

# Atomic structure of carbon clusters laser-produced diamond-like carbon films

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## ABSTRACT

Structural state of thin diamond-like carbon films has been studied by high-resolution transmission microscopy. Diamond-like carbon films have been obtained by vapor-gas phase carbon concentration on glass substrates, using defocused NTS 300 laser beam for graphite targets evaporation in vacuum. Defocused laser beam provided an area of 3 mm in diameter on the target for carbon direct evaporation. It has been established that diffraction of electrons identifies diamond reflections (111) and (220), and this corresponds to interplane spacing  $d_{111} = 0.207$  nm,  $d_{220} = 0.119$  nm of the diamond lattice. The obtained values of interplanar distances are close to the values of interplanar distances of carbon macroscopic crystals with  $d_{111} = 0.205$  nm and  $d_{220} = 0.125$  nm. The research of the film atomic structure shows that sp<sup>3</sup>-bonding generally participate in assembling carbon atoms into diamond clusters having the size less than 1 nm. The ratio of graphite clusters formed by sp<sup>2</sup>-bonds within the structure of diamond-like carbon films is negligible. In spite of the pronounced cluster pattern of the structure, the film is not an analogue of the polycrystalline one with graded junction from one crystalline domain to another observed. As distinguished from polycrystals, there is no structure stepwise changing on the mating clusters boundaries. It is shown that clusters are linked with each other into homogeneous cluster structure by sp<sup>3</sup>- and sp<sup>2</sup>-bonds. These bonds are well-identified in the diamond-like carbon film structure, as the length of sp<sup>2</sup>-bonds exceeds considerably the length of sp<sup>3</sup>- bonds. Carbon film properties are determined by diamond clusters due to domination of clusters with tetragonal diamond lattice, for instance, the film is a good dielectric.

## 1. Introduction

The first studies of thin carbon films demonstrated their complex structure with crystalline and amorphous fractions included. The structure was seen as a mixture of amorphous and crystalline phases where crystalline structure was that of a diamond [1,2]. Carbon exists in two crystalline modifications – diamond and graphite with sp<sup>3</sup>- and sp<sup>2</sup>-bonds, respectively. Combination of these two bond types makes up carbon films, with some amount of sp<sup>1</sup>-bond possible [3]. Relative ratio of sp<sup>3</sup> and sp<sup>2</sup>-bonds can be regulated by altering deposition conditions, for instance, by increasing or decreasing carbon ions energy while depositing on the substrate. This makes it possible to obtain films with very low electrical conductivity, high hardness and high optical transparency, high wear-resistance qualities and low friction ratio. The film properties tend to reach values as those characteristics to diamond when the amount of sp<sup>3</sup>- bonds is sufficient. This kind of carbon films are called «diamond-like carbon (DLC)». An in-depth survey of carbon films

properties and structure is provided [3–7].

Experimental results make it possible to separate a vast group of amorphous carbon films (denoted as a-C) with no visible crystalline film structure as their major structural property. These films demonstrate a wide range of varying proportions of sp<sup>3</sup>/sp<sup>2</sup> bonds from greater portion of sp<sup>2</sup>-bonds to sp<sup>3</sup>-bonds domination. Investigation of neutron scattering shows that the structure of the a-C films synthesized under certain conditions is mainly a tetrahedral network of carbon atoms, that is typical to diamond lattice bonds [8,9]. It has been called tetrahedrally bonded amorphous carbon - ta-C to structurally distinguish it from other a-C forms [10]. This a-C tetrahedral form has the density close to that of a diamond, high hardness and may prove to be a significant novel carbon form.

Thin carbon films obtained from tetrahedrally bonded amorphous carbon have high sp<sup>3</sup>-bonds content up to 87% [11–14]. It is just the high sp<sup>3</sup>-bonds content in ta-C films that provides high hardness, chemical inertness, low friction ratio, thermal stability and high electric

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resistance [6,15–17]. That means that ta-C films unique properties depend substantially on  $sp^3$ -bonds content [13]. For example, such characteristics as density and Young's modulus are directly determined by  $sp^3$  and  $sp^2$  bond proportions. Measuring these quantities is an indirect method of defining a diamond bond share that is used to study the film graphitizing processes [3,10,18–20].

