

## INFLUENCE OF DIAMOND-LIKE STRUCTURE OF NANOSIZED LAYERS ON THEIR ELECTRICAL CONDUCTIVITY

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**Abstract.** DLCs films of polyimide as substrates with a thickness of 200 micrometers obtained by magnetron sputtering at small (30 and 90 s) and large (of the order of tenths minutes and) deposition times were studied. In addition, the structure and properties of the polyimide substrate were studied for reference. Methods of X-ray diffraction analysis (XRD), atomic force microscopy (AFM), absorption and transmission of light in the visible and IR ranges, as well as Raman spectroscopy were used to study the structure. Electrical resistance and current-voltage characteristics (IVs) were studied in the temperature range from 50 to 300 K.

**Keywords:** thin films, spectroscopy and microscopy, electric transport mechanisms, amorphous semiconductor

**Introduction.** Diamond-like coatings (DLC) may have some properties similar to diamond, such as high mechanical strength and hardness, chemical inertia, optical transparency, etc. In the electrical sense, these films the most often looks like amorphous semiconductor or a dielectric. They usually consist of a metastable form of amorphous carbon containing a significant proportion of  $sp^3$  bonds, the presence of which gives the listed properties at the DLC. At the same time, due to some technological peculiarities of the obtained the DLC films, they may contain other phases, with  $sp^2$  bonds, in particular. As a result, their final properties are determined by the phase composition, including the ratio of  $sp^3$  to  $sp^2$  bonds. If the  $sp^3$  configuration is prevailed, four  $\sigma$ -bonds with neighboring carbon atoms are formed. If the  $sp^2$  configuration predominates, three  $sp^2$   $\sigma$ -bonds and one weak  $\pi$ -bond are formed. As a consequence, in the electrical sense, the DLC looks like an amorphous coating with semiconducting or insulating properties [1,2].

The combination of high mechanical strength and chemical inertia with the necessary electrical characteristics makes the DLC coatings useful for gas electronic multiplier (GEM) detector. The latter are a type of gas ionization detector used in nuclear and particle physics, as well as for detection of radiation. The GEM uses such electrical characteristics of the DLC as high electrical breakdown voltages (to suppress breakdowns in the working gas) and at the same time maintaining some electrical conductivity (to use the DLC coating as an electrode). Since the combination of such electrical properties of the DLC depends on the  $sp^3/sp^2$  ratio, the purpose of this work was to study the relationship between the structure of DLC and mechanisms of electron transport through them [3,4].

X-ray diffraction analysis, Figure 1, shows some amplifying of reflexes in polyimide substrate (XRD spectra 3 and 4) and DLC film on polyimide (XRD spectra 1 and 2), that indicates an increase in the proportion of  $sp^2$  hybridization. Lines  $2\theta = 23.8^\circ, 29^\circ, 39.45^\circ$  and  $43.25^\circ$  at XRD spectra indicate the presence of the crystalline phase nuclei.

Figure 2, a, shows the morphology of the film with a shortest (30 seconds) deposition time, and Figure 2, b shows the same for about 30 minutes when a DLC thickness was about of 200 nm. The roughness coefficients  $R_a$  and  $R_q$  are 0,7 and 0,4 nm for the films shown in Figure 2, a, and 13,2 and 5,7 nm for Figure 2, b, respectively. The presence of sharp peaks in Figure 2, b indicates the combined mechanism of thin film growth, namely the Stransky-Krastanov layer-by-layer and islands-like mechanisms.

The DLC coatings lead to changes in the reflection spectra of the initial polymer substrate (Fig. 3). In particular, for long deposition times we can see in Fig. 3,a the masking of the maxima which are characteristic for polyimide films. At the same time, for the mostly thin DLC coatings prepared at low deposition times of 30 and 90 s, we observe in Fig. 3,b the reflection spectra which

