Graphene produced by carbon diffusion through nickel foil

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This paper presents results of obtaining graphene and few-layer graphene nanostructures by unconventional method consisting in the diffusion of carbon through a thin nickel foil. The production of graphene and few-layer graphene nanostructures by the diffusion method was carried out under high vacuum conditions, with resistive heating of nickel. The growing method presented by us makes it possible to control the process of graphene formation by changing parameters such as: temperature, time and thickness of nickel. Data on the time dependence of the diffusion process on the nickel thickness and temperature are given. From the obtained experimental data was found the parameters determining the diffusion dynamics: E_a - the activation energy and concentration diffusion coefficient. The obtained samples were investigated by optical and electron microscopy, as well as by Raman spectroscopy. The experimental results are in good agreement with the theoretical Arrhenius relation, which confirms the diffusion nature of the process.

1 Introduction

Graphene attracts wide attention due to its physical and mechanical properties, and also represents a huge potential for various scientific and practical applications. Graphene is characterized as a two-dimensional sheet of sp^2-hybridized carbon atoms located in a hexagonal lattice [1]. Graphene synthesis is the production of graphene of the desired size, purity, and defect level using various methods [2-6]. The most commonly used methods of graphene synthesis are mechanical exfoliation; epitaxial growth; chemical vapor deposition (CVD); electrochemical exfoliation; chemical oxidation / reduction of graphite [7].

To obtain graphene by mechanical exfoliation, thin layers of highly oriented pyrolytic graphite are placed between the adhesive tapes, and the graphite films are separated again and again until a thin layer is obtained [1].

Another important method is the epitaxial growth of graphene, where graphene is grown on single-crystal silicon carbide (SiC). In this method, silicon carbide (SiC) is heated at a temperature of about 1200 °C under vacuum, resulting in the sublimation of Si atoms, forming carbon layers on SiC, which can be bilayer, multilayer or monolayer. In the CVD method, graphene is grown directly on various substrates of transition metals such as Ni, Cu, Co, Au and Ru by saturation of carbon under the influence of various gaseous hydrocarbons such as methane, ethylene, acetylene and benzene at high temperature.

In the CVD method, the difference between a cold wall and a hot wall is that the hot wall chamber is heated by an external energy source, while the temperature is everywhere relatively constant, and the substrate is heated by radiation from the heated walls of the chamber. In the reactor of the cold wall system, the sample is heated by the following different methods: passing current through the sample; using the heater that contacts the substrate; induction and the walls of the chamber are at room temperature [8].

The next method for obtaining graphene is electrochemical exfoliation of graphite. In this method, such electrodes as highly oriented pyrolytic graphite, graphite, Cu, Pt are used. In electrochemical separation, one of the important processes is the choice of the electrolyte, because

from it depends the increase of the charge transfer and the functionalization of the obtained graphene sheets. Many different electrolytes for electrochemical exfoliation, including HBr, HCl, HNO$_3$ and H$_2$SO$_4$, have been investigated, and the most commonly used of them are acid electrolytes containing H$_2$SO$_4$ and alkaline KOH electrolyte diluted with distilled water, which are ideal for exfoliation graphite [9-11]. To obtain graphene by this method, at first, two graphite electrodes or other types are inserted into the solution and about 10 V are applied to them, then the intercalating ion in the solution penetrates between the graphite layers exfoliates into few-layer graphene sheets, after which to separate the graphite particles from graphene solution is subjected to centrifugation or ultrasound is used to improve the cleavage, and then the solution is dried at the end [10, 12].

The last common method of producing graphene is referred to as the Hummer method [7]. In this method the starting material is graphite. The graphite is converted to graphene oxide by treatment with super acids, oxidizers and heat. The graphene oxide is then dispersed into water down to predominantly single sheets. These individual sheets of graphene oxide are then reduced with strong reducing agents to graphene. This process has two main problems. The first is that many defects remain in the hexagonal lattice after reduction, Secondly, the reduced graphene sheets have a strong tendency to restack into nano-graphite.

