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Chemical Vapor Deposition of Graphene on Copper

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There are several methods for obtaining graphene. They could be divided into three main groups: mechanical exfoliation, wet chemical methods, chemical vapor deposition (CVD). In this work CVD method was used for synthesis of graphene. The aim of the work was to obtain samples of graphene and to determine the influence of the synthesis parameters. Synthesis of graphene was carried out in thermal reactor under ambient pressure. Methane was used as a precursor gas. Copper foil was used as a substrate. Experiments were carried out at different temperatures (970-1010 °C), varying consists of gas mixtures (Ar/He+H2+CH4), different exposition times (5-30 min) and different rates of samples cooling. Synthesized films were analyzed by Raman-spectroscopy method. In our experiments were obtained samples of few-layered graphene. It showed that the parameters of cooling significantly affect the properties of films.

1. INTRODUCTION

Graphene is a single layer of graphite. The carbon atoms in graphene are connected by sp2 bonds in a two-dimensional hexagonal lattice. Not only the single-layer graphene attracts interest, but bi-layer and multi-layer (up to 10 layers) too.

Development of methods for obtaining graphene is important because it has unique properties. The graphene has a high electrical and thermal conductivity, transparency and mechanical strength, which makes it an interesting material for many applications. Above all, it's application in opto- and nanoelectronics (touch screens, solar cells, flexible electronic devices, high-frequency transistors, logic transistors), photonics (photodetectors, optical modulators and polarizers), composite materials, paints and coatings. The graphene is considered as a good candidate to replace ITO electrodes [1]. There are several methods for obtaining graphene. They could be divided into three main groups: mechanical exfoliation, wet chemical methods, chemical vapor deposition.

This work is devoted to development of CVD method for the synthesis of graphene.

2. EXPERIMENTAL DETAILS

Synthesis of graphene was carried out in thermal reactor (Fig. 1). Thermal reactor consists of a furnace (a thermally insulated enclosure with a heater). A cylindrical quartz tube (1 m long, 19 mm internal diameter) is placed into it. It was used as a gas chamber of the thermal reactor. The tube can be moved up and down in the direction of the gas flow. It is necessary for removal of the substrate-catalyst from the hot zone to effect rapid cooling of the substrate. Temperature of the hot zone was controlled by temperature controller with an accuracy of 1°C. Watercooled vacuum connection fastened to the ends of the tube. Gas is supplied
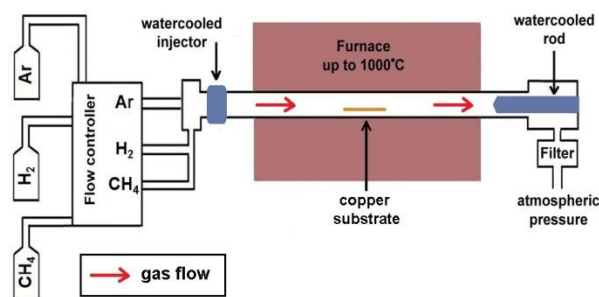
through the flow controller.

Fig. 1 – A schematic view of a setup for CVD synthesis.

Copper foil thickness of 30 microns was used as a substrate. Before experiment, the copper substrate was placed in the reaction zone. The chamber pumped with forvakuum pump and filled with Ar/He buffer gas up to 1.1 bar. It is necessary for creating the gas flow through the chamber. Then the procedure followed for the synthesis of graphene. It can be divided into four stages, as shown in Fig. 2.

1. During the first stage, chamber heated to a temperature of 970-1010 °C, in a stream of buffer gas Ar/He with flow rate of 300 sccm.

2. The temperature was stabilized at the desired value. The copper substrate was annealed in the flow of H2 with rate 100 sccm for 30 min. During annealing in H2, oxide layer is etched off from the surface of copper and the grain size is increased, as said in [2].

