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Structural state of diamond-like amorphous carbon films, obtained by laser evaporation of carbon target

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ABSTRACT

A homogeneous diamond-like film was obtained on an area of 75 × 25 mm^2. Study of the film structure, using transmission electron microscopy and Raman spectroscopy, showed a mixture of carbon atoms with sp^2- and sp^3-bonds. Structure of carbon film is determined by the presence of randomly oriented carbon clusters bound by diamond sp^3-bonds (tetrahedral amorphous carbon, ta-C). Electron diffraction patterns demonstrate strongly distorted interfacial distances. Raman spectra show that there are carbon atoms with graphite sp^2-bonds in the film, but a signal of graphite crystal lattice is absent in electron diffraction: This implies that hexagonal units are not shaped into a graphite crystal lattice. Broad D-band in Raman spectra shows strongly distorted carbon bonds in graphite. If diamond phase dominates, the space between diamond clusters is filled with carbon atoms with sp^2-bonds (turbostratic structure). Thus, diamond areas are bound into a single discontinuous aggregate of carbon diamond-like film.

1. Introduction

The properties of carbon films are determined by a large diversity of structures which have not only crystalline, but also amorphous state. This diversity of structures and the unique properties of diamond films can be explained by the features of interatomic bonds between carbon atoms. The most widespread chemical bonds in amorphous and crystalline carbon films are the sp^3- and sp^2-bonds which are a result of electronic orbitals hybridization. At sp^3-hybridization carbon atoms have four sp^3-orbitals, which allows them to form four strong bonds with the neighboring atoms. In some carbon films, the portion of sp^3-bonds reaches 80% and more [1–3], which results in their high hardness. Such films consist of tetrahedral amorphous carbon, in which diamond sp^3-bonds dominate [1,2,4,5]. In sp^2 configuration carbon bonds form three sp^2 orbitals (three strong covalent bonds) and a weak π-bond (Fig. 1b), and the structure consists of flat rings which are joined into the graphite phase with the help of π-bond [6].

To describe the structure of amorphous films, the cluster model was suggested [7,8]. The substance of this model is as follows. Carbon atoms tied by sp^2 bonds are joined into plates consisting of rings. These rings are joined by π-bonds into stacks and form graphite clusters. These clusters are buried into the matrix of carbon atoms bound by sp^3-bonds. The sp^2-clusters determine the electrical properties whereas sp^3-matrix controls the mechanical properties. The heterogeneity of film structure follows from this model: the areas with sp^2 and sp^3 bonds are alternating here.

Thus, in amorphous and nanocrystalline carbon films the areas with coordination numbers 3 (sp^2-bond) and 4 (sp^3-bond) may exist: they form a mixture of structures with different types of bonds [7]. At first, the high hardness was considered to be determined by diamond sp^3-bond, but recent studies showed that sp^2-bonds also form carbon films of high hardness. This means that the existence of this or the other bond does not attest to the predominance of properties typical of diamond or graphite, provided that sp^2 and sp^3 clusters are nanosized [9,10].

Amorphous state in materials with covalent bonds differs considerably from amorphous state in metals. Amorphous metals have a liquid-like structure, in which the nearest environment of atom follows the principle of the closest packing, the neighbors being located at a distance of atomic diameter to each other, whereas coordination number is close to 12. In covalent crystals the distance to the nearest neighbors is determined by the length of covalent bond, whereas the number of nearest atoms is determined by the element valency. In diamonds, the nearest atoms are located at a distance of 0.154 nm, number of nearest neighbors is 4. In graphite, these parameters are

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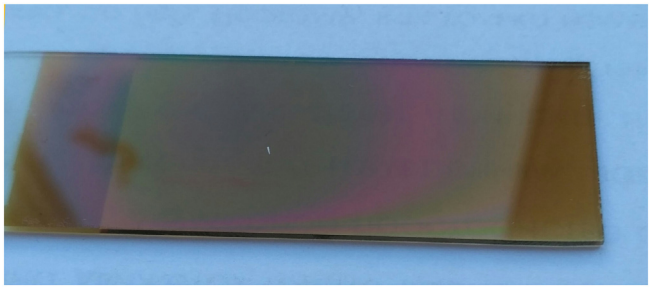

Fig. 1. A diamond-like amorphous carbon film deposited on the silicate glass substrate obtained by laser evaporation of carbon target. The dimension of the area covered with film is 75 × 25 mm^2.