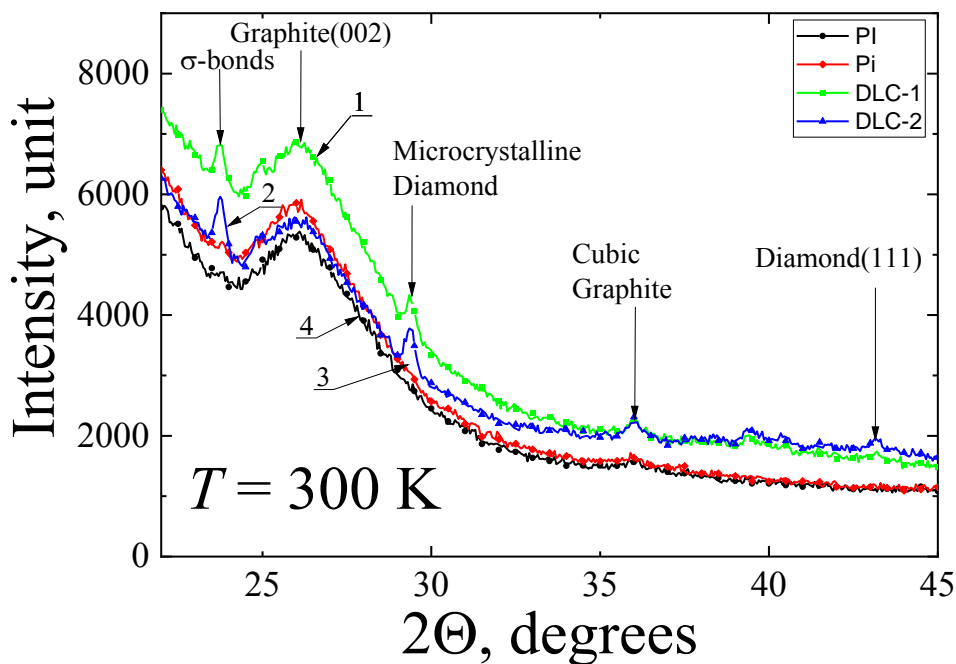


Figure 1 – XRD spectra of polyimide substrate (1,2) and DLC coatings (3,4)

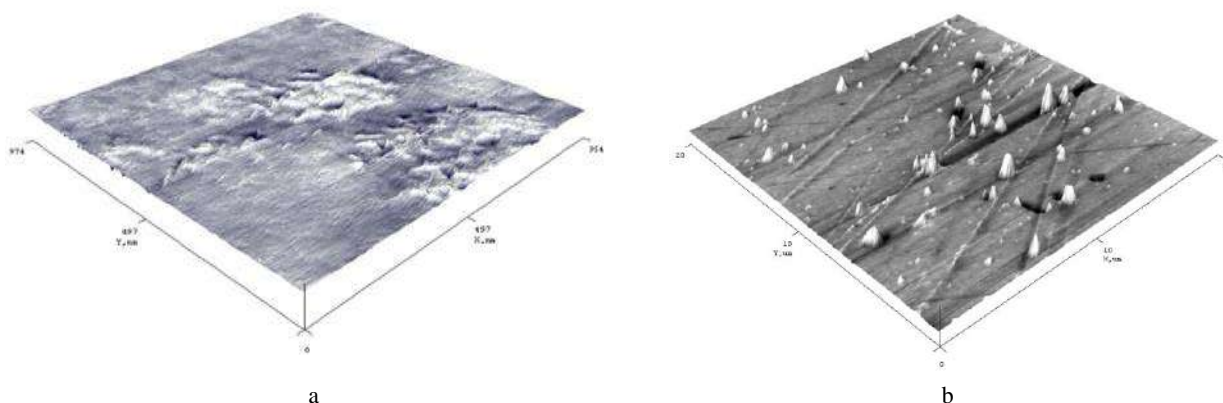


Figure 2 – AFM patterns of DLC coatings for the low (a) and high (b) deposition times

practically repeat those for polyimide substrates. This effect can be explained by island-like growth of DLC coatings for low-time deposition giving non-continuous coatings. Raman spectra in Fig. 3c show a superposition of  $D = 1389 \text{ cm}^{-1}$  and  $G = 1564 \text{ cm}^{-1}$  peaks, which correspond to vibrations of aromatic rings with the presence of C-C-bond with  $sp^2$  hybridization (graphite phase) and vibrations of C-C-bond with  $sp^3$  hybridization (almazopobodnaya phase) accordingly. It is most likely that the used deposition method results in *a*-C type DLC growth.

