

## Flame Synthesis of Graphene Layers at Low Pressure

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**Abstract**—The synthesis of graphene layers on a nickel substrate in a butane–benzene–oxygen premixed flame at a pressure of 40–100 Torr is studied. It is demonstrated that, the temperature of 900–950°C and exposure time of 0.5 min are sufficient for synthesizing graphene layers on a nickel substrate. It is shown that, at a pressure of 45–55 Torr, single-layer graphene is predominantly formed. It is found that, at a pressure of 90 Torr and an exposure time of 0.5 min, monolayer graphite can be produced, but with a lower yield as compared to that prepared at 45–55 Torr. It is demonstrated that the degree of defectiveness of graphenes decreases with the exposure time, reaching a minimum value of  $I_D/I_G = 0.36$ .

**Keywords:** graphene, graphene layers, flame, combustion, butane, pressure, benzene, Raman spectrum

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### INTRODUCTION

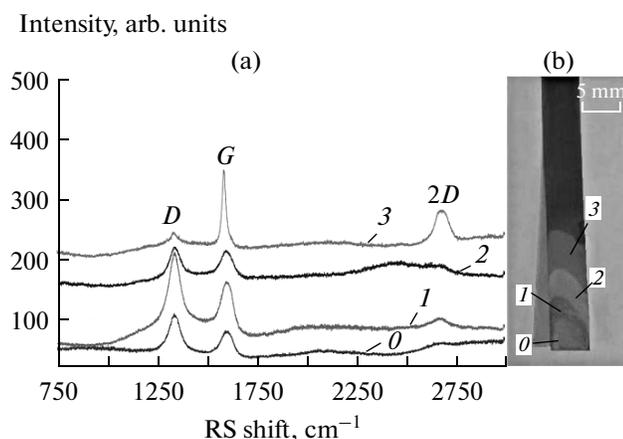
Studies of graphene have a long history. Back in 1859, Benjamin Brodie observed a new form of carbon, produced by treating graphite with a strong acid [1]. Brodie named the resulting suspension “carbon acid” and the new form of carbon, with a molecular weight of 33, “graphon”. Currently, we know that he produced and observed a suspension of graphite oxide crystals [2]. In the following century, just a few papers describing the layered structure of graphite oxide appeared; note, however, that the existence of individual atomic planes in the latter has been established. In 1948, Ruess and Vogt, using a transmission electron microscope (TEM), observed a graphite oxide flakes with a thickness of a few nanometers, which were formed as a result of evaporation of a suspension droplet deposited on the TEM grid [3]. In 1962, Hofmann and Boehm, while examining reduced graphite oxide flakes to find the thinnest, revealed that some of them consist of one monolayer [4]. This work can be regarded as the one wherein graphene was first identified. Note also that, in 1986, Bohm and his colleagues were first to introduce the term “graphene”, as a combination of the word “graphite” and the suffix denoting a polycyclic aromatic hydrocarbon [5].

Initially, studies of thin graphite films were aimed mainly at their visualization, without trying to examine the remarkable properties of graphene. Geim and Novoselov were first to investigate the electronic properties of a single graphite layer produced by micromechanical cleavage of graphite, starting a new stage in

the study of graphene [6]. They have discovered unique electronic properties of graphene, thereby giving a new impetus to its further studies. Graphene is a single-layer two-dimensional carbon structure composed of regular hexagons with sides of 0.142 nm. Graphene has high electrical and thermal conductivity, the ability to add radicals of different natures capable of changing its properties depending on the nature of the radical, an extremely high charge carrier mobility, a high elasticity, and good electromechanical characteristics [6–8]. All this makes graphene an indispensable material for producing new nanomaterials with improved mechanical, electrical, and thermal characteristics, as well as an element for nanoelectronic devices.

Currently, graphene layers are synthesized by a variety of methods, such as the delamination of graphite in the liquid phase, graphite oxidation, chemical vapor deposition, epitaxial growth of graphene on a metal surface, thermal decomposition of carbide, and production of graphene in the electric arc [8]. However, these methods for graphene synthesis are very laborious and time-consuming. Therefore, many research laboratories are engaged in searching for new, faster, and less labor-intensive methods of graphene synthesis.

