

SPECTROSCOPY OF CONDENSED STATES

The Effect of Nonequilibrium Synthesis Conditions on the Structure and Optical Properties of Amorphous Carbon Films

A. P. Ryaguzov^{a,*}, R. R. Nemkayeva^{a,b}, O. I. Yukhnovets^a, N. R. Guseinov^a, S. L. Mikhailova^c,
F. Bekmurat^c, and A. R. Assembayeva^{a,d}

^a National Nanotechnology Open Laboratory, Al-Farabi Kazakh National University, Almaty, 050040 Kazakhstan

^b Engineering Laboratory, Al-Farabi Kazakh National University, Almaty, 050040 Kazakhstan

^c Department of Solid State Physics and Nonlinear Physics, Al-Farabi Kazakh National University, Almaty, 050040 Kazakhstan

^d Satpaev Kazakh National Technical University, Almaty, 050040 Kazakhstan

*e-mail: ryaguzov_a@mail.ru

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Abstract—Amorphous carbon (a-C) thin films are synthesized using a nonequilibrium method of ion-plasma sputtering of a graphite target under argon atmosphere at a constant plasma current. The local structure of carbon films is studied by the Raman spectroscopy method. Using the normal distribution in the decomposition of the Raman spectra, it is found that a peak typical for a phonon density of states with sp^3 bond hybridization appears in the frequency region of 1260 cm^{-1} at synthesis temperatures of less than 150°C . In addition, the influence of the dimensions of nanostructures composed of sp^2 sites on the width of optical bandgap and their correlation with the results of X-ray photoelectron spectroscopy (XPS) in a-C films is shown.

Keywords: carbon film, synthesis, optical properties

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INTRODUCTION

There are various allotropic forms of carbon in both the crystalline and disordered states [1]. The diversity of allotropic forms of carbon is determined by the spatial arrangement of the sp^1 -, sp^2 -, and sp^3 -hybridized bonds. The degree of hybridization and orientation of chemical bonds has an effect on the distribution of the density of energy states of π and σ electrons, which causes differences in the electronic properties of the substance.

Over the past three decades, particular attention has been focused on the study of thin amorphous diamond-like carbon (DLC) films [2–7]. There are many ways to synthesize DLC films as coatings that possess the best antifriction, strength, and chemical resistance characteristics [8–10]. Conditions under which atoms condense determine the formation of the atomic structure of the films. Unlike many other synthesis methods, the magnetron ion-plasma method allows one to grow amorphous DLC film with a given structural modification in a wide range of kinetic and thermodynamic parameters of the synthesis. Nonequilibrium conditions of condensation of carbon atoms enable to create different cluster structures of sp^2 and sp^3 sites in the amorphous carbon matrix and, consequently, the possibility appears to form nanohetero-

morphous carbon films with various electronic properties.

For adjusting synthesis conditions and stabilizing the process of growth of a-C films, a magnetron based on an electromagnet was used. The use of an electromagnet allows one to control the density of magnetic field lines on the target surface, which gives rise to the adjustable plasma current and cathode voltage. The ability to monitor the plasma state makes it possible to fix the processes of sputtering, condensation, and structure formation during the synthesis of carbon films. Thus, it becomes possible to obtain amorphous DLC films with a given structural configuration comprised of sp^2 and sp^3 sites.

To estimate the sp^2/sp^3 site ratio and to determine the size of cluster formations comprised of sp^2 sites, the Raman spectroscopy (RS) method was used. The RS method can be attributed to the relatively mild methods for studying the local atomic structure. Using the accumulated spectral data on RS, one can estimate the sp^2/sp^3 bond percentage ratio, as was done in [11–14]. In the Raman spectra of a-C films, the half-width of the main G peak, the $I(D)/I(G)$ peak intensity ratio, and the position of the G peak and its variance [12] are characterized by vibrational modes of molecular groups comprised of sp^2 sites. This is due to the scat-

tering cross section of sp^2 sites in the visible range of the exciting radiation, which is 50 to 250 times larger than the scattering cross section of sp^3 sites and characterized by resonance transitions between π and π^* states [12, 15, 16]. The energy of visible radiation is much lower than the excitation energy of deeper lying σ states. However, the RS studies of the structure of amorphous diamond-like carbon films can be useful for determining the formation of sp^3 sites in DLC films.