0.142 nm and 3, respectively.

In this paper, we have carried out the investigation of the structure of a thin carbon film obtained by laser evaporation of carbon targets in vacuum.

2. Experimental

Structure of carbon films depends on the regime of carbon atom condensation on the substrate. Varying this regime, one can control the film properties in a broad range. Laser evaporation produces mainly sp^3-bonds in condensed carbon, the so-called ta-C carbon [8]. We used direct evaporation of graphite target at 1064 nm laser irradiation from a Nd:YAG laser NTS300 to condense carbon on amorphous substrate of silicate glass. Defocused laser beam is introduced into the vacuum chamber of the vacuum unit (the residual pressure is less than 10^{-5} Torr), where graphite targets and silicate glass substrates were placed. On a graphite target with a diameter of 5 mm and a thickness of about 2 mm, the defocused laser beam, whose energy was 1.1–1.9 J, created a spot with a diameter of about 3 mm. The exposure time was about 5 min. The resulting stream of evaporated carbon was deposited on glass substrates, which were arranged in a circle with a diameter of about 20 cm at a distance of about 10 cm from the target and at an angle of about 30° to the axis of the vapor-gas torch, forming a carbon film. If the target is heated by a defocused beam, target fragmentation is absent. The resulting diamond-like amorphous carbon film is shown in Fig. 1. Carbon condensation from the vapor phase was carried out on the silicate glass substrate 75 × 25 mm^2 in size. Detonation ultra-nanocrystalline diamonds, studied for comparison, were produced according to technical specifications TU 84-112-87 in the Federal Research and Production Center “Altai”, Biysk, Russia.

Structural studies were carried out on a transmission electron microscope *Philips CM-30* in the Material science center of collective usage at Tomsk State University. Raman spectra were recorded at room temperature using a micro-Raman *LabRAM HR* spectrometer with 325 nm excitation from a He-Cd laser (IGM SB RAS).

3. Results

3.1. Transmission electron microscopy of thin carbon film

The structure of thin carbon film was studied using transmission electron microscopy (TEM). A typical section of such film is shown in Fig. 2a with magnification which is sufficient to reveal details smaller than 1 μm. Film structure is a homogeneous matrix the main feature of which is the absence of any boundaries. Some contrast observed in the bright-field TEM image is due to variations in the film thickness, i.e., to the weak relief on the film surface.

To determine the structural state of the carbon film, the electron-diffraction patterns were obtained for several sections. The image of carbon film and corresponding electron-diffraction (ED) pattern are given in Fig. 1. Analysis of such patterns showed that the rings (diffraction maxima) correspond to the diffraction from (111) and (220) faces of diamond lattice. Interfacial distances are d_{111} = 0.207 nm and d_{220} = 0.119 nm. One can see that these values differ from the table values for diamond (d_{111} = 0.205 nm and d_{220} = 0.125 nm). For the film, the interfacial distance d_{111} is larger whereas distance d_{220} is smaller in comparison with the values for a diamond single crystal. Such distortion of the lattice is typical of thin diamond-like films. For example, in [11], thin carbon films obtained by laser evaporation and carbon condensation were studied and values of interfacial distances d_{111} = 0.208 nm and d_{220} = 0.117 nm were given. The authors of [12] obtained d_{111} = 0.207 nm. One can suppose that interfacial distances do not change and the length of the C—C bond remains permanent but the angles between bonds vary similar to carbon nanotubes and fullerenes [13,14]. This results in lattice distortion with a decrease in some interfacial distances and with an increase in the others.