Considering the disadvantages of the above methods, we proposed a method for obtaining few-layer graphene structures and graphene on a nickel substrate, the essence of which was the diffusion of carbon through a nickel foil. This method is realized in conditions of high vacuum during resistive heating of nickel foil with tightly pressed pyrolytic graphite on one side.

Carbon diffusion in various materials was published in [13-16]. The diffusion and dissolution of carbon in nickel are considered in [17-19].

2 Experiment

In this paper, we investigated the diffusion of carbon through a nickel foil. As the initial material, we used highly oriented pyrolytic graphite (HOPG) from NT-MDT, nickel foil with a purity of 99.99%.

To confirm the diffusion nature of the process and to determine the concentration diffusion coefficient, we considered the theoretical Arrhenius relation.

$$D=D_{0exp}(-E_a/kT) \qquad (1)$$

D – is the diffusion coefficient [m²/s]; E$_a$ - activation energy [J]; k – is the Boltzmann constant [J/K]; T – is the temperature [K]. The average distance that a particle travels during a time τ is estimated by the relation

$$L=\sqrt{D*\tau} \qquad (2)$$

For example, at a temperature of about 900 ^{0}C, the value of the concentration diffusion coefficient is estimated at 8.23 * 10^{-12} m^2/c. Table 1 shows the values of the process parameters.

Table 1 –The time dependence of the process (τ) on the substrate thickness (L) and temperature (T)

L (µm)	T (°C)	t (c)
40,2±4,2	903,7±5,5	182,31±22,40
60,5±3,4	900,5±6,4	431,64±7,05
80,3±3,8	902,7±4,0	736,32±25,69

We have proposed a method of growing graphene, few-layer graphene by the diffusion method on nickel foil in a high-vacuum chamber. The essence of this method is that in the case of resistive heating, the tightly pressed pyrolytic graphite on the nickel foil diffuses through the nickel foil and graphene and few-layer graphene layers are formed on the reverse side of the surface. Figure 1 shows the scheme of obtaining graphene on nickel by the diffusion method.
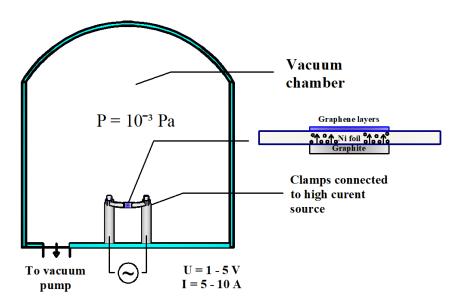
Figure 1 – Experimental setup of graphene production method

Before obtaining graphene or few-layer graphene by diffusion method on nickel, an experiment was first done to obtain the graphite layer. To perform this experiment, we took a thin nickel foil with a thickness of about 40 μm, with a size of 3.5 * 0.5 cm and highly oriented pyrolytic graphite (HOPG). HOPG was tightly pressed with nickel foil and under high vacuum conditions it was heated at a high temperature of about 900 °C until a graphite layers was formed on the other side of the nickel foil. Figure 2 shows a SEM image of graphite layers.

This figure clearly shows the folds, wrinkles on the surface of the graphite layers grown by the diffusion method on nickel foil.

After diffusion growth of the graphite layers, the surface of the nickel foil becomes defective and folds. According to the known literature data, during the process of growing graphene nanostructures, the interaction between the substrate and graphene strongly influences the formation of wrinkles, folds and pulsations due to the opposite polarity of the coefficients of thermal expansion of graphene nanostructures and metals [20]. Wrinkles, folds are more likely to occur due to the influence of thermal stress and compression when cooling graphene, graphene nanostructures.

The next process of our experimental part is the production of graphene, a few-layer graphene by the diffusion method on nickel foil. To obtain graphene or few layer graphene, we used the same initial materials that were used to obtain a graphite layer

by the diffusion process. In this experiment, the thickness of the nickel foil ranged from 40 to 80 μm, the temperature of the resistive heating was 900 °C, and the time of obtaining a certain graphene layer depended on the size of the nickel foil and on the temperature (Table 1). Figure 3 shows the nickel foil before and after diffusion.
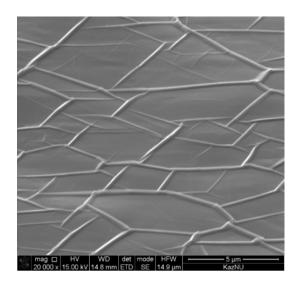