The width of optical bandgap is an important criterion for evaluating the RS results. The optical bandgap width calculated from the transmission and reflection spectra refers to the structurally sensitive parameters and, therefore, may be a specific estimate of the sp^2/sp^3 -hybridized bond ratio [1, 12]. This is connected with the difference in the energy states of the π and σ electrons forming a band structure. The energy states of the π and σ electrons are determined by the bond configuration between nearest neighbors of the sp^2 and sp^3 sites [17].

The effects of the substrate temperature, gas pressure, and discharge power density on the structure and optical properties are studied. The findings are correlated with the sp^2/sp^3 site ratio values determined from the XPS spectra.

The main objective in the study of electronic properties of nanoheteromorphous carbon media is to reveal the influence of synthesis conditions on the formation of an atomic structure and the sp^2/sp^3 site ratio. This is especially important for the formation of fine structures in the nanotechnological processes. Knowledge of the dependence of the structure and properties of a-C films on the synthesis conditions makes it possible to increase the understanding of their formation origin and to control electronic processes in new nanoelectronic devices.

EXPERIMENTAL

A cooled magnetron with unbalanced plasma and a magnetic flux density (\mathbf{B}) adjustable in magnitude was used in the synthesis of carbon films. The input voltage (U) from a DC power source and the electron-ion current (I) in the discharge plasma was further adjusted by variation of \mathbf{B} during the synthesis of films. The \mathbf{B} value varied within 25–40 mT. The sustainability of the ion-plasma discharge and the plasma-sputtering process stability are determined by the E/p ratio, where E is the electrical field strength between the anode and cathode of the magnetron, and p is the pressure of Ar in the chamber for the synthesis of films. The adjustment of magnetic flux density \mathbf{B} allows to maintain $E/p = \text{const}$ under certain synthesis conditions (U and I of the discharge). The constant E/p ratio during the synthesis made it possible to study in detail the influence of thermodynamic and kinetic parameters on the structure and optical properties of

synthesized amorphous carbon films. All samples were prepared with the same current (DC) in the plasma.

The power density (P_d) of the ion-plasma discharge during the synthesis of films took values of 2.1, 2.4, and 2.6 W/cm². Carbon films were grown on quartz and silicon substrates at three temperatures T_{sub} (50, 150, and 250°C) and under pressures of argon in the range of 0.5–1.2 Pa. The purity grades of argon and a graphite target were 99.999%. The synthesis time of all a-C films was constant and equaled 40 min; the average growth rate was about 15 Å/min. The film thickness was determined on the face of a fresh cleavage of a silicon wafer in a Quanta 200i 3D scanning electron microscope and varied in the range from 50 to 70 nm depending on the synthesis conditions. The condensation of carbon atoms on a substrate was carried out in the range of angles from 15° to 30° between the normal to the substrate surface and the direction of atoms' movement. These synthesis conditions are poorly investigated and of certain interest in the technology of preparation of thin-film structures for nanoelectronics.

The local structure of amorphous carbon films was studied by the RS method on an NTegraSpectra instrument (NT-MDT, Russia). A solid-state laser with a wavelength of 473 nm (2.62 eV) was used in the RS method. The diameter of a spot of the exciting laser light on the sample was 2 μm, which determined a sufficiently large irradiation area on the film surface. The spectral resolution was $\pm 4 \text{ cm}^{-1}$. The exposure time of spectral measurements was 30 s. In addition, the exposure was carried out under motion with a speed of 10 μm/s in order to avoid the impact of laser radiation with 1.5 mW in power on the atomic structure of the films.

The width of optical bandgap was calculated from the reflection and transmission spectra obtained on a UV3600 device (Shimadzu, Japan). All measurements of the structure and optical properties were performed on freshly prepared samples.

The XPS measurements were carried out on a KRATOS AXIS 165 XPS system (Missouri University of Science and Technology). The electron flow from the surface layer of a film with a thickness of 10 nm was recorded in the spectra. The measurements were carried out in a vacuum (2×10^{-8} Torr) using monochromatic Al K_{α} radiation (1486.71 eV). The instrumental error of measurements was ± 0.05 eV. It should be noted that the surface charging took place when measuring films on silicon substrates. Therefore, the charge offset was taken into account in the data processing.

RESULTS AND DISCUSSION

Raman Spectroscopy

According to [1, 12–16], Raman spectra of carbon films with a disordered structure can be described by two sharp peaks, the vibrational modes of which are referred to as the “*D* (Disordered) peak” and “*G* (Graphitic) peak” in the frequency ranges of 1350–1400 and 1575–1600 cm^{-1} , respectively. The change of the *D* and *G* peak positions and the ratio of their intensities determine the degree of hybridization of C–C bonds and variation of the allotropic forms in the synthesized a-C films from the graphite-like structure to the diamond-like one.