Strong broadening of the rings is an important feature of the ED pattern. If the size of diamond crystals is 4 to 7 nm, then broadened but rather well-pronounced diffraction reflections are observed [15,16]. Thus, it is possible to suppose that the size of areas forming the diffraction ring is considerably smaller, supposedly about 1 nm. Similar broadening of the rings in the ED pattern for a diamond-like film was described in [3]: This was due to 80% of the sp^3-bonds. Such structure corresponds to ta-C amorphous diamond [17]. Thus, amorphous carbon can be considered to be a mixture of sp^2- and sp^3-bonds [18].

The situation with carbon materials with strong covalent bonds is much more complicated. It is impossible to interpret the amorphous state as the liquid-like state in covalent crystals. If the closest neighbors are located at a distance from the first coordination sphere as in the case of metallic amorphous materials, then coordination number will be determined by the bond type (sp^2 or sp^3). However, in any case the principle of the closest packing is not realized in carbon amorphous materials. Amorphous carbon material is characterized, first of all, by the random chaotic combination of interatomic sp^2- and sp^3-bonds.

Electron microscopy and electron diffraction allow us to unambiguously interpret the structural state of the carbon film as diamond-like. But highly diffused reflexes indicate extremely small size of diamond clusters and strong distortion of interatomic distances. According to publications such ED pattern determines that the structural state of the carbon film is amorphous, so-called ta-C (tetrahedral amorphous carbon) [19]. However, the relative position of the rings clearly indicates some crystallinity in the diamond component of the film. On the other hand, no reflexes from the hexagonal crystal lattice of graphite were found. The question arises whether there is carbon with sp^2-bonds in the structure of such film. The answer is given by the Raman spectroscopy.

3.2. Raman spectroscopy of thin diamond-like films

Raman spectra were recorded in 14 points, distributed evenly, with an interval of 0.5 cm, along a line parallel to the long edge of the substrate. These Raman spectra were found to be very similar and one of them is given in Fig. 3. Main features of Raman spectrum are two broad bands near 1393 and 1607 cm^{-1}. A band at larger wave number is attributed to the optical stretching mode of E_{2g} symmetry (G-mode). This band is located at 1585 cm^{-1} in well-ordered, perfect crystalline graphite, but it is shifted to 1607 cm^{-1} in our case because of the graphite disordering [19]. For natural crystalline graphite, this band is narrow and the full width at half-maximum (FWHM) is about 13 cm^{-1}. Broadening to 80 cm^{-1} is commonly explained by the presence of glass-like graphite. Line near 1355 cm^{-1} is D-mode or a disorder peak. Tuinstra & Koenig attributed to the breathing mode of A_{1g} symmetry with phonons corresponding to the point k = 0 [20]. This mode is absent in perfect graphite and appears only at its disorder. Its position varies in the 1310 to 1450 cm^{-1} range whereas FWHM values cover the 80 to 400 cm^{-1} range. A possible origin is disordered or nanocrystalline graphite, disordered glass-like carbon, sp^2-hybridizated carbon phases

