Production of the thin carbon films using a Plasma Focus Installation

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Abstract. In the paper, the possibility of obtaining thin carbon (C) films on glass substrates using the Plasma focus installation is considered. The films were sprayed through a slit diaphragm made of graphite under the action of nitrogen plasma. The obtained films were inhomogeneous, which is due to the non-uniform energy distribution in the plasma jet. The measured transmission spectra and temperature dependences of the surface electrical resistivity (in the temperature range 78-300K) indicate the cluster formation of films on glass substrates. At 300K, the resistance of the films with is from 10^5 to 10^7 Ohms.

1. Introduction
The plasma focus devices are used to produce high-temperature plasma [1]. High temperatures make it possible to obtain nanosized particles of any refractory materials [2]. When particles are deposited on substrates, nanofilms are formed that have a number of properties different from those of materials of macroscopic dimensions [3]. A number of techniques are known that allow to obtain such films [4, 5]. However, after the deposition of films, they are almost always subjected to thermal or other treatment in order to improve their parameters, which requires additional energy and material costs. Therefore, the search for new methods of film production remains relevant at the present time.

The aim of the work was to obtain thin carbon films on glass substrates using a Plasma focus type installation.

2. Experimental technique
Deposition of carbon films was carried out on the PF-5M Mather type installation (IMET RAS). The stored energy in the capacitor bank of the unit was ~ 2 kJ. The duration of the plasma pulse was ~50 ns. The working gas was nitrogen (N2) at a vacuum chamber pressure of ~ 1 Torr. The central electrode of the anode assembly was made of stainless steel Fe-18%Cr-10%Ni-Ti, the cathode was made of copper. The plasma energy at the installation axis was measured by a copper calorimeter. The dependence of the integral energy density in the nitrogen plasma jet on the distance to the anode of the installation is shown in figure 1.
Figure 1. The energy density in the nitrogen plasma jet as a function of the distance to the anode of the PF installation.

The deposition of carbon films on glass substrates was carried out through a slit nozzle made of graphite according to the scheme shown in figure 2. The sputtering regime was chosen so that at a given energy density in a plasma jet (figure 1) and the width of the slit (d = 0.5-2 mm), there were no mechanical damages on the surface of the glass plates and thin film was deposited on it. Graphite plates had a size of 2×10×20 mm. The height of the cone of the slit diaphragm (h) was ~8 mm.

Figure 2. Scheme of deposition of carbon films on glass substrates: 1 - copper cathode; 2 - anode (stainless steel Fe-18%Cr-10%Ni-Ti); 3 - slit diaphragm from graphite plates; 4 - glass plate; 5 - sample holder; x - the distance from the anode to the slit diaphragm; h - height of the slit diaphragm cone; d - the width of the diaphragm slit.

Glass plates had a size ~ 20x20 mm at a thickness of 1.5 mm. Before the deposition of films, the glass plates were washed in distilled water and was degreased in ethyl alcohol. Deposition of films on glass substrates was performed at an initial temperature of ~ 300K. The structure of the C films was studied using a NEOPHOT microscope. The transmission spectra of C films were measured by SF-14 spectrophotometer at 300K. The resistance of the film strip (figure 3) measured by two-probe method with a step of 1 mm by the method [7]. Measurement of surface resistance of the films by four-probe method in the temperature range 78 – 300K was carried out in a nitrogen cryostat according to the Valdes method [8].

3. Results
Figure 3 shows a typical carbon strip deposited on a glass substrate through a slit diaphragm. It can be seen that the distribution of carbon along the strip is inhomogeneous. This feature is associated with the non-uniform distribution of energy in the plasma jet, in the central region of which the energy
density and temperature are higher. Homogeneity of the film was determined by measuring the electrical resistance along a strip of 14 mm length and ~2 mm width (figure 4).

**Figure 3.** A glass plate with a thin carbon film sputtered through the slit diaphragm when exposed to a nitrogen plasma: the number of plasma pulses is 10; the energy density is 0.4 J/cm². The width of the diaphragm slit is 2 mm. The distance from the anode to the slit diaphragm is 40 mm.

**Figure 4.** Distribution of electrical resistance along the carbon film (figure 3).

It is seen from the dependence $R(x)$ (figure 4) that the film C is very inhomogeneous, the resistance value along the film varies by two orders of magnitude from $10^5$ to $10^7$ Ohms. Figure 5 shows microstructure of the deposition area in the center of the film and on the periphery. It is seen that the density of C particles in the center of the film is significantly higher than at the edge, where fractal structures of carbon particles in the form of long and short branched chains are visible. The length of carbon chains varies from units to tens of microns.