Diverse methods were applied to research ta-C thin films structure [10,12,21,22]. X-ray, electron- and neutron diffraction methods [8,9,18] have proved that  $sp^3$ -bonded carbon is dominant in these films. The structure of carbon films synthesized by diverse methods is presented [23,24] with the results shown in a triple phase diagram that is based upon three phases of these films formation – diamond ( $sp^3$ -bonds), graphite ( $sp^2$ -bonds) and hydrogen. Hydrogen in such films can be linked with carbon by  $sp^3$ -bond to substantially result in carbon film properties. Metallic additives to the structure of carbon materials also have great influence upon their properties. Metallic inclusions change the character of the interatomic links and causes changes in their optical, electrical and mechanical properties of carbon films [25–27].

Defining amorphous carbon structure has still been a challenge. Experimental research has made it possible to develop structural models that account for thin carbon films properties. The dominant model presents the film as a tightly linked 3-D network of carbon tetrahedral groups with  $sp^3$ -bonds, with small graphite clusters embedded. Tetrahedrally-coordinated carbon atoms ( $sp^3$ -hybrids) make up 3-D scaffold providing high hardness to ta-C films.  $sp^2$ -bonds-grown graphite clusters determine generally optical properties, such as optically-forbidden zone. It has been established by measuring optically-forbidden zone width in carbon films that the optical band gap width changes roughly in inverse proportion to the graphite cluster size [28]. Considering this ratio, it was found that diamond-like carbon films mainly consist of disordered graphite clusters with sizes up to 1.5 nm.

The analysis shows that graphite clusters are the major constituent of diamond-like carbon films where the diamond element of the structure serves as environment (matrix) with graphite clusters placed into it. It is stated that even in films with  $sp^3$ -bonds fraction of 80% and more, the structural state of films is determined by graphite clusters. Thus, the structural state of carbon diamond-like films with high percentage of  $sp^3$ -bonds is still not clear. The paper covers research of the structural state of diamond-like carbon films with high percentage of  $sp^3$ -bonds obtained by laser-beam evaporation of carbon targets and by carbon aggregation from the vapor-gas phase onto the substrate.

## 2. Methods of obtaining carbon films

To get diamond-like carbon films we used graphite targets direct vaporization technique with 1064 nm-wavelength laser beam from NTS300 neodymium laser, and with subsequent carbon condensation on amorphous silicate-glass substrate. The structural state of diamond-like carbon films depends on the mode of carbon atoms condensing upon the substrate. Changing the mode makes it possible to control the film properties within a wide range of values. It is known that laser evaporation brings mostly  $sp^3$ -bonds in condensed carbon.

A defocused laser beam was introduced into a vacuum set vacuum chamber (residual pressure not less than  $10^{-5}$  Torr), with graphite targets and silicate-glass substrates being there. The defocused laser beam, with its energy changing from 1.1 to 5 J, made a spot of about 3 mm in diameter on the graphite target having 5 mm diameter and about 2 mm thickness. Exposure time was approximately 5 min. The obtained flux of carbon being vaporized was plating upon glass substrates placed about 10 cm from the target and at the angle of about 30 grades to the vapor-gas torch axis, thus forming carbon film.

The structure of diamond-like carbon films was studied with the use of high-resolution transmission electron microscopy (transmission electron microscope Philips CM-30) at Centre for Research in Materials and Technologies (Tomsk State University).

## 3. Research results

The typical structure of a diamond-like carbon films obtained by transmission electron microscopy and also the electron diffraction pattern of this fragment are shown in Fig. 1. Heterogeneous grain structure of the film on a nanoscale is evident. The grain size is in the range of about 1 nm. Examination of the dark-field image indicates that the contrast emerging in the bright-field image is completely similar to that of the dark-field image. It proves a high degree of the film homogeneity at macroscopic scale and dominating of one structural element. The film's every local area makes an equal contribution into diffraction rings intensity.