3. After annealing, the synthesis gas mixture (Ar/He + H2 + CH4) enters the chamber. Methane (99,9%) was used as a precursor gas. Synthesis was carried out at different temperatures (970-1010 °C), varying consists of gas mixtures and different exposition times (5-30 min).

4. Stage of cooling of the sample completed the pro-

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cedure for the synthesis of graphene.

In the first experiments, the copper substrate cooled with the camera in the flow of buffer gas Ar/He with flow rate of 300 sccm. Cooling to 200 °C took ~ 4 hours. Graphite coating were not detected in samples (№1, 2) of the thus obtained. It was decided to replace the flow of buffer gas to synthesis gas mixture (sample № 3). Later the setup was adapted to the rapid cooling of the substrate. For this purpose, a quartz tube shifted so that the copper substrate coming out from the hot zone upstream of gas. Water cooling was attached to the outside of the tube in the area where the substrate was situated. Thus substrate cooled from 1000 °C to 100 °C for 3 min. The substrate is cooled in the flow of buffer gas (Ar / He), or in the flow of synthesis gas mixture (Ar / He + H2 + CH4).
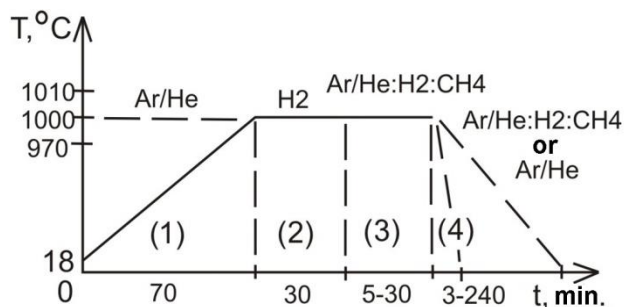

Fig. 2 – Temperature regimes used during the synthesis.

The following experiments on the synthesis of graphene films have been carried out (values in brackets - the gas flow rate in sccm):

№1. Ar(100)+H2(10)+CH4(10)*10 min, 1010°C + slow cooling in the flow of gas Ar(300);

№2. Ar(100)+CH4+(10)*10 min, 1010°C + slow cooling in the flow of gas Ar(300);

№3. Ar(100)+CH4(10)*10 min, 1010°C + slow cooling in the flow of synthesis gas mixture Ar(100)+CH4(10);

№4. Ar(100)+H2(10)+CH4(10)*10 min, 1010°C + rapid cooling in the flow of gas Ar(300);

№5. He(100)+CH4(10)*10 min, 1010°C + rapid cooling in the flow of gas He(300);

№6. Ar(100)+CH4(10)*10 min, 1010°C + rapid cooling in the flow of gas Ar(300);

№7. Ar(100)+H2(10)+CH4(1)*10 min, 1010°C + rapid cooling in the flow of gas Ar(300);

№8. H2(100)+CH4(10)*10 min, 1010°C + rapid cooling in the flow of gas Ar(300);

№9. Ar(400)+H2(6)+CH4(20)*10 min, 1010°C + rapid cooling in the flow of gas Ar(300);

№10. He(400)+H2(6)+CH4(20)*10 min, 1010°C + rapid cooling in the flow of gas He(300);

№11. Ar(100)+H2(10)+CH4(1)*10 min, 990°C + rapid cooling in the flow of gas Ar(300);

№12. Ar(100)+H2(10)+CH4(1)*5 min, 1010°C + rapid cooling in the flow of gas Ar(300);

№13. Ar(100)+H2(10)+CH4(1)*10 min, 970°C + rapid cooling in the flow of gas Ar(300);

№14. Ar(100)+H2(3)+CH4(10)*30 min, 1000°C + rapid cooling in the flow of gas Ar(300);

№15. Ar(100)+H2(3)+CH4(10)*30 min, 1000°C + rapid cooling in the flow of synthesis gas mixture Ar(100)+H2(3)+CH4(10);

№16. H2(100)+CH4(10)*30 min, 1000°C + rapid cooling in the flow of synthesis gas mixture H2(100)+CH4(10);

№17. H2(100)+CH4(1)*30 min, 1000°C + rapid cooling in the flow of synthesis gas mixture H2(100)+CH4(1).