As is known, the appearance of the *G* peak is caused by the mode of stretching vibrations of hexagonal carbon rings in the central region with the E_{2g} symmetry [1]. At the same time, the presence of the *G* peak in the Raman spectra of amorphous carbon films with disordered structure may be associated with the stretching modes of C–C atomic pairs of sp^2 sites. The absence of hexagonal C_6 molecules cannot exclude the existence of C–C sp^2 bonds. Therefore, the position of the *G* peak in disordered structures of carbon films varies in the range from 1500 to 1630 cm^{-1} [15].

The appearance of the *D* peak is associated with the breathing mode of hexagonal molecules of carbon. This is possible owing to the structural disorder involving phonons near the edge of the *K* region [15, 16]. The absence of the hexagonal rings gives rise to the absence of the *D* peak [12, 14–16]. In pyrolytic graphite, the *D* peak is also absent. The film structure can be attributed to either the diamond-like or graphite-like structure by comparing the intensity values and positions of the *D* and *G* peaks.

The Raman spectra of amorphous carbon films synthesized with a plasma discharge power density of 2.1 W/cm^2 and substrate temperatures of 50 and 250°C are given in Fig. 1. The Raman spectra of DLC films are characterized by a single *G* peak and a shoulder in the low-frequency region. The shape of these spectra is typical of amorphous carbon films prepared in this study under different synthesis conditions.

As can be seen from Fig. 1a, the position of the *G* peak at $T_{\text{sub}} = 50^\circ\text{C}$ does not depend on the argon gas pressure in the working chamber and corresponds to 1545 cm^{-1} . In the spectra given in Fig. 1b, the *G* peak at $T_{\text{sub}} = 250^\circ\text{C}$ substantially changes the position with an increase in the pressure and shifts to 1570 cm^{-1} at $p_{\text{Ar}} = 1.2$ Pa. In addition, we see an increase in the *D* band in the region of 1360 cm^{-1} . The blueshift of the *G* peak at $T_{\text{sub}} = 250^\circ\text{C}$ and an increase in the intensity of the *D* band indicates an increase in the number of sp^2 C–C sites and hexagonal C_6 rings.

The dependence of the position of the *G* peak (PosG) on the synthesis conditions (T_{sub} , gas pressure p , and plasma discharge power density P_d) is shown in

Fig. 2. One can see that the PosG(p) functions for 150 and 250°C are almost parallel lines with a small deviation of about 4 cm^{-1} , depending on the P_d values. Thus, it can be assumed that the gas pressure at these temperatures has a similar effect on the structure formation. However, the position of the *G* peak at $T_{\text{sub}} = 50^\circ\text{C}$ does not depend on the synthesis parameters (p and P_d) and remains unchanged at 1545 cm^{-1} .

Previously, we have investigated the influence of the substrate temperature on the structural properties of a-C films with other synthesis conditions and observed the *G* peak at 1555 cm^{-1} for temperature $T_{\text{sub}} = 50^\circ\text{C}$ [11]. Thus, it should be noted that the stabilization of the E/p ratio during the synthesis allows one to get a film with a large percentage of sp^3 -hybridized bonds, since the redshift of the *G* peak indicates an increase in the number of sp^3 sites. As follows from the results obtained in [16], carbon films with the *G* peak at 1545 cm^{-1} for more than 60% consist of sp^3 sites.

Using the method of synthesis of a-C films with filtered cathodic vacuum arc (FCVA), it was found in [18] that there is a certain activation temperature of T_1 , at which a sharp change in the process of formation of a short-range order in the atomic structure takes place. Moreover, it was found that the percentage of sp^3 sites decreases sharply at temperatures above 200°C. In addition, it was shown that the T_1 value depends on the energy of condensing atoms.