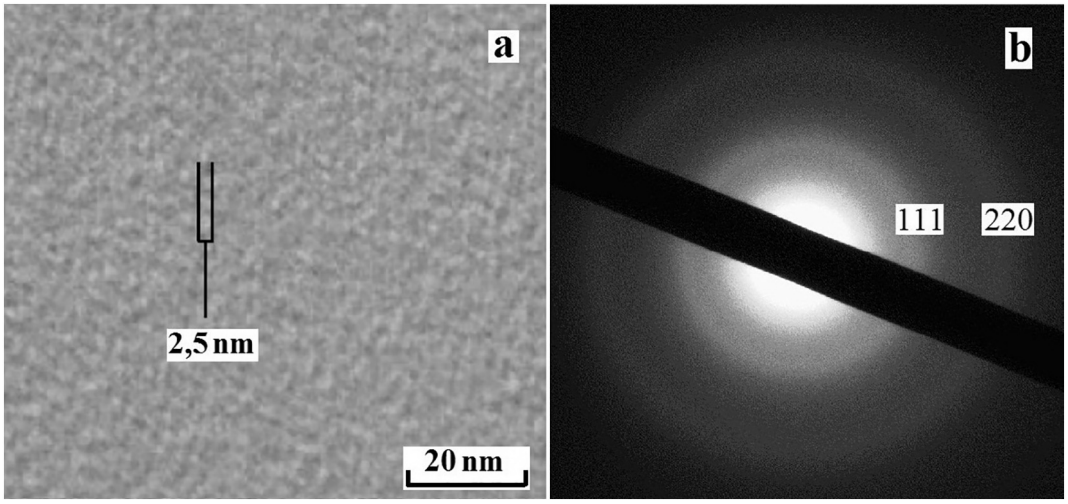

Fig. 2. Bright-light TEM image of carbon film (a) and electron-diffraction pattern for the same area (b).

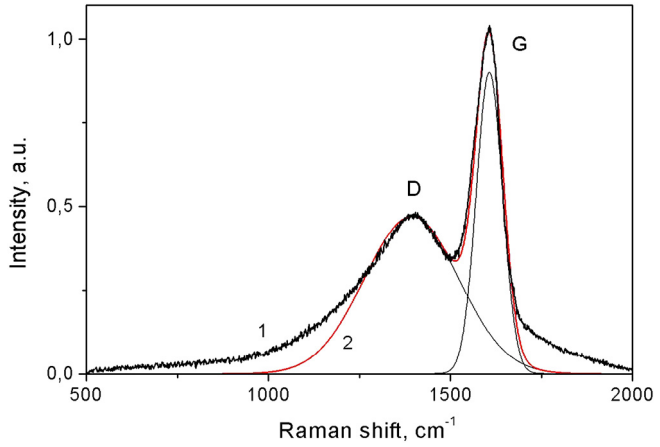

Fig. 3. Raman spectrum for point 6 on diamond-like carbon film (1) and results of its decomposition into two Gaussian components with maxima near 1393 and 1607 cm^{-1} and FWHM values 300 and 88 cm^{-1}, respectively. Curve 2 is a sum of two Gaussian components whereas thin black lines show individual components. For given point 6 the ratio I_D/I_G is about 0.53.

or microcrystalline defect graphite [21]. The intensity of D peak changes depending on the number of aromatic rings in the graphite-like clusters. Although Raman spectra are not a measure of the sp^2- or sp^3-input, some parameters of these spectra (for example, position of G-peak or the I_D/I_G ratio) provide such information. Thus, the shift of G-peak to high energies and increase in the I_D/I_G value indicate an increase in sp^2 π-π* bonding or, per contra, a decrease in diamond-like sp^3 bonding [18].

Decomposition into two, D and G, components was carried out for all 14 Raman spectra, recorded in different points. The dependences of the intensities of the peaks D and G, as well as of the ratio I_D/I_G between these two values on the coordinates of the measurement points distributed uniformly along the substrate about 7.5 cm long are shown in Fig. 4a. In Fig. 4b similar dependencies are shown for the width of these peaks. It can be seen that the latter are virtually independent of the coordinates. As for the intensities of the bands D and G, they gradually increase (by 25–35% from left to right on the film in Fig. 1) and further in the last two points fall to the initial level. The I_D/I_G ratio in the same range varies from 0.48 to 0.58.