The flame synthesis of graphenes under atmospheric conditions was demonstrated [9–12] to be promising because it is continuous, simple, and fast. Mansurov proposed [11, 13] a scheme of soot formation complemented by a graphene formation stage, which was confirmed experimentally [9–11].



**Fig. 1.** (a) Raman spectra of the carbon structure formed in zones 0, 1, 2, and 3 and (b) photograph of the relevant zones of formed carbon structures ( $P = 90$  Torr,  $C/O = 0.8$ ,  $T = 900^\circ\text{C}$ , and  $t = 0.5$  min).

This paper reports new results on graphene synthesis in a flame at low pressures, which are of a certain interest, filling a gap in this field of knowledge.

## EXPERIMENTAL PART

Graphene layers were synthesized at 40–100 Torr in a butane–benzene–oxygen premixed flame. For this purpose, the burner was placed in a quartz glass tube in which a low initial pressure, 5 Torr, was created. The experiments were performed at butane, oxygen, and benzene flow rates of 450, 740, and 70–120  $\text{cm}^3/\text{min}$ , respectively, which corresponds to C/O ratios of 0.8–0.9. The flame temperature in the graphene synthesis zone was 900–950 $^\circ\text{C}$ , as measured by a Chromel–Alumel thermocouple. The substrate was a 0.2-mm thick (111) surface nickel plate pretreated in a 20%  $\text{HNO}_3$  solution for 30 min.

The plate was placed vertically in the central part of the flame parallel to its axis. The substrate was introduced into the flame upon full stabilization of combustion and kept therein from 0.5 to 3 min. After a predetermined time, the substrate was taken out of the flame, burning was stopped, and the pressure was raised to atmospheric. The obtained samples of carbon structures were not separated from the nickel substrate and were not purified, being examined on the substrate in the form in which they were produced in the flame. The samples of carbon structures synthesized on nickel catalyst substrates were studied using a Raman spectrometer (INTEGRA Spectra Raman,  $\lambda = 473$  nm, signal from an area with a diameter of 80 nm), and optic (DFC 490), atomic force (INTEGRA Force Microscope), and scanning (Quanta 3D200i) microscopes.