In our study, an increase in the synthesis temperature leads to a change in the *G* peak position and its dependence on the gas pressure at $T_{\text{sub}} = 150$ and 250°C. Hence, there is a synthesis temperature (T_1) between 50 and 150°C, at which structure formation and its dependence on the additional kinetic and thermodynamic parameters change the character. As can be seen from Figs. 1a and 2, the position of the *G* peak at $T_{\text{sub}} = 50^\circ\text{C}$ is retained at 1545 cm^{-1} and does not depend on the discharge power and gas pressure. Moreover, it should be noted that variation of the power density of the ion-plasma discharge (within the range from 2.1 to 2.6 W/cm^2) at $T_{\text{sub}} = 50^\circ\text{C}$ does not have a significant effect on short-range order formation in the structure. An increase in the synthesis temperature causes the *G* peak to shift and its position to start to depend on the gas pressure (Figs. 1b, 2). As is seen from the obtained results, a 200°C change in the substrate temperature leads to shifting the peak position by 20 ± 5 cm^{-1} , which determines a substantial change in the sp^2/sp^3 ratio and, consequently, a change in the structure formation.

For more detailed comprehension of the influence of synthesis conditions on the structure of amorphous carbon films, the Raman spectra were decomposed into components by the Gaussian method. The Gaussian decomposition of the Raman spectra shown

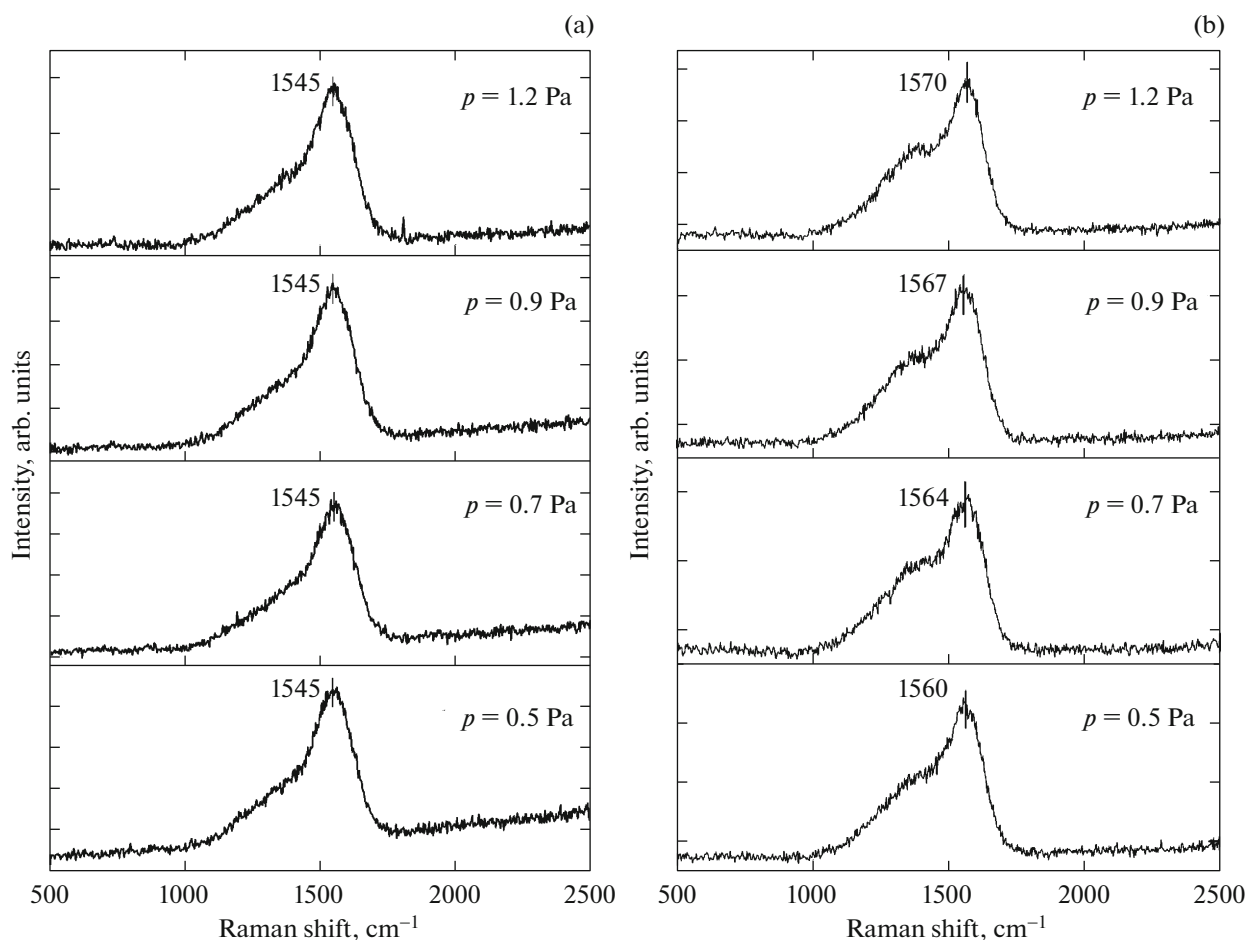


Fig. 1. Raman spectra of a-C films synthesized at (a) $T_{\text{sub}} = 50$ and (b) 250°C with a DC-discharge power density of 2.1 W/cm^2 on quartz substrates.