The electron diffraction pattern (insert in Fig. 1) shows diffraction rings strongly widened, but distinct to identify, to prove crystalline structure of the film material. We must note that we applied the diaphragm with diameter 1  $\mu\text{m}$  for obtaining the diffraction pattern. That means that electron beam overlays the whole of the image. Part of it is shown in Fig. 1.

The ring-shaped diffraction pattern illustrate the grains mutual disorientation, i.e. non-monocrystalline film structure. The rings radial blurring relates to the grain small size. Interpretation of the electron diffraction pattern shows that the film material has diamond lattice, and the rings correspond to surface diffraction (111) and (220). Interplane spaces have values  $d_{111} = 0.207$  nm,  $d_{220} = 0.119$  nm. The values obtained in the study are close to the tabulated values of diamond macroscopic crystals.

High-resolution electron microscopy was applied to investigate the film thin structure. Fig. 2 shows a film microphotography with atomic resolution. Substantial close-ups demonstrate that the key structural element of the film are clusters – groups of atoms having the size considerably less than 1 nm. Fig. 2 illustrates atoms of clusters with crystallographically-favorable orientation as bright points, whereas dark fields relate to clusters with unfavorable focusing conditions.

Individual clusters can be selected in the film structure and their crystal structure subjected to an analysis. Direct observation of atoms provides an opportunity not only to examine the film atomic structure, but also to get numerical characteristics, such as individual clusters size, interatomic and interplane spacing.

The main mass of clusters in the film has the size less than 0.5 nm. The largest discovered clusters have the size not more than 1 nm. Clusters of such size have a well-formed crystal lattice and may be classified as crystals. Fig. 3 presents images of such crystals with typical (a, b) diamond (cubic) crystalline structure that have been oriented

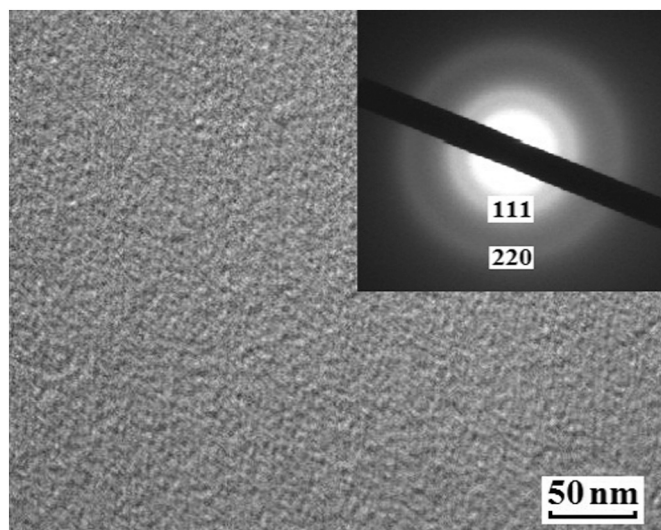


Fig. 1. Bright-field electron microscopy image of a carbon film.

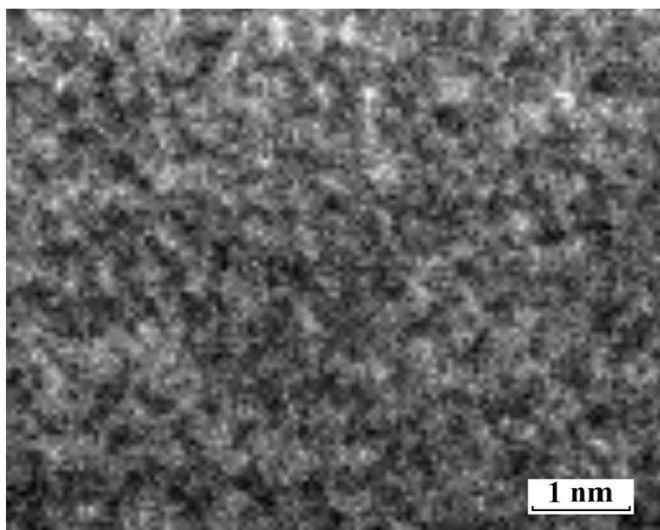


Fig. 2. Carbon film cluster structure.

towards electron beam by planes (100) and (110) (Fig. 3a, b), and graphite crystals oriented by plane (0001) (Fig. 3c, d).