## RESULTS AND DISCUSSION

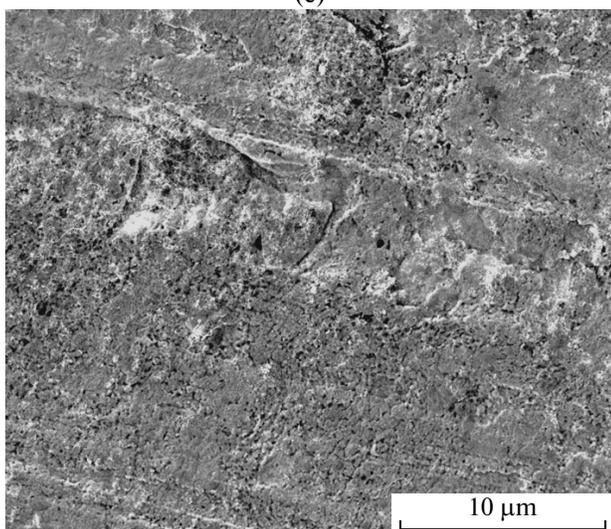
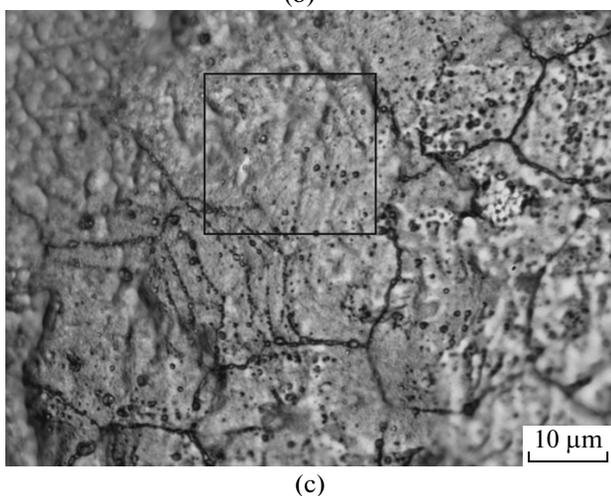
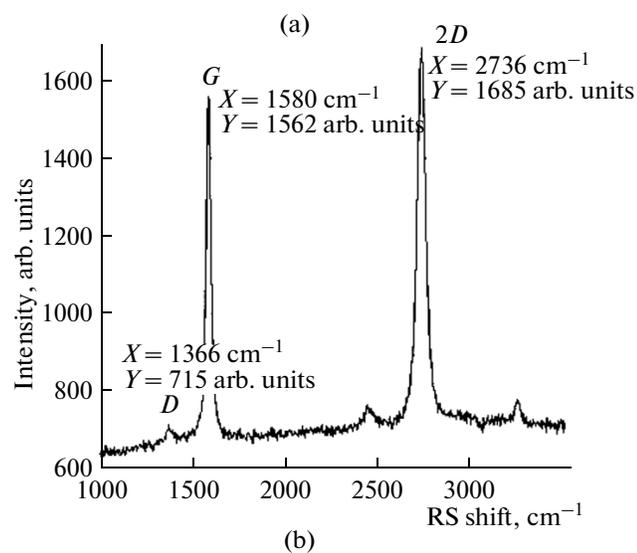
It is known that the mechanisms of the formation of carbon structures in rich premixed flames at low and atmospheric pressures are different [14]. At atmospheric pressure, carbon structures are largely formed from acetylene, since heavier acetylenic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) appear later than the majority of carbon structures [14]. At low pressure, the formation of carbon structures is preceded by the production of polycyclic aromatic hydrocarbons. The combustion of hydrocarbon fuels at low pressure is also characterized by a reduced soot formation and the pyrolysis of unburned fuel on the substrate surface, a factor that has a positive effect on the synthesis of graphenes. With decreasing pressure, the thermal width of the flame front increases approximately inversely proportional to the pressure. Thus, at low-pressure, the reaction zone, where PAH formation begins, is wider, a feature that provides a larger surface area for the synthesis of graphene layers.

As is known, a typical spectrum of graphene exhibits three peaks: peak  $D$  at  $1351\text{ cm}^{-1}$ , peak  $G$  at  $1580\text{ cm}^{-1}$ , and peak  $2D$  at  $2700\text{ cm}^{-1}$  [9, 10]. The ratio between the intensities of peak  $G$   $I_G$  and peak  $2D$   $I_{2D}$ ,  $I_G/I_{2D}$  gives an estimate of the number of layers [10]. For monolayer graphene, this ratio is less than unity. The ratio between the intensities of peak  $D$   $I_D$  and peak  $G$   $I_G$ ,  $I_D/I_G$  evaluates the defectiveness of graphene layers [10].

