Formation of graphene on the surface of copper under the conditions of chemical deposition from the gas phase

I A Kostogrud¹, E V Boyko¹² and D V Smovzh¹²

¹ Kutateladze Institute of Thermophysics SB RAS, Novosibirsk, Russia
² Novosibirsk State University, Novosibirsk, Russia

E-mail: ikostogrud@gmail.com

Abstract. This work is devoted to experimental studies of the effect of synthesis conditions on formation of single-layer graphene on the copper surface. Under the conditions of formation and growth of single-layer graphene, it is shown that characteristic times of graphite nuclei formation are about 1 min and times of primary layer growth are about 0.5 min. The subsequent layers form in 10 min. It is shown that hydrogen concentration at the initial stage of synthesis affects the growth rate of the second layer significantly.

1. Introduction

Since the moment when graphene was first obtained by splitting highly oriented pyrolytic graphite (HOPG), there were many studies of its exceptional mechanical, electrical and thermophysical properties [1]. Thus, it was found out that graphene has high mobility of charge carriers, superconductivity under certain conditions, high optical transparency and mechanical strength [2, 3, 4, 5]. Despite the high quality of graphene obtained by HOPG splitting, this method does not involve the production of large-area samples. To solve the problems of this type, graphene is produced by epitaxial growth on carbide-silicon (SiC) substrates [6] or by chemical vapor deposition (CVD) on the metal surface [7]. The latter method is most suitable for manufacturing graphene samples of large areas in industry because of its low cost, efficiency and high quality [8, 9]. The CVD process allows production of one-layer and multi-layered graphene different degree of defectiveness depending on the synthesis parameters. Solubility of carbon in copper is low, therefore, even at high temperatures, graphene is formed on the surface with a negligible dissolution of carbon in the bulk of metal, leading to the process of self-limiting graphene growth. In addition, thin copper sheets are relatively inexpensive material. All these characteristics make the CVD method with the use of copper as a catalytic substrate, an attractive technology for producing high quality graphene.

An important parameter for the CVD graphene synthesis is the size of crystal fragments of the 2D film covering the copper substrate. This size is determined by the morphology of copper, where the graphene films (grain size, roughness) are formed, parameters of copper foil pretreatment and synthesis conditions.

It was shown in [10] that hydrogen plays a key role in formation and growth of graphite nuclei on the copper surface. The regimes using various mixtures at the stage of nucleation and active growth are described in the literature [11]. The characteristic times of nucleation, nuclei growth and formation of a continuous graphene coating on the surface of copper represent an important issue of experimental search for the optimal regimes. The parameters of the formed graphene coatings at
different growth times under the conditions of constant hydrogen concentration and change in hydrogen concentration at the initial stage are studied here.

2. Experimental section

Graphene was synthesized in a thermal reactor. Copper foil AlfaAesar13382 (99.8% Cu) with the thickness of 25 μm and dimensions of 15 x 35 mm was used as a catalyst-substrate. Initially, the synthesis chamber was filled with Ar and heated to the annealing temperature of 1070°C in the flow of this gas. After that, this gas was replaced by H₂, and the copper substrate was annealed during 30 min. The synthesis of graphene occurred at the temperature of 1070°C. The temperature was set by a thermoregulator with an accuracy of 1°C. Chromel-alumel thermocouples located near the copper substrate were used to measure the temperature. They were calibrated according to the melting point of copper (1085°C). In experiments, two regimes of gas mixture supply for synthesis were investigated. In the first case, immediately after annealing in the atmosphere of H₂, the mixture of gases Ar(90) + H₂(20) + CH₄(0.2) sccm was fed to the synthesis chamber. Thus, at the initial stage, the atmosphere in the synthesis chamber consisted entirely of H₂, and it was gradually replaced by the mixture of Ar + H₂ + CH₄ (regime 1). In the second case, after annealing, the gas chamber was blown by gas mixture Ar(90) + H₂(20) sccm during 10 min. After this, we proceeded to the synthesis stage and CH₄(0.2) sccm (regime 2) was added to the mixture. In a series of experiments, the synthesis was stopped at 1, 1.5, 2, 3, 5 and 10 minutes; the time of the synthesis was counted from the moment when gas was fed to the reactor. The process ended by a stage of rapid cooling in the synthesis mixture.

Raman spectroscopy (RS) was used to determine the number of layers. A T64000 Raman spectrometer produced by Horiba Jobin Yvon with the wavelength of exciting radiation of 514.5 nm was used for RS. The size of graphene crystals and degree of copper coating with graphene layers were analyzed using an optical microscope after sample annealing in the air atmospheric during 10 min at the temperature of 190°C. Optical images were obtained with the Olympus BX51M optical microscope.

3. Results and discussion

An important stage of graphene synthesis is preparation of a copper surface. The usual procedure of copper foil preparation consists in washing it in various solvents [12] to remove surface contamination and annealing in atmosphere containing hydrogen. Annealing is carried out at the temperatures equal or higher than the synthesis temperature to remove the oxide layer and smooth the grain surface. The effect of the annealing temperature on the copper surface was studied experimentally. For this purpose, the samples of copper substrate were annealed in the H₂ atmosphere at the temperatures from 500 to 1090°C during 10 minutes. Then, the surface of samples was analyzed by optical microscopy. The average size of copper grains was measured by the images. The data are presented in figure 1a. They show that a linear increase in sizes takes place at the temperatures from 500 to 900°C. This is

![Figure 1. a) Dependence of copper grain size on temperature of annealing in H₂. b) Optical image of the copper surface after annealing in the H₂ atmosphere at 1070°C during 30 min.](image-url)
Figure 2. Optical images of the copper surface covered with graphene after oxidation. Left column (a, c, e, g, i) relates to regime 1 (beginning with H$_2$ atmosphere). Right column (b, d, f, h, j) relates to regime 2 (beginning with Ar + H$_2$ atmosphere).
due to manifestation of the grain boundaries and smoothing copper surface deformations formed at foil rolling. At the temperatures above 900°C, an exponential increase in grain size occurs, and this corresponds directly to the growth of grains due to coagulation of grains with close orientation. When the melting point (1085°C) is reached, the foil melts, and this leads to irreversible deformations. Under the effect of surface tension forces, it merges into droplets. The maximal annealing temperature that could be achieved avoiding destruction of copper foil was 1080°C. At that, there was a significant increase in the average grain size to 100 μm. It can be also seen in the microphotographs that the bands left on the surface of copper at foil production are smoothed out.