The crystal presented in Fig. 3a is oriented so that crystallographic plane (100) is parallel to the imaging plane. Square structure of this plane that is typical of diamond, is well seen. High accuracy measurements showed that angles make up  $90^\circ$ , and interplane distances are equal to  $d_{220} = 0.206$  nm and  $d_{400} = 0.09$  nm. The lattice parameter is 0.36 nm. These values correspond to the massive diamond. The crystal has a regular cuboctahedron form relevant to the crystal equilibrium faceting by planes (110) and (111). The crystal is equiaxed having the size 0.75 nm. Another crystal oriented by the plane (110) is shown in Fig. 3b. Rows of atoms in the crystal make up an angle of  $109^\circ$ , and this is a proof of the diamond lattice presence in the crystal. The crystal has an elongated form and the size of  $0.6 \times 0.8$  nm.

Graphite crystals can be also found in the thin film structure. Their amount is very small. Fig. 1 shows about five graphite crystals oriented

to expose their lattice for visual observation. More than 100 diamond crystals with the size of 0.5 nm have been discovered in this fragment. That is why graphite renders no reflections in the electron diffraction pattern. Fig. 3c and d show two graphite crystals. The crystals are oriented by the basic plane {0001}, hexagonal arrangement of atoms is evident. Rows of atoms correspond to crystallographic planes of the  $\{1\bar{1}00\}$  type that are perpendicular to the imaging. Measurements of the interplane distances  $d_1$ ,  $d_2$ ,  $d_3$  for the three differently-oriented planes showed that two of the values are equal to the tabulated meanings  $d_1 = d_2 = 0.12$  nm for graphite, and the third one is  $d_3 = 0.11$  nm being 10% less. Such changes of interplane spacing indicate presence of directed stresses resulting in the lattice distortion.

The major part of the carbon lattice is presented by groups of atoms (clusters) with  $sp^3$ -bonds of tetrahedral configuration. These clusters constitute the crystalline lattice, even though a number of atoms to make it up are small. Interatomic distances and interlink angles in the clusters mostly correspond to these properties in the mass lattice. Some distortion of these links is related mostly to the atoms on the clusters surface.

Fig. 4 illustrates examples of typical clusters that make up the carbon film structure. A group of three interrelated diamond clusters is shown in Fig. 4a. Atoms in the clusters are placed in correct tetrahedral positions, interatomic distances correlate with  $sp^3$ -bonds. The clusters are oriented in the way so as to provide that the plane (100) and the imaging plane coincide. It is well observed that the lattice is regular, distances between the clusters atoms are equal and they make up a correct square-shaped lattice. Cluster 1 and cluster 2 are linked together via neighboring atoms, the clusters size in cross-section is  $0.13 \times 0.25$  nm and  $0.25 \times 0.25$  nm respectively. Cluster 2 is linked to the remaining matrix via  $sp^2$ -bonds having greater interatomic distances. Cluster 3 is a small group of atoms linked with cluster 1 via  $sp^3$ -bond. Thus, the diamond-like carbon films structure defined as amorphous, is a complex of carbon atoms with  $sp^3$ - and  $sp^2$ -bonds providing transition in between the clusters.