**Figure 5** Structure of carbon films in the center (a) and at the edge (b) of the deposition area (see figure 3).
Film resistance measurements in the temperature range 78-300K (the central region of the $R(x)$ curve in figure 4) showed that the conductivity of the films is nonlinear and is largely determined by the hopping conductivity of the current carriers (figure 6). Analysis of the temperature dependence of the films $R(T)$ shows that in the temperature range 78-150K it can be described by the expression of the form (1)

$$R = R_0 \cdot \exp(\frac{T}{T_0})^m$$

Here $T_0$ - is the energy parameter of hopping conductivity;
$T$ – current temperature;
$R_0$ – some initial resistance;
$m$ – a exponent that characterizes the hopping conductivity mechanism.

In our case, in the temperature range 78-150K, the dependence $R(T)$ can be described by expression (1) with exponent m=1/2, which for highly inhomogeneous media, which are obtained C films, points to the tunneling mechanism of hopping conductivity between small clusters with metal conductivity [6].

The presence of various chemical elements in C films was observed by a scanning microscope LEO 430i (Carl Zeiss, Germany) equipped with an x-ray microanalyzer ISYS300 (Cambridge, England) (figure 7). Elements were found in the films: Cu, Fe, Ni, Cr, which come from the anode unit of the installation. The presence of other impurities in the films is due to the chemical composition of the glass. Thus, C films obtained at the PF-5M are doped with a variety of chemical elements, and the formation of metal clusters based on: copper, iron, nickel and chromium is quite possible.
Optical transmission spectra of carbon films measured after different regimes of nitrogen plasma treatment are shown in figure 8. As can be seen, there are no noticeable absorption peaks in the transmission spectra of carbon films in the wavelength range of 0.35–1.0 μm. The shape of the spectra is smooth. In the wavelength range <350 nm, a strong absorption is observed, associated with the fundamental absorption of light in the band gap of the carbon film. The estimation of the optical slit width by extrapolation of the transmission curve to zero gives a value of about 3.9 eV, which indicates the amorphous structure of the films associated with the formation of clusters [9]. At low energy plasma densities, thin optical films C (curve 3) are obtained, which in their characteristics are close to pure carbon films [10].

Figure 8. Transmission spectra of carbon films: 1- energy density 0.2 J/cm², N = 10 imp.; 2 – 0.4 J/cm², N = 15 imp.; 3 – 0.1 J/cm², N = 15 imp.

4. Discussion
From the presented experimental results it follows that at low-energy PF type installations it is possible to coating of optical thin films of carbon. However, the films are very heterogeneous due to the peculiarities of the energy distribution in the plasma jet and doped with various chemical elements coming from the anode unit of the installation. The resistance of the films at 300 K varies within a wide range from $10^5$ to $10^7$ Ohms, which corresponds to a resistivity of $10^1$-$10^3$ Ohm·cm for a thickness of the skin layer of optical films <2 μm. It is close to the resistance of graphites of the PGE, GMZ, 30PG, etc. Electrophysical and optical properties of films are significantly determined by the formation of metal and carbon clusters arranged randomly relative to each other. The results of the
studies performed in this work are consistent with similar studies performed in [9, 10]. But in contrast to these works, we observed an increase in $R(T)$ in the temperature range 150-300K, the behavior of which can be explained by the presence of two types of clusters: carbon and metal. At low temperatures <150K, the effect of carbon clusters, which are characterized by semiconductor properties, is predominant. This is indicated by an exponential increase in resistance. In the high temperature range >200K, the contribution of metal clusters prevails; their conductivity decreases with increasing temperature. Similar dependences of $R(T)$ in this temperature range were observed in [11] in the study of carbon nanotube clusters. However, the formation of carbon nanotubes cluster in our case is doubtful and requires additional research.

5. Conclusions
The results of the research allow us to conclude that a thin carbon films can be deposited by plasma focus installations. However, during deposition of films using graphite nozzle, they are obtained inhomogeneous and have a large content of impurities that come from the anode unit of the installation. The presence of metal impurities (copper, iron, nickel and chromium) leads to the formation of metal clusters, which along with carbon clusters determine the electrical and optical properties of the films. The production of homogeneous films by PF installations is possible provided that the most intense homogeneous part is extracted in the plasma jet and the deposition region on the substrates is diaphragmed. Reduction of impurity concentration in the films can be achieved by selecting the anode and cathode material, as well as by choosing lower energy densities in the plasma jet. However, all these issues require further research.

Acknowledgements
In memoriam of our colleague, leading researcher Aleksandr Vladimirovich Dubrovskii.
The work was performed under state assignment No. 007-00129.18-00.

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