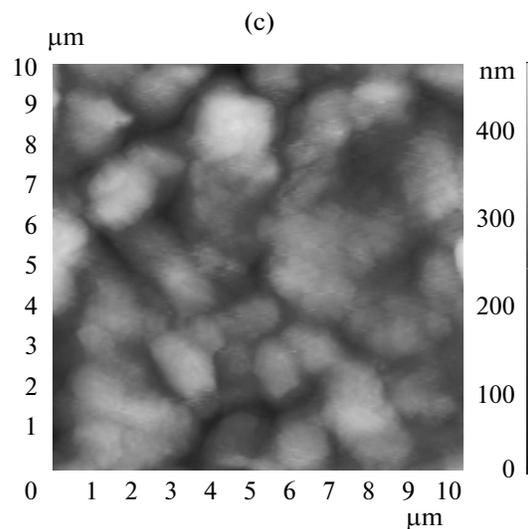
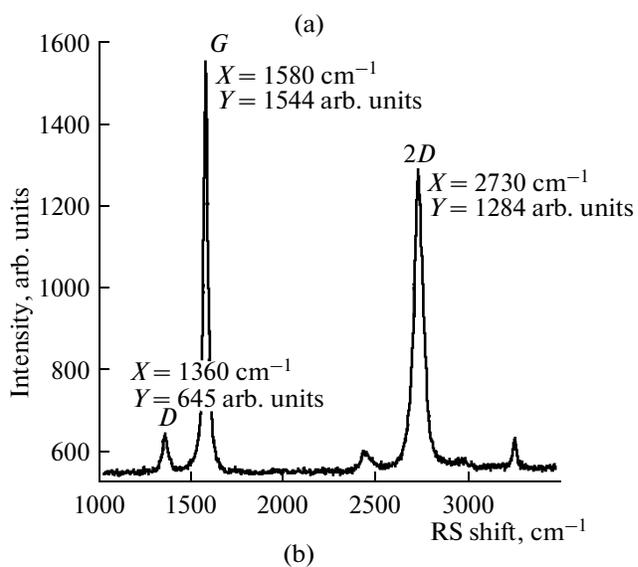
Based on studies of the carbon–nickel phase transition with the formation of graphene layers on the substrate surface [15–17] and some previous results, it was found that, for the formation of layered graphene films, it is preferable to use a nickel substrate with plane orientation (111). Under our experimental conditions, a copper substrate in a vacuum environment catalytically burns out the carbon structure deposited on its surface, thereby preventing the formation of graphene. Twisting, graphene layers appear to be able to follow the relief of the substrate, covering its defects with a continuous layer.

It was shown [11] that, at low pressure, as at atmospheric pressure, graphene layers are formed in the presooting zone. Figure 1a shows Raman spectra typical of carbon structures formed on a nickel plate in zones 0, 1, 2, and 3 (Fig. 1b). In zones 0, 1, and 2 (Figs. 1a and 1b), amorphous carbon structures are formed, whereas in zone 3, graphene layers are synthesized. Note that, at low pressure, the width of the graphene formation zone ( $\sim 5$  mm at 40 Torr) is larger than that at atmospheric pressure. Above zone 3, a soot-like structure is observed (Fig. 1 b).

Analysis of the results on the synthesis of graphenes at an exposure time of 3 min and different pressures showed that an increase in pressure, all other experimental conditions being equal, leads to an increase in the number of graphene layers on the nickel substrate. In the pressure range covered, 40–100 Torr, the maximum number of graphene layers is less than three, as



**Fig. 2.** (a) Raman spectrum of a single-layer graphene synthesized on a nickel substrate placed in a butane–benzene–oxygen flame and (b) optical and (c) SEM microimages of the graphene film synthesized on a nickel substrate ( $P = 90 \text{ Torr}$ ,  $C/O = 0.8$ ,  $T = 900^\circ\text{C}$ ,  $t = 0.5 \text{ min}$ ,  $I_G/I_{2D} = 0.93$ , and  $I_D/I_G = 0.46$ ;  $X$  is the Raman scattering shift,  $\text{cm}^{-1}$ ;  $Y$  is the intensity, arb. units).



**Fig. 3.** (a) Raman spectrum of a multilayer graphene synthesized on a nickel substrate placed in a butane–benzene–oxygen flame and (b) optical and (c) atomic-force microimages of the graphene film synthesized on a nickel substrate ( $P = 90 \text{ Torr}$ ,  $C/O = 0.8$ ,  $T = 900^\circ\text{C}$ ,  $t = 1.5 \text{ min}$ ,  $I_G/I_{2D} = 1.2$ , and  $I_D/I_G = 0.42$ ;  $X$  is the Raman scattering shift,  $\text{cm}^{-1}$ ;  $Y$  is the intensity, arb. units).