As is seen in Fig. 4,a, at  $U < 20 \text{ V}$ , the I-V characteristics are linear, that indicates the formation of ohmic contacts and lack of overheating. At higher bias voltages, Figure 4b, the I-V characteristic becomes non-linear, that can be explained by either the non-ohmic behavior of the contact metal-PI or its overheating when electric current flows through it at high voltages. Note that after every I-V measurement in Figure 4, a and b, the electrical resistance, measured as  $R = (U/I)$  at  $U < 20 \text{ V}$ ,

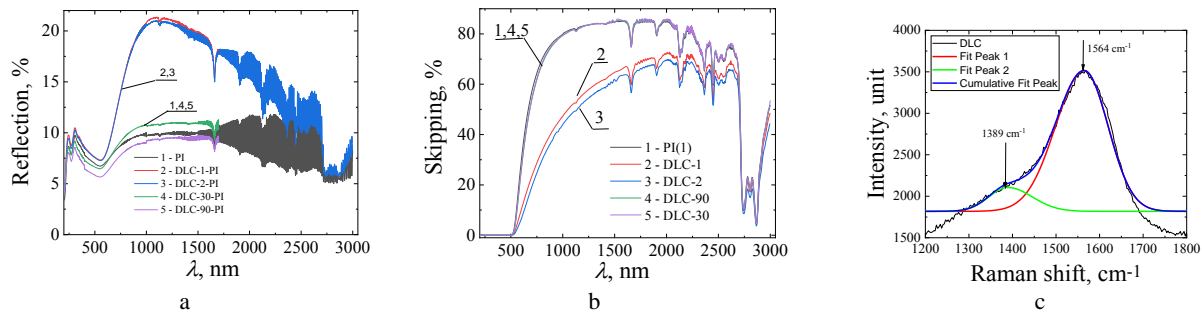
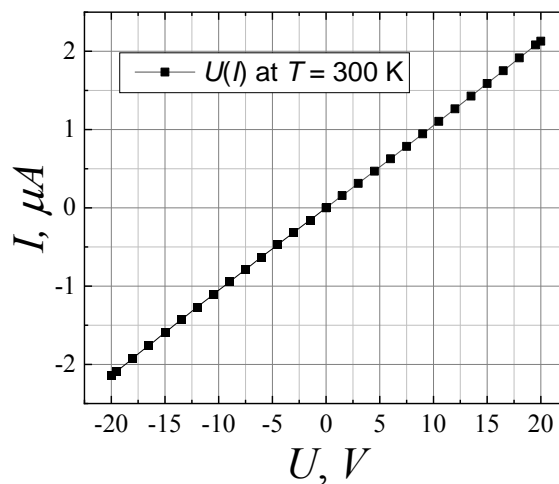
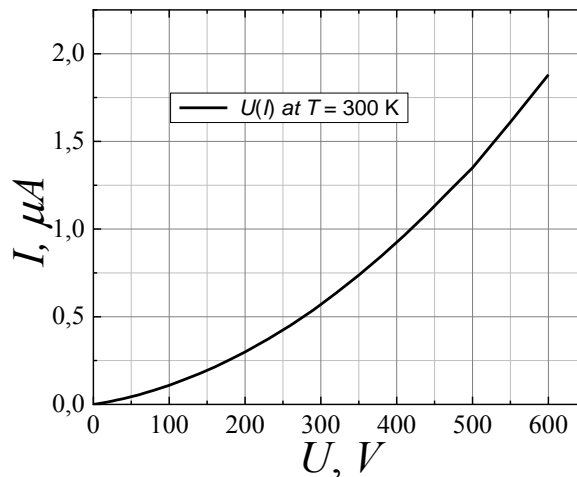


Figure 3 – Reflection (a), transmission (b) spectra and AFM patterns of DLC coatings on polyimide

increased probably due to “burning out” of the film areas with  $sp^2$  bonds under application of bias voltage to the DLC film.