4. Discussion

According to the results of electron microscopy, a typical structural

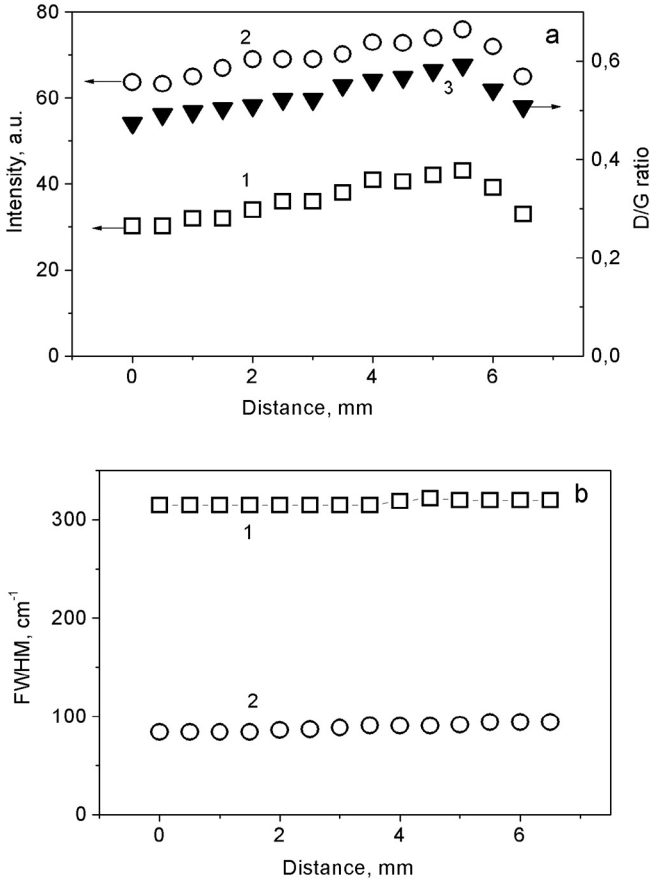

Fig. 4. Parameters of Raman spectra recorded in 14 points of the diamond-like carbon film (see Fig. 1):
(a) Intensities of Gauss components D (1) and G (2), and I_D/I_G ratio (3) versus coordinate;
(b) FWHM values for D and G peaks versus coordinate (1 and 2, respectively).

feature of thin carbon film is the absence of well-pronounced boundaries between grains, which attests to the amorphous state. However, electron-diffraction patterns show unambiguously the presence of a diamond crystal lattice, though it has changed interfacial distances. Graphite reflections are absent in these patterns.

On the contrary, analysis of Raman spectra attests to the presence of both the D line of disordered graphite and the G line of perfect

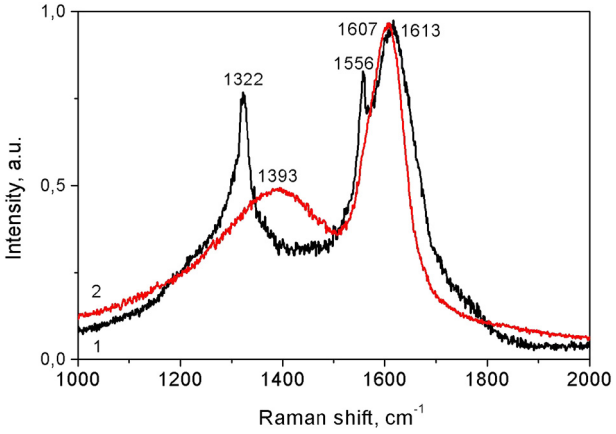

Fig. 5. Raman spectrum for detonation nanodiamond (1) and carbon diamond-like film (2).

crystalline graphite. The results of these two techniques used for studying the structure state of diamond-like films seem to contradict one another. However, this contradictory situation is solvable. The high symmetry of diamond lattice is known to determine the simplicity of vibrational spectrum. There is a single triply degenerated fundamental vibration which is located at 1332.5 ± 0.5 cm^{-1} at room temperature in a perfect diamond lattice [22]. In nanocrystalline diamond the FWHM value increases, but in tetragonal and amorphous films this peak is completely absent [22]. Indeed, in nanocrystals of detonation diamond a broadened 1322 cm^{-1} line is present (Fig. 5): it is superimposed on the broadband spectrum of graphite with main maxima near 1317 and 1613 cm^{-1} (D and G lines, respectively). The position of these maxima depends considerably on the sp^2 configuration of carbon [19] and the size of graphite grains.

