrid solar modules, Graphene, Methanol artificial photosynthesis.



**Sang-Yeop Kim** received his Bachelor's degree in Department of Advanced Materials and Engineering, Kumoh National Institute of Technology, South Korea. He is currently pursuing his Master degree under the supervision of Prof. Sungjin Kim at Kumoh National Institute of Technology. Current research interests: Graphene, ZnO thin film nanostructure, light emitting diode (LED).



Heung-Woo Jeon is a professor. He obtained Ph.D. at Kumoh National Institute of Technology, Department of Electronic Engineering, South Korea. His current research interests are communication, networking & broadcasting; components, circuits, devices & systems; engineered materials, dielectrics & plasmas.



**Soon-Wook Jeong** is a professor. He obtained Ph.D. at Kumoh National Institute of Technology, Department of Advanced Materials and Engineering, South Korea. Current research interests are ZnO nanostructures, chemical vapor deposition, Silicon wafer processing, thin films manufacturing.



**Sungjin Kim** is a professor. He obtained Ph.D. at Kumoh National Institute of Technology, Department of Advanced Materials and Engineering, South Korea. Current research interests are ZnO nanostructures; silicon, dye sensitized (DSSC), organic-inorganic solar cells, spark plasma sintering (SPS), photocatalyst, composite materials, graphene.