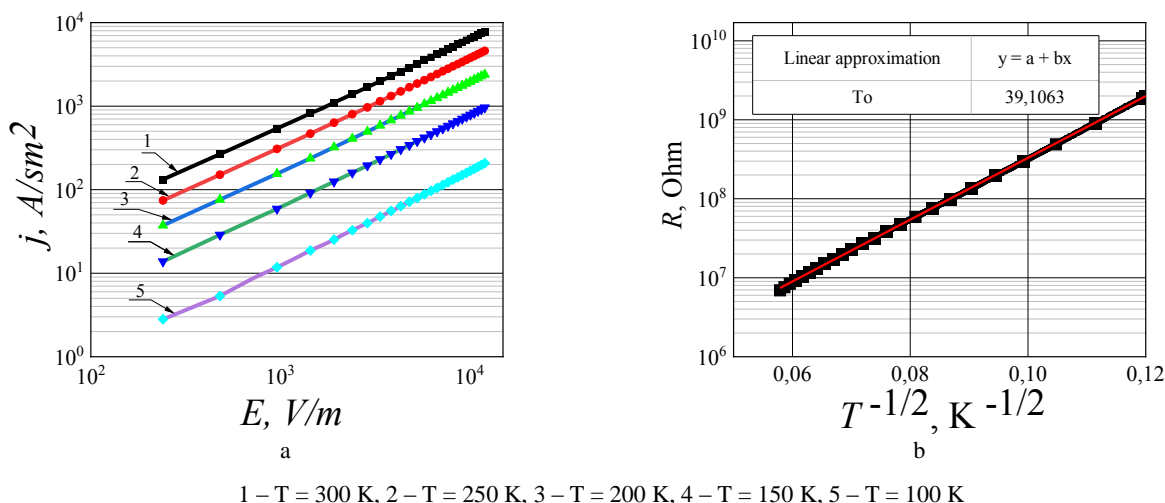
a



b

Figure 4 – Room temperature I-V characteristics of DLC coatings at low (a) and high (b) bias voltages applied to the sample

The  $J(E)$  dependences of the DLC coatings at different temperatures  $T$  in Fig. 5,a show linear behavior. At lower temperatures in the studied range of bias voltages  $U < 20$  V, a weak nonlinearity is observed on the sample studied, which can be caused by its overheating by the electric current. The plotting of  $R(T)$  curves in Mott coordinates  $\lg R - (1/T)^\alpha$  in Fig. 5,b gives straight line with an exponent  $\alpha = -0.5$ . This linearization indicates to the hopping mechanism of conductivity with


 Figure 4 –I-Vs (a) and electrical resistance  $R$  for temperatures  $50 < T < 300$  K in Mott coordinates

variable range hopping by localized states in amorphous DLC layers described by the Shklovsky-Efros model [2]. The localization radius for electron wave functions at the localized centers (traps) estimated from this model is close to 7,8 nm.

**Conclusion.** The study of diamond-like films has been carried out. X-ray diffraction analysis observed the features of nucleation of the diamond-like crystalline phase in the films studied. Atomic force microscopy shows the difference between samples with short and long deposition times in terms of roughness coefficients and characteristic «peaks» by heights. The deposited DLS layers in the entire thickness range studied have a high electrical resistance (from  $10^7$  to  $10^{10}$  Ohm), which depend on structure of the samples. At low applied bias voltages  $U < 20$  V, the I-V characteristics are linear that indicates the formation of ohmic contact. At higher bias voltages, the non-ohmic behavior was observed. This nonlinearity in I–V characteristics can be caused both by the properties of the metal–DLC contact and by the overheating of the samples by the current flowing through it. The temperature dependences of the electrical resistance  $R(T)$  of the DLC layers are characterized by negative temperature coefficient of resistance, which indicates the semiconducting behavior of the DLC layers. Carriers transport in DLC layers is provided for the hopping mechanism described by the Shklovsky-Efros model. The deposition of DLC on PI substrate leads to the change in the reflection spectra of the initial polyimide, which, in particular, manifests itself in the masking of the maxima characteristic for PI films after long times deposition.

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### References

1. J. Robertson, "Diamond-like amorphous carbon," *Mater. Sci. Eng. R Rep.*, vol. 37, no. 4–6, pp. 129–281, May 2002, doi: 10.1016/S0927-796X(02)00005-0.
2. B. I. Shklovskii and A. L. Efros, "Dependence of Hopping Conduction on the Impurity Concentration and Strain in the Crystal," in *Electronic Properties of Doped Semiconductors*, B. I. Shklovskii and A. L. Efros, Eds. Berlin, Heidelberg: Springer, 1984, pp. 137–154. doi: 10.1007/978-3-662-02403-4\_6.
3. A. Breskin et al., "Ion-induced effects in GEM and GEM/MHSP gaseous photomultipliers for the UV and the visible spectral range," *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.*, vol. 553, no. 1–2, pp. 46–52, Nov. 2005, doi: 10.1016/j.nima.2005.08.005.
4. I. Vankov and S. E. Vasiliev, "Thick GEM with resistive coating", pp. 1274–1281, 2013, doi: PACS: 29.40.Cs.