The method of Raman spectroscopy was used to analyze the synthesized films. Raman spectrometer HoribaJobinYvon T64000 with the excitation wavelength of 514.5 nm was used for this. Spectra were recorded with the sample surface at several points in the range from 100 to 3000 cm^{-1}. Also the spectra of reference samples (CVD-graphene on copper foil and highly oriented pyrolytic graphite HOPG) were recorded. Peaks D, G, D ', 2D typical for graphite structures present in the recorded spectra. Also, the background signal created by luminescent emission of copper observed in the spectra. Background was subtracted as a baseline. Peaks D, G and 2D were approximated by a Gaussian and Lorenz distribution. Center position, intensity and width at half maximum were determined from the observed peaks. Then these parameters were compared.

3. RESULTS AND DISCUSSION

Graphite peaks (D, G, 2D) was not detected on the spectra of several samples (№ 1, 2, 9, 10, 14). In case of № 1, 2 it was assumed that the film was destroyed on slow cooling stage in Ar (300) due to the weak leakage of oxygen through the exhaust system. Considering this reason, cooling procedure was changed. Slow cooling was replaced by a rapid cooling. The flow of buffer gas was replaced by flow of synthesis gas mixture. In the experiments № 9, 10 the gas does not have time to warm up to the synthesis temperature due to the high velocity of the flow. This fact has been taken into account in subsequent experiments

Data of Raman spectra are shown in Fig.3. Samples can be compared with each other (the number of layers and defects) in the data.

The vertical axis in Fig. 3 plotted the values of the ratio of the peak intensity D to the peak intensity G. D-line in the spectrum of graphite materials is responsible for the oscillation of defective rings. In an ideal lattice D-line is disabled (within the noise of the reference graphene and HOPG). The lower value of the normalized intensity of the D-line on the intensity of the G-line corresponds to less defective material. The horizontal axis represents the values of the center of 2D lines. For single-layer graphene is the value of ~ 2680 cm-1, which corresponds to the measured value of the reference sample. This peak is shifted to the blue area (to the right in the figure) with the number of graphene layers. Accordingly, the increase in this parameter indicates the increase in the number of graphene layers [3]. The measured value for HOPG is 2725 cm-1. The graph shows that the values of the synthesized samples are between the values of the reference graphene and HOPG. This indicates that the synthesized samples are multi-layered graphene films.

Based on the experimental data one can conclude that the monotonic temperature influence on the syn-

thesis of graphene structure is not observed (samples № 7, 11, 13). Decrease in the D/G comes with an increase in exposure time, which is associated with an increase in the number of layers and the reduction of defects (samples № 7, 12). By increasing the partial pressure of methane in the mixture from 1 to 10% was found a slight increase in defects of graphene layers (№ 4 and 7, № 16 and 17), it is probably caused by an increased rate of growth of carbon structures. An experiment was conducted (№14) wherein a sample after 30

