Formation of submicron thickness films under processing graphite by proton beam

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Abstract. Modification of graphite surface under irradiation by beam of protons with energy 50 keV was studied. Protons flux was equal $4 \times 10^{15}$ and $2 \times 10^{16}$ cm$^{-2}$. It was established that under the proton action the sample surface was converted into a periodic structure in the form of ridges, located in increments of less than 1 µm. The height of ridges was about of 2 µm; their longitudinal size was about of 10 µm. Increase in radiation dose led to a more intensive growth of discovered structures. The transparent thin films were detected on the graphite surface with help of scan electronic microscope. The action of the arc discharge on the modified surface of graphite was described.

1. Introduction

Graphene is a layer of carbon atoms forming a two-dimensional crystal with a hexagonal lattice. Due to unique optical, electrical and mechanical properties, graphenes are widely in demand, including in micro- and nanoelectronics, the creation of new composite materials, etc [1]. The possibilities of practical use of graphene are determined by the technology of its production, while the purity of the final product plays an important role for a number of applications. Technological processes of the graphene production are accompanied by the formation of graphite-like films. For the first time, graphene was obtained by the method of splitting (exfoliation) of layers from ordinary crystalline graphite [2]. This method did not allow obtaining graphene in a significant amount, besides it was difficult to ensure its purity. Different chemical methods have a higher productivity [3, 4]. In the intercalation process described in [3], graphite is saturated with sulfuric and nitric acids, and then it is rapidly heated to approximately 1.3 kK. As a result of explosive evaporation of intercalant molecules, graphite flakes are formed, which contain many layers of graphene. Then oleum and tetrabutylammonium hydroxide are introduced between the graphene layers, and then graphene is separated by centrifugation. The thermal decomposition of silicon carbide is a more promising method for the production of graphene [1]. Usually, this process is carried out in ultrahigh vacuum at temperatures from 1.3 to 1.8 kK. After the sublimation of silicon, thin graphite-like films are formed, which serve as a starting material for the production of graphene. In general, the production of graphene by chemical methods is a
complex multi-stage process, in which thorough purification of the product from used chemical reagents is required.

In work [5], it was assumed that irradiation of graphite samples with neutrons of energy up to 2 MeV should produce Frenkel defects, which can contribute to the separation of graphene layers. The neutron fluence was \(3.6 \times 10^{16} \text{ cm}^{-2}\) under exposure duration of \(\approx 300\) min. However, in the study [5], no evidence of graphene formation was recorded. Also, no formation of the flat graphite-like structures (GLS) was observed upon irradiation of graphite with alpha-particles with the energy of 40 keV and 3.5 MeV [6].

In this paper, we report the results of obtaining GLS of submicron thickness under exposure of the graphite surface to a proton beam. The advantage of the studied method is the possibility of obtaining GLS without chemical and mechanical impurities.

2. Experimental set
The samples were made from rods of the spectral graphite, the total percentage of impurities in which was less than 0.01%. The graphite of this grade is used in electric arc standards of brightness. The specific resistance of the graphite used at room temperature is 11 Ohm µm; density is 1.7 g/cm³. The length of the samples was 80 mm, the initial diameter of the rod was 6 mm. The cylindrical groove with a diameter of 3 mm and a length of 20 mm was made in the middle of the rods. The geometry of the sample allowed to heat its central part with an electric current around 150 A to a temperature around 3 kK.

The samples were irradiated with a beam of protons with the energy of 50 keV in a vacuum chamber at a residual gas pressure of \(10^{-5}\) Pa. Under the fixed current of the beam, two series of samples with a proton fluence \(F_p\) of \(4 \times 10^{15}\) and \(2 \times 10^{16} \text{ cm}^{-2}\) were obtained. It should be noted, that the maximum proton flux was equal to the dose of irradiation that a sample would receive during five years in a geostationary orbit. The maximum duration of irradiation with a beam power density of 10 mW/cm² was 330 min. In graphite, the protons fully lose their initial energy of 50 keV on the length \(R_p \sim 1\) µm [7]. Protons that lost their energy could react with carbon atoms. After irradiation, the fraction of the reacted carbon atoms in the surface layer of the samples did not exceed \(\sim 0.1\%\).

Surface investigations of graphite samples before and after irradiation were carried out using a Veeco Dimension V scanning probe microscope and FEI Quanta 600 FEG scanning electron microscope.

After the irradiation, the samples were heated by electric current in argon at the pressure of 50 kPa. The heating scheme was similar to the one that was used in the study of processes during prolonged heating of unirradiated graphite samples [8–10].

3. Experimental results
The initial surface of the sample was a plateau, dotted with hills and hollows with a height of \(\sim 1\) µm (figure 1). The surface appearance changed qualitatively after the exposure to proton processing. Figure 2 presents scan of the sample surface irradiated by protons with fluence \(2 \times 10^{16} \text{ cm}^{-2}\). The periodic structure in the form of ridges, arranged in \(\approx 1\) µm steps, could be seen on this figure. Length of the ridges reached \(\sim 10\) µm, their height was \(\approx 2\) µm, i.e., it was comparable with length of the proton energy loss in graphite \(R_p\). Under the proton fluence of \(F_p = 4 \times 10^{15} \text{ cm}^{-2}\), this structure manifested itself less clearly. The areas with ridges were located in the form of islands on the initial surface. This allows assuming that the radiation dose had influence on the formation of the detected structures.