in Fig. 3 is typical for all amorphous carbon films synthesized in this work. The decomposition was carried out into a minimum number of Gaussian peak com-

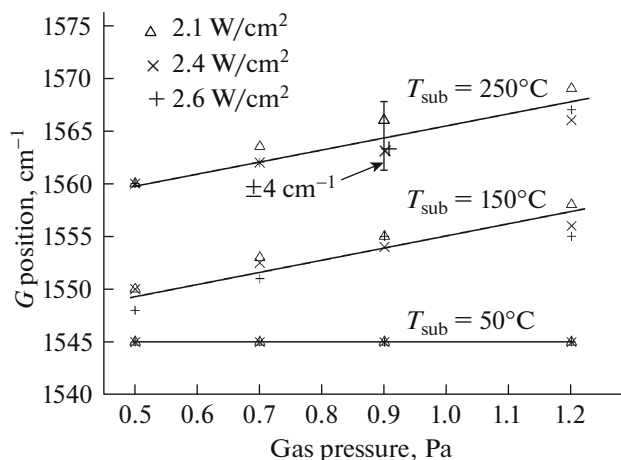


Fig. 2. Position of the G peak as a function of synthesis conditions of amorphous carbon films on quartz substrates.

ponents, with which the resulting curve described the experimental curve with a confidence level of $>0.99\%$ [11].

Before decomposition, the operation of background subtraction was applied. The experimental curves are given by a black line, the Gaussian distribution peaks are marked with a green line, and the resulting decomposition is shown in red. As can be seen from Fig. 3, the RS spectra were decomposed into two and three peaks in accordance with the maximum confidence level.

The spectra of vibrational density of states (VDOS) of graphite and diamond are published in [15, 19, 20]. The main bands of the VDOS are in the frequency range of $1000\text{--}1335 \text{ cm}^{-1}$ for diamond and $1350\text{--}1600 \text{ cm}^{-1}$ for graphite.

According to [1, 14–16], peak 3 in the frequency range of $1500\text{--}1600 \text{ cm}^{-1}$ can be attributed to the G peak (Fig. 3). Peak 2 in the frequency range of $1350\text{--}1400 \text{ cm}^{-1}$ corresponds to the position of the D peak. Decomposition of the Raman spectra of a-C films synthesized at temperatures of 50 and 150°C shows

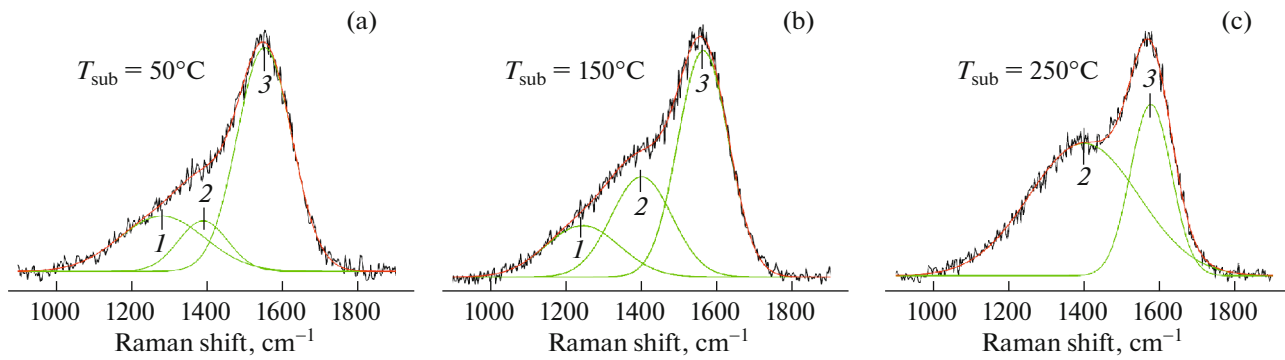


Fig. 3. Raman spectra of amorphous carbon films synthesized with $p = 1.2$ Pa and $P_d = 2.1$ W/cm² at different synthesis temperatures with decompositions by the Gaussian method.

that a peak near the frequency region of 1260 cm⁻¹ appears in the spectra (peak *I*), which corresponds to the phonon density of states of diamond [15]. Hence, it can be assumed that the synthesized amorphous carbon films are structured with diamond-like nanoparticles at substrate temperatures of less than 150°C. Peak *I* is absent in Fig. 3c, which is consistent with the results published in [18] about a sharp decrease in the amount of *sp*³ sites at $T_{\text{sub}} > 200^\circ\text{C}$.