#### 4. Discussion of the results

Measurements of the interplane distances made by the electron diffraction pattern from the thin film showed their values of  $d_{111} =$

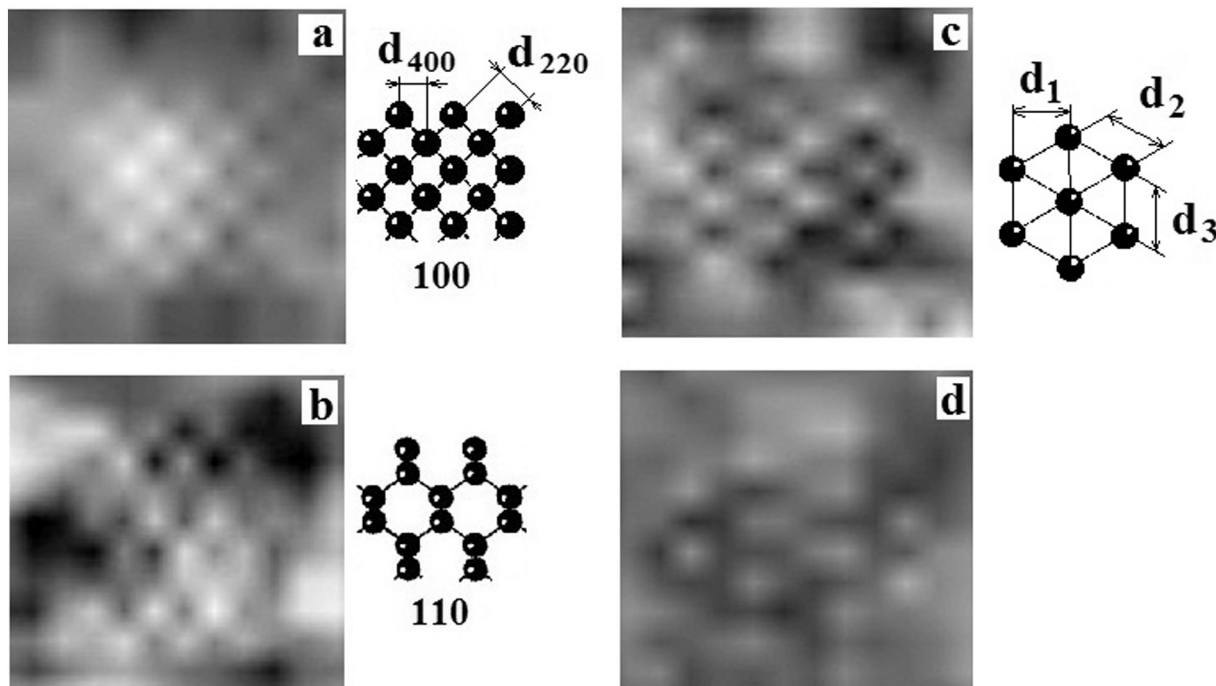


Fig. 3. Crystalline structure of the diamond (a, b) and graphite (c, d) clusters.



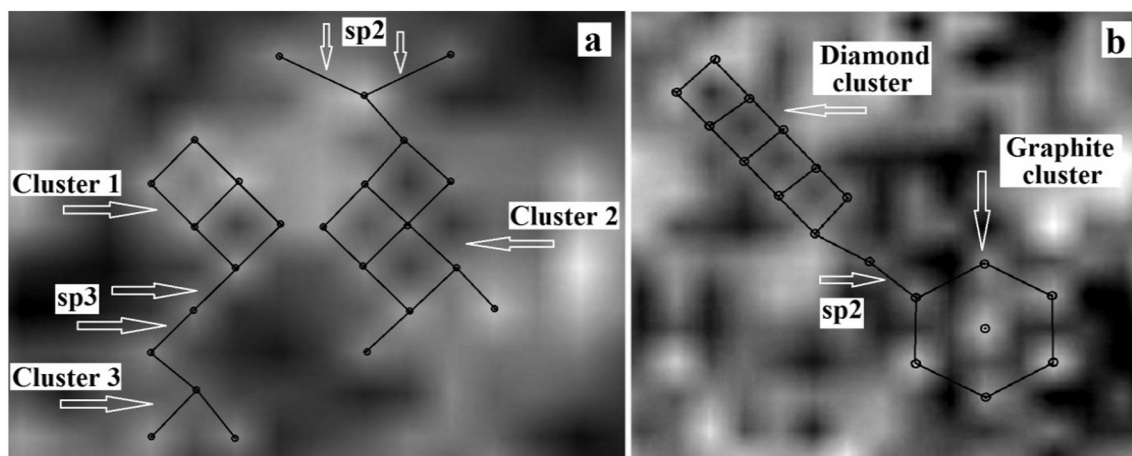


Fig. 4. Atomic structure of the clusters.