**Table 1.** Pressure dependences of  $I_G/I_{2D}$  and  $I_D/I_G$  as obtained from the Raman spectra of graphenes synthesized in a butane–benzene–oxygen flame at  $C/O = 0.8$  and  $t = 3$  min

Pressure, Torr	$I_G/I_{2D}$	$I_D/I_G$	Number of layers
45	0.99–1.27	0.6–0.69	1–2
55	0.58–1.25	0.49–0.73	1–2
60	1.1–1.25	0.67–0.77	2–3
65	1.2–1.35	0.6–0.75	2–3
90	1.27–1.33	0.63–0.78	2–3

**Table 2.** Exposure time dependences of  $I_G/I_{2D}$  and  $I_D/I_G$  as obtained from the Raman spectra of graphenes synthesized in a butane–benzene–oxygen flame at  $C/O = 0.8$  and  $P = 90$  Torr

Exposure time, min	$I_G/I_{2D}$	$I_D/I_G$	Number of layers
0.5	0.88–1.53	0.36–0.46	1–3
1.0	1.51–1.80	0.42–0.49	3–5
1.5	1.56–1.62	0.44–0.53	3–5
2.0	1.47–1.62	0.48–0.53	3–5

indicated by the ratio between the peaks' intensities  $I_G/I_{2D}$ . It was shown [18] that the ratio of  $I_G/I_{2D} = 1.3$  corresponds to three layers of graphene, whereas the authors of [19] found that  $I_G/I_{2D} = 1.8–2.4$  corresponds to 5–10 layers of graphene. For monolayer graphene, this ratio is less than unity [18, 20]. It was found that, at pressures of 45 to 55 Torr, single-layer graphene is predominantly formed. The results of analysis of the Raman spectra of the synthesized graphene layers are listed in Table 1. The degree of imperfection of graphene, as characterized by the  $I_D/I_G$  ratio was demonstrated to range within 0.49–0.78.

That the number of layers on the substrate increases with the pressure, all other things being equal, can be attributed to a rise in the contribution from soot formation. Accordingly, it was assumed that the number of layers formed on the substrate at high pressure can be reduced by decreasing the residence time of the substrate in the flame.

To test this assumption, we performed a series of experiments at a pressure of 90 Torr and exposure times of 0.5, 1.0, 1.5, and 2.0 min. Analysis of the results showed that, at the exposure time of 0.5 min, single-layer graphene is formed, a characteristic Raman spectrum of which is shown in Fig. 2a. Figure 2b shows an optical microscope image of a graphene film on a nickel substrate. The selected area in Fig. 2b was examined on a scanning electron microscope (Fig. 2c). The optical and SEM images are indicative of a wavy surface structure of the graphene sample and its defects.

At an exposure time above 0.5 min and a pressure of 90 Torr, single-layer graphene is predominantly formed, a characteristic Raman spectrum of which is displayed in Fig. 3a. Figures 3b and 3c show, respectively, optical and atomic-force images of multilayer graphene on a nickel substrate. The atomic force image (Fig. 3c) of a  $10 \times 10 \mu\text{m}^2$  area on the Ni(111) substrate and the optical image (Fig. 3b) show that the graphene film surface has folds and irregularities, which follow the relief of the nickel crystal surface. The characteristics of the Raman spectra of the synthesized graphene layers are given in Table 2.

Analysis of the results showed that, at the pressure of 90 Torr, soot formation more strongly influences the process of graphene formation than it does at 45 Torr. In this case, typically 3 to 5 layers of graphene are formed. However, reducing the time of exposure of the substrate in the flame to 30 s makes it possible to obtain a graphene monolayer at the pressure of 90 Torr as well. The degree of imperfection of graphenes decreases and reaches a minimum value of  $I_D/I_G = 0.36$ , which brings them closer in quality to graphenes synthesized by the CVD method.

## CONCLUSIONS

Analyzing the results of studies on the formation of graphene films in a butane–benzene–oxygen low-pressure flame led us to the following conclusions:

- the formation of graphene layers at low pressure, as at atmospheric pressure, occurs in the pre-sooting zone, but the graphene formation zone at low pressure is more extended;
- with pressure increasing from 40 to 100 Torr, all other experimental conditions being equal, the number of graphene layers formed on a nickel substrate increases from one to five;
- at pressures of 45 to 55 Torr graphene monolayers of size  $10 \times 10 \mu\text{m}^2$  are predominantly formed;
- reducing the time of exposure of the substrate in the flame to 0.5 min enables to obtain single-layer graphenes even at a pressure of 90 Torr;
- the defectiveness of graphenes decreases with reducing exposure time from 3 to 0.5 min, reaching a minimum value of  $I_D/I_G = 0.36$ .

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