Optical and mechanical properties of fluorocarbon coatings formed in a matrix mode of deposition using an atmospheric pressure plasmatron

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Abstract. This paper is devoted to study of the formation of fluorocarbon coatings, which were obtained by using a low-frequency plasmatron of a low-temperature plasma at atmospheric pressure. The possibility of forming fluorocarbon coatings on silicon, and PET and polystyrene substrates is shown. The spectra of the UV and visible ranges were obtained, the width of the band gap of the obtained coatings was established by the Tauc method. The nanohardness of the obtained coatings was studied by the Oliver-Farr method.

The intensive development of modern electronic and optical devices requires new approaches and solutions in the field of their protection from the negative influence of the environment. The more important is the issue of protection of components, which include polymeric materials [1], subjected to degradation in conditions of high humidity and microbiological activity. The creation of thin protective coatings based on fluorocarbon minimizes the negative effect of an aggressive environment [2]. This can be achieved due to the qualities of carbon itself, in particular, the possibility of forming compensated valence bonds and a wide range of properties [3], as well as due to the chemical activity of fluorine [4]. The use of ion-plasma vacuum methods for obtaining carbon-containing coatings has proven itself over the past 30 years, however, at the same time, more and more attention has been paid to the use of gas discharges at atmospheric pressure to conduct deposition from the gas phase [5]. Due to the lack of the need to create and maintain a vacuum, the availability of equipment and ease of process control, these methods are already widely used for processing various materials [6–8]. Among the many types of gas discharges, the most promising is a low-frequency arc gas discharge of atmospheric pressure, as it is able to provide local formation of the required coating by low-temperature plasma with minimized environmental influence on the processes taking place [8]. For reproducible formation of carbon-containing coatings over the entire area of the substrate or product, it is necessary to choose the matrix mode of deposition: multipoint deposition from the gas phase with a fixed distance between points (figure 1).

In this work, we used an experimental setup consisting of a low-frequency plasma torch of a low-temperature plasma (LF plasmatron) operating at atmospheric pressure, mounted on a CNC machine for precise control of the geometric parameters of the formation process (figure 2).
This model has the ability to use multiple gas streams to form a coating with controlled concentrations of various gases (figure 3).

The formation of coatings was carried out according to the following technological parameters: used plasma-forming / transport gas (Ar), the plasmatron-substrate distance (15–24 mm), the deposition time (5–20 s), the distance between points (3–6 mm). The total gas flow was $7.1 \pm 0.1$ l/min. The formation was carried out on substrates of monocrystalline silicon, polyethylene terephthalate (PET) and polystyrene.

The study of the thickness of the obtained coatings was carried out on samples on a silicon substrate at several points: in the center of the coating, at the points of the triangle's vertices, and in the middle of one of the triangle hips. The study showed that the growth rate of fluorocarbon coatings significantly depends on the plasmatron-substrate distance and the time of deposition (figures 4 and 5). This is due to the increased energy input to the gas discharge between the plasma torch nozzle and the substrate on which the application was made. In addition, increased diffusion of gas particles from the plasma jet into the environment has an effect.

Absorption spectra were studied using a PhotoLab 6600 spectrophotometer (WTW, Germany). The study was conducted on PET substrates coated with fluorocarbon coatings. As can be seen from the above spectra, up to 310 nm fluorocarbon coatings have a different set of absorption peaks, which is associated with different chemical compositions of the coatings. In the visible range (380–740 nm), the coatings are almost transparent and have the same intensity of transmission of the visible range of light. At a distance of the plasmatron substrate 15–18 mm, the coating shows itself to be the most stable.
The thickness of the coatings obtained with a distance between the points of 3 mm.

The thickness of the coatings obtained with a distance between the points of 5 mm.

The forbidden zone was calculated using the Tauc method, which averaged $4.22 \pm 0.04$ eV. This band gap corresponds to the dielectric material. The influence of technological parameters on the width of the forbidden zone is insignificant.

The nanohardness was measured by using a Nanovea nanohardness meter (USA) according to the Oliver-Farr method [9]. Indentation was carried out with a load of 2.5 mN on the indenter. The load on the indenter was chosen minimal, but ensuring the reliability of measurements. The exposure time of the indenter at maximum load was 20 seconds, the speed of loading and unloading - 5 mN per minute. As a result of the measurements, load-unloading curves were obtained (figure 7) and the mechanical characteristics of the surface were calculated: the nanohardness of fluorocarbon coatings varied from 0.314 to 0.447 GPa depending on the technological parameters. The plasmatron-substrate distance and the distance between the points of application had the greatest effect, since they had the most significant effect on the coating density, as well as on the resulting relief. The modulus of elasticity of Young showed similar dynamics and ranged from 4.94 to 6.1 GPa.
As a result of the work, the possibility of forming carbon and fluorocarbon coatings in a matrix deposition mode was demonstrated. It was shown that the thickness of carbon coatings depends linearly on the plasmatron-substrate distance, the deposition time and the distance between the vertices of an equilateral triangle. The photoabsorption spectra were determined and the band gap was established by the Tauc method for fluorocarbon coatings, which was $4.22 \pm 0.04$ eV. The mechanical properties of the coatings were tested and the nanohardness values of the Young’s modulus of elasticity of the coated surface were obtained.

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