Figure 2 – SEM image of graphite layers

Figure 4 shows the optical image of the graphene obtained by the diffusion method on nickel at a temperature of 900 °C.
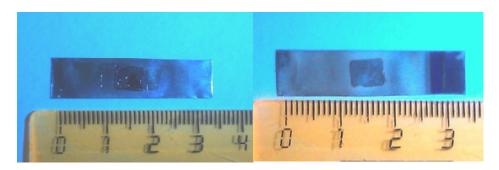
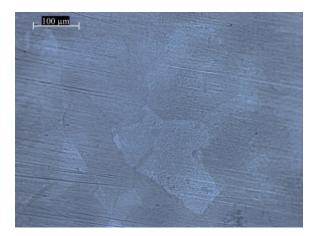**Figure 3** – Nickel foil before and after diffusion

Figure 4 – Optical image of graphene

Optical image clearly shows graphene and few-layer graphene sheets grown by the diffusion method on nickel foil. This figure shows the grains of the nickel substrate and the boundaries on which the few-layer graphene sheets were grown, as well as the possibility of growing the larger size of graphene sheets, regardless of the morphology of the substrate surface and small nucleation centers. According to [21], the number of nucleation sites for graphene growth is extremely small on the Ni (111) surface, which is an important growth factor for large single-domain graphene crystals. According to the literature data, carbon diffusion in Ni (111) can occur mainly through grains and their boundaries or in other defective places in the graphene layer [22-25].

The average grain size of nickel and few-layer graphene was estimated in the analysis using optical microscopy. It was $10*15$ μm^2 and Raman spectroscopy analysis confirmed the presence of few-layer graphene (FLG) on the obtained sample.

Figure 5 shows the Raman spectrum of graphene obtained by the diffusion method on nickel. The main modes of Raman spectroscopy of graphene, few-layer graphene are D, G, 2D peaks. D line (disorder, defects) this peak corresponds to defects inside the carbon lattice. D mode is due to the disordered structure of the graphene and is located in the region of 1370 cm^{-1}. G – the peak is located in the region of 1580 cm^{-1} and arises due to the E_{2g} mode at the G point, also the G-peak arises due to the expansion of the C-C bond of the graphite materials and is characteristic for all sp^2 carbon systems. In the Raman spectrum the 2D peak is located in the 2730 cm^{-1} range and the number of graphene layers can be determined with this peak [26, 27].
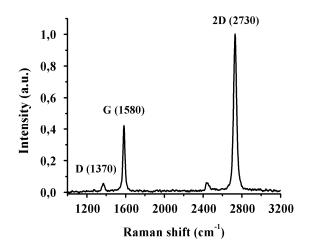

Figure 5 – Raman spectrum of graphene obtained by the diffusion method at the temperature of 900 °C.

According to [28], the number of layers of graphene is determined by the ratio of the intensities of the I_{2D}/I_G peaks. The ratio $I_{2D}/I_G \sim 2\text{-}3$ is characteristic for monolayer graphene, for two-layer graphene $2 > I_{2D}/I_G > 1$ and for multilayer $I_{2D}/I_G < 1$ [28, 29]. Based on the ratio of the intensity of the Raman scattering I_{2D}/I_G peaks, it can be concluded

that the graphene obtained by the diffusion method on nickel foil is a two-layer one (Figure 5).

3 Conclusions

We studied the production of graphene on nickel by diffusion method. The following problems were solved: the features of graphene production on nickel by diffusion method were studied; the most optimal process parameters for this method were determined; the obtained samples were investigated using optical microscopy, electron microscopy and Raman spectroscopy.

The obtained results of this method show the possibility of controlling the process of graphene formation by changing parameters such as temperature, time and thickness of nickel. During the experiment, the main parameters of carbon diffusion in nickel were estimated. In this case, the theoretical limiting possible size of the formed graphene is limited only by the size of the reaction chamber. The experimental results are well correlated with the theoretical Arrhenius ratio, which confirms the diffusion nature of the process.

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