minutes of synthesis was stood for 1 minute in a flow of Ar(300) (corresponds to the complete replacement of the gas in the reactor). In this sample, only a weak G peak is detected that is not consistent with the data obtained by cooling the sample without pre-purge chamber argon (№ 15). This fact indicates a significant impact of the cooling stage on the growth of graphene films. Perhaps carbon structures are destroyed when replacing the synthesis gas mixture to argon.
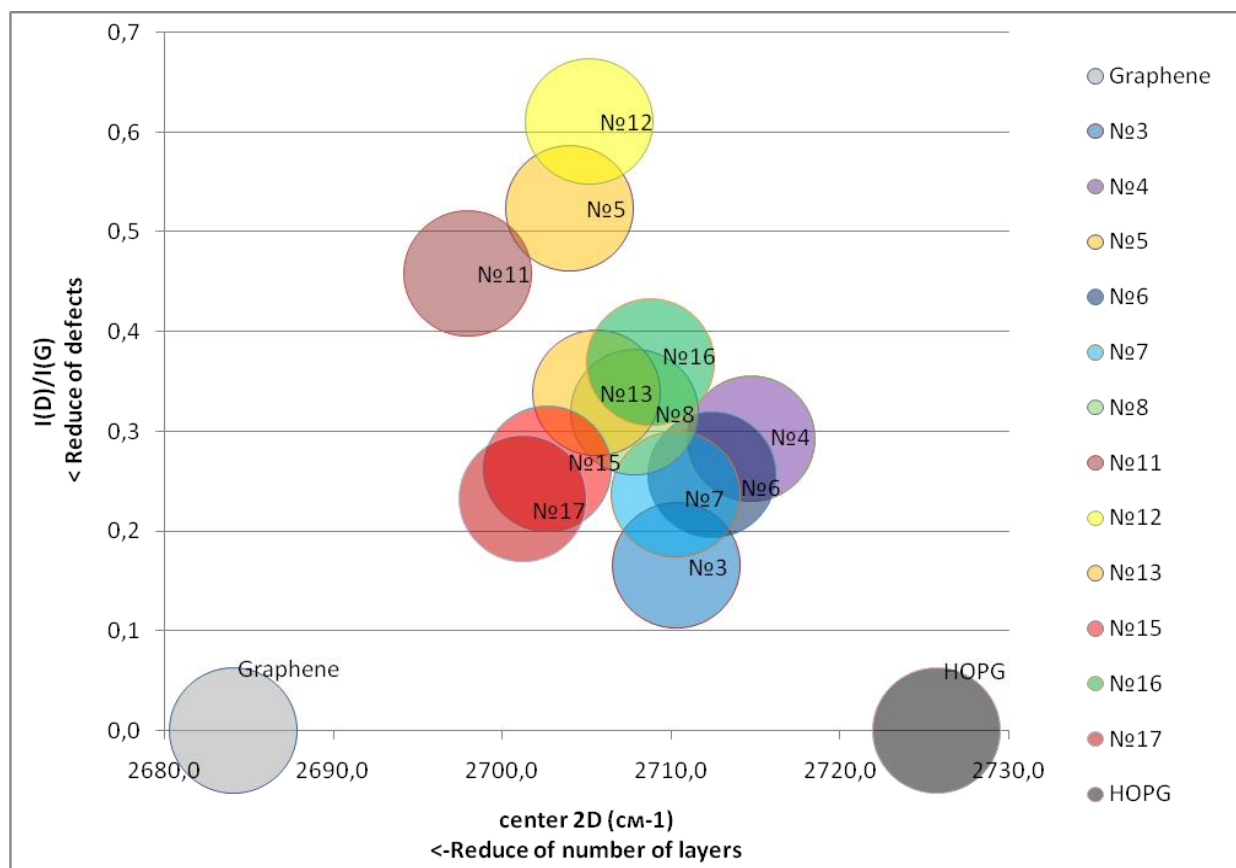

Fig. 3 – Data of Raman spectra of synthesized samples.

4. CONCLUSIONS

In this paper we carried out experiments on the synthesis of graphene by chemical vapor deposition. Various modes of synthesis were tested. In the experiments, the samples of multi-layer graphene were obtained. Analysis of the synthesized films was held by Raman spectroscopy. It was found that the cooling parameters significantly affect the resulting films. It is

shown that the rapid cooling in the synthesis gas mixture is the best way. It is shown that the least defective graphene films obtained in the synthesis of low concentration of methane (~ 1%). The smallest amount of the graphene layers (2-5) is obtained at a reactor temperature of 1000 °C, using the gas mixture (Ar: H2: CH4 = 100:3:10 sccm), exposure time 30 minutes and rapid cooling in the same gas mixture.

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