It should be noted that a-C films were synthesized in [18] by the FCVA method with a fixed condensation energy of 90 eV in a wide temperature range (from 100 to 200°C) and contained up to 85% of *sp*³ bonds. The magnetron ion-plasma method of synthesis used in this study relates to non-equilibrium conditions of structure formation, i.e., these synthesis conditions are characterized by a large energy spread of condensing carbon atoms, molecules, and ions. Condensing particles with different energies create structure formation conditions that are substantially different from the conditions used in the FCVA method. This is why the appearance of peak *I* in our films substantially depends on the substrate temperature. In addition, diamond-like grain with dimensions of about 10 Å or less may have, as noted in [21], softer phonons in contrast to bulk diamond, which leads to the appearance of VDOS in the region of 1260 cm⁻¹. As is seen from Fig. 3, peak *I* shifts into the low-frequency region to the band at 1230 cm⁻¹ with an increase in the synthesis temperature ($T_{\text{sub}} = 150^\circ\text{C}$) and disappears completely at $T_{\text{sub}} = 250^\circ\text{C}$. Such behavior of peak *I* shows that the concentration of *sp*³ sites in the amorphous carbon film is significantly reduced. In this case, the priority in the film structure formation goes to *sp*²-hybridized bonds.

As can be seen from Fig. 3, the intensity and half-width of peak 2 increase with an increase in the synthesis temperature. The Raman spectra of a-C films with $T_{\text{sub}} = 250^\circ\text{C}$ are decomposed only into two components, i.e., peaks 2 and peak 3. Thus, the structure

is described, as determined above, only by the *D* and *G* peaks, i.e., by vibrational modes of hexagonal molecules and *sp*² C–C bond. This pattern of changing the structure, which was revealed by decomposition of the spectra into Gaussian components, is observed for all a-C synthesis conditions used in this study.

The size of structural units forming a carbon film matrix is estimated by the Tuinstra–Koenig rule:

$$I_D/I_G \propto 1/L_a, \quad (1)$$

where L_a is the nanocluster size. However, a further increase in the degree of disordering of the atomic structure in strongly disordered structures leads to a decrease in the number of hexagonal molecules, which leads, in turn, to a decrease in the intensity of the *D* peak [15]. Therefore, intensity ratio I_D/I_G of the *D* and *G* peaks starts to decrease with an increase in the degree of structural disordering and the Tuinstra–Koenig equation is not relevant in this case [15, 22].

The appearance of rings in the amorphous matrix indicates the occurrence of certain ordering in the amorphous structure, which gives rise to an increase in the intensity of the *D* peak. In this case, the I_D/I_G ratio is proportional to the number of rings in the cluster. When the size of the nanocluster composed of hexagonal rings do not exceed 20 Å, the following expression should be used:

$$\frac{I_D}{I_G} = C(\lambda)L_a^2. \quad (2)$$

At the same time, it is correct to use the I_D/I_G ratio of the peaks intensity rather than the ratio of their FWHM (full width at half maximum) values [11, 22]. This is because the radiation intensity of Raman spectra is determined by the phonon modes of molecules involved in the most probable resonant Raman processes. Similar reasoning can also be applied to three-dimensionally structured clusters of *sp*³ sites. In [21], the intensity of vibrational modes and their depen-

dence on the wave vector and selection rules were discussed. It was argued that the phonon confinement allows participation of phonons with a wave vector of $q = 2\pi/d$, where d is the cluster size, but no individual sp^2 or sp^3 structural units.

According to [15], the calculated proportionality factor in Eq. (2) for a laser with a wavelength of 473 nm is approximately $C'(473) \approx 0.00376$. Thus, the calculation performed in accordance with the I_D/I_G ratio showed that the size of graphite-like clusters increases from about 6 to 12 Å with an increase in the temperature.