0.207 nm and  $d_{220} = 0.119$  nm. The obtained values differ from the tabulated ones. Corresponding interplane distances in macrocrystalline diamond are  $d_{111} = 0.205$  nm and  $d_{220} = 0.125$  nm. Thus, the film under study shows interplane distance  $d_{111}$  larger, and  $d_{220}$  less than the same values in the equilibrium lattice. This kind of lattice distortion is characteristic of the diamond-like carbon thin films. For example, the paper [29] explores thin carbon films obtained by laser sputtering, with the values of interplane distances as  $d_{111} = 0.208$  nm,  $d_{220} = 0.117$  nm, and in the paper [30] -  $d_{111} = 0.207$  nm. It can be assumed that the distortions were caused by changing angles between the links, but not by changing interatomic distances. This results in reducing some interplane distances and increasing others, with C-C-bond constant length as it occurs in carbon nanotubes and fullerenes [31,32].

The findings correlate with experimental data received by neutron, X-ray and electron diffraction methods. Application of these methods makes it possible to find the radial density function, which in its turn provides essential structural data on the closest interatomic distances ( $r_1$ ), angular directions of links ( $\alpha$ ) and coordination number ( $z$ ) [10]. These data for amorphous diamond-like carbon films were received from the neutrons scattering spectrum [8,9]. Reliable arguments have been received to prove that these values are close to those of crystalline diamond ( $r_1 = 0.154$  nm,  $z = 4$ ,  $\alpha = 109.47^\circ$ ). The second neighbors have also been found that correspond to the diamond, interatomic distances in the second coordination sphere are somewhat varying explained by random distribution of neighboring tetrahedrons mutual orientation in ta-C films. Neutron investigations show that correlations are getting lost behind the third coordination sphere. The angle between the links has practical coincidence with the corresponding values of diamond. These results are explained by the fact that carbon systems with rigid covalent links have certain values of the links length and of the angle correlations even in small groups of atoms.

Analysis of Raman spectroscopy of carbon diamond-like films shows that there are two lines present - D-line corresponding with the disordered defect graphite and G-line corresponding with the reflection from the defect-free graphite crystals [33]. It is known that Raman spectroscopy of diamond contains no first order phonon mode, but it contains a triple degenerate fundamental oscillation that exists for a structurally perfect diamond lattice for  $1332.5 \pm 0.5$   $\text{cm}^{-1}$  at 300 K [34]. The peak's width is growing with the transition to nanocrystalline diamond and it is moving towards low-frequency region, but this peak never appears in tetragonal and amorphous films [34]. Experiments with detonation diamond nanocrystals demonstrated [33] that Raman spectroscopy features a broadened  $1322$   $\text{cm}^{-1}$  line imposed upon graphite broadband spectrum with major maximum  $1317$  and  $1613$   $\text{cm}^{-1}$  (D and G respectively). In case with carbon diamond-like film peak D shows anomalous broadening being placed in the approximate spacing of  $1000$ – $1600$   $\text{cm}^{-1}$

with maximum about  $1393$   $\text{cm}^{-1}$ . Thus, Raman spectroscopy indicates presence of considerable amount of carbon with sp<sup>2</sup>-bonds in the film structure, but it is not arranged into the graphite structure.