Figure 3 demonstrates scans of the samples obtained with the scanning electron microscope. At both values of the proton fluence, transparent GLS of different geometries are observed on the sample surface. The maximum size of the films along the surface of the sample, as well as
Figure 1. Scanning of the reference surface of the sample.

The ridges in figure 2, reached $\sim 10 \, \mu m$. Upcoming folding of the GLS film on the surface of the sample could be seen in figure 3(b).

Perhaps, figure 3(b) illustrates the initial stage of the formation of the structure in the form of ridges, which are shown in figure 2. The degree of transparency of GLS depends on the number of layers. Through one or two layers of GLS at the surface of the sample, distinct fragments of $\approx 0.2 \, \mu m$ in size are clearly visible. If the number of such layers reaches 4 [the lower part of figure 3(b)], then the transparency of the film significantly decreases. From the picture of superposition of film layers on each other, which is visible in figure 3(b), it can be concluded that its thickness does not exceed $\sim 0.1 \, \mu m$.

The appearance of the structures formed during the proton irradiation of graphite is similar to the GLS, produced by the thermal decomposition of silicon carbide. If this process is carried out in an argon at atmospheric pressure, the surface roughness decreases, and graphene films with a length of up to 50 $\mu m$ are obtained with distances between them $\approx 2 \, \mu m$ [11]. Externally, the graphene samples described in [11] are quite similar to the structures shown in figure 2.
Figure 2. Surface of graphite after proton irradiation with $F_p = 2 \times 10^{16} \text{ cm}^{-2}$.

Irradiated samples were heated by a fixed current for $\approx 10 \text{ min}$ at a temperature about 3 kK. During the exposure, a monotonous increase in the temperature of the sample and the voltage drop on it took place. The increase in the temperature of the sample and its resistance at a fixed current was probably due to solid-phase transformations in graphite. A similar change in the temperature of unirradiated samples is described in works [8–10]. In these studies it was shown that a prolonged holding ($\approx 10^2 \text{ min}$) with the fixed current and starting temperature of the sample above 2.5 kK leads to a gradual increase in its temperature and voltage drop on it. Moreover, the growth rate of the sample temperature at a fixed current increased with the increase of initial temperature. Comparison of the results of experiments on heating by electric current of samples irradiated and not irradiated by protons showed, that at the same initial temperature, the rate of its growth for irradiated samples is approximately twice as high. This may indicate that solid-state transformations in irradiated samples occur not only at the surface, but also at the depth of the sample.
Figure 3. Scans of graphite surface obtained by electron microscope for $F_p = 2 \times 10^{16}$ (a) and $4 \times 10^{15}$ cm$^{-2}$ (b).

Figure 4. Scan of the anode surface.

It can be noted, that ridges, similar to those, shown in figure 2, were observed in work [12] on the image of the unirradiated sample surface, that recorded by scanning probe microscope. This sample was held at the fixed current for 70 min at argon pressure of 34 kPa. The initial
Figure 5. Scan of the cathode surface.

Temperature of the sample was 2.78 kK, the final temperature was 3.08 kK. The height of these ridges ($\approx 1 \mu m$) was somewhat less than in the ridges in figure 2, and they were located like islands on the original surface. The appearance of the surface approximately corresponded to the surface of the samples, which were exposed to protons with the fluence of $4 \times 10^{15} \text{ cm}^{-2}$.

If the temperature of graphite exceeded about 3.3 kK, the sample was destroyed, and the arc discharge was ignited. The main properties of the arc, which appeared after the sample destruction, were described in our work [12]. Figure 4 shows a scan of the surface of the anode part of the sample, which was irradiated with protons with fluence of $4 \times 10^{15} \text{ cm}^{-2}$. The arc with a current of 140 A burned for $\approx 5$ s. The argon pressure was 52 kPa, the arc voltage was about 20 V, and the anode temperature was 3.3–3.4 kK. As can be seen in figure 4, after the arc GLS, which are similar to those shown in figures 2 and 3, were preserved on the sample surface. After the arc action, GLS fitted tightly together and spread along the surface. At the cathode part of the sample (figure 5), GLS was not recorded, but carbon filaments with a diameter of 20–170 nm were observed. It can be noted that similar filamentary carbon structures were observed in our experiments on the surface of the cathodes of the arc that appeared after the destruction of unirradiated graphite samples. In our experiments, the maximum cathode temperature reached 3.7 kK [12].

4. Conclusion
The presented results demonstrate that treatment of graphite with protons of energy 50 keV led to the formation of super-pure thin-film graphite-like structures on its surface. An increase in the proton fluence from $4 \times 10^{15}$ to $2 \times 10^{16} \text{ cm}^{-2}$ caused more intensive growth of these structures.
The discovered structures survived the heating to the temperature of 3.4 kK. To determine the nature of these structures and recognize their properties, further research is needed, primarily with the help of Raman spectroscopy [13]. The surface treatment of graphite by protons has ample opportunities to optimization of the expose process due to possible alteration in their energy and radiation dose. Apparently, it is of interest to irradiate graphite with high-energy deuteron fluxes.

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