As is shown in [21], the existence of peak I in the case of the diamond-like phase is due to softer phonons comprised of sp^3 sites, the dimensions of which are about 10 Å. In addition, an increase in the synthesis temperature gives rise to a decrease in the dimensions of these clusters, as can be seen from Fig. 3. At a synthesis temperature of 250°C, sp^3 are not assembled into clusters, but formed as connecting bridges between the ordered sp^2 -structure regions. In this case, inelastic light scattering on the regions structured by sp^2 sites takes place. Therefore, the phonon spectrum of sp^3 sites is suppressed and peak I disappears.

The decompositions of the Raman spectra of a-C films synthesized with other values of the argon pressure and power density of DC discharge at a substrate temperature of 50°C into components are roughly the same and similar to the decomposition shown in Fig. 3a. As was found from estimating the dimensions of clusters comprised of sp^2 sites, they generally tend to increase in the range from 6 to 10 Å with an increase in the power density. At the same time, they decrease with an increase in the gas pressure in the same range of L_a variation at $T_{\text{sub}} = 50^\circ\text{C}$. The opposite pattern is observed for clusters comprised of sp^3 sites.

Thus, it is possible to find a relationship between changes in the formed structure of a-C and condensation conditions and to obtain more information about the dimensions of structural units by applying the normal distribution in decomposition of the Raman spectra.

It should be further noted that the sublimation energy of diamond-like phases is less than the sublimation energy of diamond, as was found in [23], which indicates their lower thermodynamic stability. Therefore, such phases cannot be obtained under equilibrium thermodynamic conditions [23].

Optical Spectroscopy

As determined above, the thermodynamic parameters have a substantial effect on the atomic structure formation in amorphous carbon films. This effect is reflected in a ratio of the sp^2/sp^3 bonds and, consequently, in the sizes of regions with a quasi-ordered

structure. The estimation of the degree of structural ordering showed that regions composed of sp^3 sites are present in the amorphous matrix at temperatures below 150°C. However, graphite-like structures growing from sp^2 sites are observed with an increase in the synthesis temperature.

In [17], the issue concerning the band structure of amorphous carbon was investigated in most detail. It was shown that the bandgap width is inversely proportional to the dimensions of nanoclusters comprised of sp^2 sites. According to the model of disordered graphite layers of about 15 Å in diameter bounded by sp^3 sites, the width of optical bandgap corresponds to about 0.5 eV. As was found in [17], the π interactions between the π states of the nearest neighbors of the first and second coordination spheres that create the short-range order of the atomic structure are behind the formation of the band structure. Therefore, the contribution of each of the $p\pi$ and $p\sigma$ states to the formation of band edges was taken into account. Depending on the sp^2/sp^3 -bond percentage ratio, the contribution of π and σ electrons in the formation of band edges and electronic density of states (EDOS) near the Fermi level (E_F) changes. At the same time, the top of the valence band, the bottom of the conduction band, and EDOS both inside the bandgap and near E_F is formed by low-energy electrons of π - π^* states. As noted in [15, 17], the energy gap between the edges of the σ - σ^* bands is about 6 eV. Therefore, the energy levels of σ states are far from the Fermi level. If the concentration of sp^3 sites in the amorphous film is more than 20%, then a decrease in the population of π electrons has a substantial effect on the EDOS near the Fermi level and at the band edges [17, 18]. This is why the E_g value increases. As is shown in [17, 18], the number of sp^2 sites and their orientation have a substantial effect on the width of optical bandgap.

The width of optical bandgap is a structurally sensitive parameter that substantially contributes to the understanding of the band structure and its formation. As was determined from the transmission and reflection spectra, the dependence of the absorption coefficient (α) on the wavelengths of light in the range of values $\alpha \sim 10^3$ – 10^5 cm⁻¹ obeys Tauc's quadratic law $\alpha h\nu = B(h\nu - E_g)^2$ [18, 24] for allowed direct-bandgap transitions. The bandgap width was determined in the region of values $\alpha \sim 10^5$ cm⁻¹ and $\alpha d \sim 1$. The dependences of E_g on the substrate temperature and Ar gas pressure are shown in Fig. 4. As can be seen from Fig. 4a, the E_g variation substantially depends on temperature and $\Delta E_g \sim 1$ eV at $\Delta T_{\text{sub}} = 200^\circ\text{C}$. A similar pattern of changes in the $E_g(T_{\text{sub}})$ dependence is also observed with other synthesis pressures and P_d .