D peak with maximum in the 1345–1358 cm^{-1} range, corresponding to polycrystalline graphite, is typical of amorphous films of diamond-like carbon. The intensity of this peak decreases as the size of graphite grains grows. Simultaneously the peak broadens and shifts to higher energies. In our case D peak is abnormally broadened, covers the 1000 to 1600 cm^{-1} range and has a maximum near 1393 cm^{-1} (Figs. 3, 4). This may attest to the considerable distortion of bonds with sp^2 hybridization. Diamond peak with the maximum at 1322 cm^{-1} is located just in this range.

In a number of papers the ratio between the intensities of D and G peaks was shown to be associated with the carbon portions in sp^2 and sp^3 hybridizations [23]. To obtain the $L = I_D/I_G$ parameter, we decomposed the Raman spectrum into two Gaussian components (Fig. 4). Here I_D and I_G are the intensities of D and G components, respectively, and L is the characteristic coefficient showing the portion of carbon atoms with sp^2 hybridization. For diamond-like films of amorphous carbon the L values do not exceed 0.6. In our case L is varies in the 0.48 to 0.58 range.

The obtained results can be explained in a cluster model [7,8]. Cluster state affects considerably the appearance of electron-diffraction patterns for carbon diamond-like films. Such patterns (electronic reflections) are solid rings for a fine-grained polycrystal, with the width of the rings being broadened as the grain size decreases. These reflections remain pronounced until atoms form a crystal lattice in the samples. At a certain size crystals transform to clusters. A cluster is a group of atoms bound by interatomic interaction and crystal lattice is not surely formed in such group. Nanocrystal, 5 nm in size, contains about $2 * 10^4$ atoms, whereas there are about 10^3 atoms in a 1 nm nanocrystal. Such a small amount of atoms cannot provide diffraction on crystallographic planes and ring formation in the ED patterns. In our case the ED pattern indicates that diamond crystal structure is already formed. Reflections from the graphite component are absent. This allows us to suppose that graphite platelets, consisting of hexagonal rings, are misoriented to each other and do not form a hexagonal lattice. This, so-called turbostratic structure [6,24] binds diamond areas into a single discontinuous aggregate of carbon film. Fig. 1a shows the cluster structure of the diamond-like film, according to which the size of the diamond cluster is about 2.5 nm.

Thus, the structural state of the film is as follows: basically, the structure of the film is diamond clusters united in a coherent homogeneous structure by carbon atoms but with sp^2 bonds. This approach is an alternative to approach, according to which carbon clusters, bound by sp^2-bonds, are organized into planes, consisting of hexagonal rings. These rings are bound by π-bonds into stacks and form graphite clusters. These clusters are immersed in a matrix of carbon atoms bound by sp^3-bonds [8]. TEM of carbon thin films attests unambiguously, and Raman spectroscopy indirectly indicates the presence of diamond sp^3-bonds and the organization of carbon atoms in nanodiamond clusters. The abnormally broadened reflexes also indicate large distortions of interplanar distances d(111) and d(220). The absence of graphite phase reflexes indicates the absence of pronounced graphite clusters. We can suppose that the structure of our film consists of diamond nanoclusters, where carbon atoms are bound by sp^3 bonds, but the space between clusters is filled with carbon atoms with sp^2-bonds.

Electron microscopy of thin carbon films attests unambiguously and Raman spectroscopy attests indirectly to the presence of diamond sp^3 bonds and to the configuration of carbon atoms into nanodiamond clusters, whereas the abnormally broadened reflections show strong distortions of interfacial distances d(111) and d(220). Absence of graphite reflections indicates the absence of graphite clusters in the film structure.

5. Conclusions

Electron microscopy of thin carbon films attests unambiguously and Raman spectroscopy indicates indirectly the presence of diamond sp^3 bonds and to configuration carbon atoms into nanodiamond clusters, whereas the abnormally broadened reflections show strong distortions of interfacial distances d(111) and d(220). At the same time, data of Raman spectroscopy show the presence of sp^2 bonds in structure of the carbon film. Absence of graphite reflections, that is the absence of pronounced graphite clusters, suggests that hexagonal rings fill the space between diamond clusters and operate as binding elements. This structure is homogeneous and its homogeneity is due to the absence of interfaces.

Acknowledgements

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