Carbon film imaging analysis showed that most crystals have such a small size that they are not crystals but clusters - small groups of atoms whose number can make up only several dozens. In spite of the pronounced cluster nature of the film's structure, the film is not an analogue of the polycrystalline one. Mating grains in polycrystals are separated by boundaries and structure changing is going stepwise. As for the film, a continual transition from one crystalline field to another occurs. Such smooth transition of one cluster's structure into another cluster's structure can be explained by a carbon film amorphous state in-between them.

Diamond clusters are chaotically-oriented, that is why crystalline lattice imaging emerges only for those crystals that have favorable orientation against electron beam in microscope. Blurred rings evenly intensity in the electron diffraction pattern throughout the whole length prove the absence of the crystals distinguished orientation. Despite their small number, carbon atoms take certain positions in the diamond lattice. Some clusters consist of only two crystallographic planes and that is enough to provide diffraction reflection in a diffraction pattern.

The diamond cluster consisting of the atoms of the first and the second coordination spheres contains not less than 17 atoms and has the size 0.35 nm. The cluster size will be about 0.5 nm, if though half of the atoms of the third coordination sphere participate in the cluster formation. Crystal structure of such a cluster will be sufficiently well-pronounced to form diffraction rings in electron diffraction pattern. Our results are in accord with the available experimental data. In fact, neutron diffraction research (analyzed above) show the links that correlate with the diamond structure and are present, at least, in the first and the second coordination spheres.

The conducted investigations prove small size of crystallites. If the diamond crystals size is 4–7 nm, they give rather distinguished, though somewhat widened reflections [35,36], i.e., the film under study provides reliable data of the size of diffraction ring-making fields being considerably less. The structure and the electron diffraction pattern definitely indicate presence of the diamond crystalline lattice in the diamond-like carbon films, though with some interplane distances changed.

The results obtained can be explained from the cluster model viewpoint [5,28]. Clusters are performed by groups of atoms linked by interatomic interaction with no crystalline lattice necessarily being formed. The cluster state renders an essential effect upon the electron diffraction pattern. Fine-grained polycrystal diffraction patterns perform an image of continuous rings, with the ring width increasing while the grain size is decreasing. The rings keep existing till the lattice

is existing in the crystals. But in our case the diffraction pattern shows distinctly pronounced rings, and this fact gives grounds to suppose that the diamond crystalline structure has been formed. Meanwhile, the diffraction pattern of the graphite component is absent, therefore, it can be assumed that the graphite lattice has not been formed.

So, the film structure consists of the diamond nanoclusters with carbon atoms linked by  $sp^3$ -bonds, and with gaps between the diamond clusters filled with carbon atoms with  $sp^3$ - as well as  $sp^2$ -bonds. This is exactly structure of the diamond-like carbon films that can be obtained by carbon condensation upon the substrate of the vapor-gas phase containing not less than 80% carbon with  $sp^3$ - bonds, obtained by carbon target laser evaporation [37]. This structure is just the ta-C amorphous diamond [5,17]. What is then the role of carbon atoms with  $sp^2$ -bonds? The data given above show that hexagonal packaging of carbon atoms in cluster aggregation is a rare phenomenon, i.e. the graphite phase is presented by small local fields. Only two clusters with graphite lattice on the area of  $6.6 \times 4.3 \text{ nm}^2$  can be specified. It is clear that the main contribution into the formation of diamond-like carbon films properties belongs to the diamond clusters.

## 5. Conclusion

The data obtained by electron microscopy prove that diamond-like carbon films produced with the application of laser method contain the cluster structure presented mostly by diamond clusters with the size less than 1 nm. The analysis of electrons diffraction leads to the conclusion that interplane distances  $d_{111} = 0.207 \text{ nm}$ ,  $d_{220} = 0.119 \text{ nm}$  are distorted to some extent as compared to the same parameters of the diamond macroscopic crystal, but such distortions are typical of the diamond-like structure of carbon film. It is essential that links between clusters are formed by  $sp^3$ - as well as  $sp^2$ -bonds that create the structure of the diamond-like carbon films that is homogenous and with no boundaries.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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