The annealed foil shown in figure 1b was used for graphene synthesis. The optical images of graphene coatings, synthesized at different synthesis times, are shown in figure 2 after oxidation. It can be seen that in the case of high concentration of hydrogen, formation of graphite nuclei on the copper surface is delayed. The characteristic delay time is about 1 minute, figures 2e and 2f. The RS spectra of the forming graphene islets and continuous coating are shown in figure 3. At the initial stage, islets are strongly defective graphene structures. Then, by 5 minutes, the boundaries of the graphene islets connect, and this leads to reduction in defectiveness and formation of a graphene layer. With an exposure of 10 min, the structure of graphene layers formed under different conditions becomes different. At constant concentration of hydrogen, a multilayered graphene is formed, and under the regime with varying concentration of hydrogen, a single-layer graphene coating is formed, figure 3.

The total gas flow rate during synthesis is so that the synthesis chamber is filled with gas during 1.2 minutes. Under these conditions, a laminar flow type is formed in the tube; the gas velocity is 0.02 m/s. Thus, during this time, concentration of hydrogen almost levels for both regimes of synthesis. According to figure 2, the structures of nuclei, formed at different concentrations of hydrogen, differ significantly. At high concentrations, the regions of a hexagonal shape are formed (figure 2c), while the regions of (figures 2b and 2d) do not have hexagonal symmetry and they are much smaller. Nevertheless, the coating structures in figures 2e and 2f are identical by optical images and RS. Differences in synthesized material appear in 10 minutes.

High concentration of H2 at the initial stage prevents formation of graphene nuclei on the surface of copper and reduces their concentration, defectiveness and the number of layers [10]. This leads to a delay in formation of the initial coating, increasing the quality of the produced graphite layer. We can distinguish three characteristic stages of graphene coating growth: 1 – formation of nuclei, 2 – growth of the first layer, 3 – growth of subsequent layers. The nuclei are generated during 1.5-2 minutes, with the characteristic time for stabilization of methane concentration of about 1 minute, then during 0.5-1 min, the first layer grows and the copper coating is almost completely covered by the primary layer. After formation of the first layer, the growth rate of graphite layers decreases noticeably [13]. Thus, at

Figure 3. RS spectres of samples: a) relates to regime 1 (beginning with H2 atmosphere); relates to regime 2 (beginning with Ar + H2 atmosphere).
5 minutes of synthesis, there are no differences between materials, figure 3. Nucleation of the next layer is possible on the defects of the previous layer, thus, the formation rate of the second and subsequent layers is higher for the more defective single-layer coating, formed in regime 2. However, it should be noted that the RS spectra of all synthesized samples (signal does not exceed noise) do not include the D line, responsible for the defects in figure 3, hence the discussed effect has a lower order of sensitivity to the number of defects.

4. Conclusion
The effect of mixture composition and synthesis time on concentration and shape of the nuclei of graphite phase, formed on the copper surface, is studied. The films with different degrees of coverage with single-layer graphene were obtained. It is shown that increased concentration of hydrogen at the initial stage of synthesis leads to formation of predominantly single-layer graphene coatings. This effect is explained by the influence of hydrogen on the number of defects in the primary layer, which determine the growth rate of subsequent layers.

Acknowledgements
This research was financially supported by the Russian Ministry of Education and Science. Project Identifier: RFMEFI60417X0157.

References
[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y and Du-bonos S V 2004 *Science* **306** 666
[2] Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M and Kim K S 2009 *Nature* **457** 706
[3] Bae S, Kim H, Lee Y, Xu X, Park J and Zheng Y 2010 *Nat. Nanotechnol.* **5** 574
[4] Reina A, Son H, Jiao L, Fan B, Dresselhaus M S and Liu Z F 2008 *J. Phys. Chem. C* **112** 17741
[5] Unarunotai S, Koepke J C, Tsai C-L, Du F, Chialvo C E and Murata Y 2010 *ACS Nano* **4** 5591
[6] Berger C, Song Z, Li T, Li X, Ogbazghi A Y and Feng R 2004 *J. Phys. Chem. B* **108** 19912
[7] Li X, Cai W, An J, Kim S, Nah J and Yang D 2009 *Science* **324** 1312
[8] Mattevi C, Kima H and Chhowalla M 2011 *J. Mater. Chem.* **21** 3324
[9] Munoz R and Gomez-Aleixandre C 2013 *Chem. Vap. Deposition* **19** 297
[10] Kostogrud I A, Trusov K V and Smovzh D V 2016 *Adv. Mater. Interfaces* **3** 1500823
[11] Vlassiouk I, Fulvio P, Meyer H, Lavrik N, Dai S, Datskos P and Smirnov S 2013 *Carbon* **54** 58
[12] Luo Z, Lu Y, Singer D W, Berck M E, Somers L A, Goldsmith B R and Johnson A T C 2011 *Chem. Mater.* **23** 1441
[13] Kim H-K, Saiz E, Chhowalla M and Mattevi C 2013 *New J. Phys.* **14** 053012