As is seen from Fig. 4a, an increase in the synthesis temperature gives rise to a decrease in the E_g value. As has been established above, the dimensions of graphite-like nanoclusters comprised of sp^2 sites increase

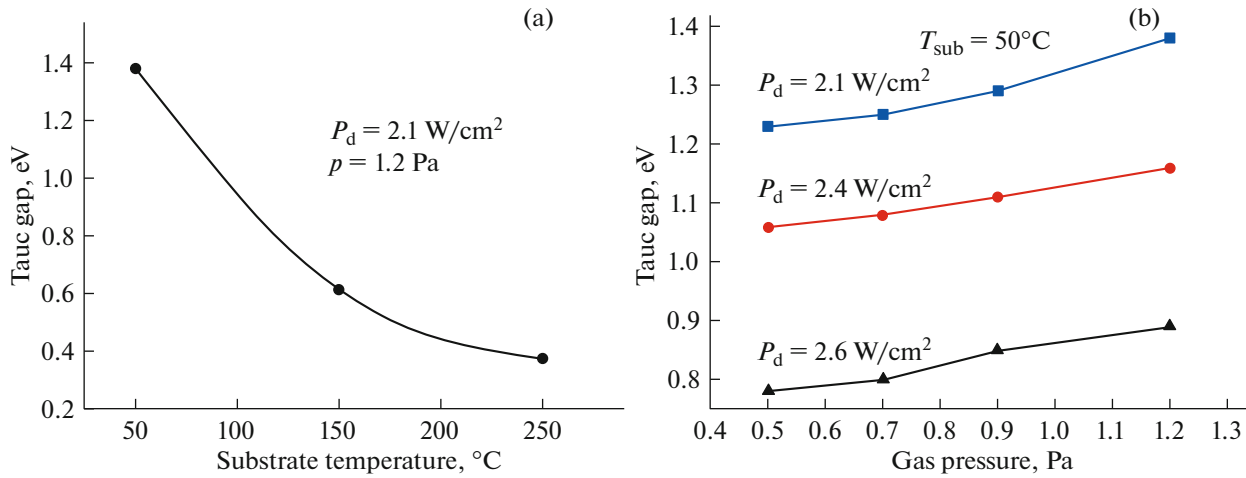


Fig. 4. Dependence of the width of optical bandgap on (a) the synthesis temperature of DLC films and (b) argon pressure for three P_d values.

from 6 to 12 Å with an increase in the synthesis temperature. That is, we observe an increase in the region with a quasi-ordered structure, the dimensions of which can be classified as a medium-range order of the atomic structure. The change in the dimensions of nanoclusters comprised of sp^2 sites correlates with the E_g value change.

As shown above (Fig. 2), the position of the G peak at $T_{\text{sub}} = 50^{\circ}\text{C}$ is the same for three P_d values and this constancy of the G peak position indicates the identical short-range order of the atomic structure. In Fig. 4b, we observe dependence of E_g on both the power density of DC discharge and Ar gas pressure under given a-C film synthesis conditions. With an increase in the P_d value by 0.5 W/cm^2 , the E_g value decreases by about 0.47 eV on average. In addition, it can be seen that the E_g change is directly proportional to the change in the gas pressure; i.e., E_g at $P_d = 2.1 \text{ W/cm}^2$ increases by 0.15 eV with an increase in p and $\Delta E_g = 0.1 \text{ eV}$ at $P_d = 2.6 \text{ W/cm}^2$. Such a change reveals a substantial effect of the power density of ion-plasma discharge and gas pressure on the structure. As was determined above, the clusters comprised of sp^2 and sp^3 sites that form an a-C film have dimensions greater than the radius of the second coordination sphere at $T_{\text{sub}} = 50^{\circ}\text{C}$. The cluster dimensions reach 10 \AA , and the calculations show that the change in the average size of regions with sp^2 sites by about 1 \AA gives rise to a change in the bandgap optical width. Thus, this confirms the hypothesis made in [17] that both the short- and medium-range orders of the atomic structure in amorphous carbon determine the formation of a band structure and the electron density distribution over the bands, which may be a unique feature inherent only to a-C carbon.

It was claimed in [1, 15] that if the bandgap energy of a-C films takes values in the range from 0.2 to 1 eV , then these films are classified as graphite-like amorphous carbon a-C. If the E_g values are in the range from 1 to 2.5 eV , then such films are structurally classified as tetragonal amorphous carbon (ta-C) films or they are also called “diamond-like films” [1, 14].

XPS Spectroscopy

To study the sp^2/sp^3 -hybridized bond ratios on the film surface, the XPS method was used. A common XPS spectrum typical for all the studied samples is given in Fig. 5, from which one can see that certain amounts of oxygen ($\leq 10 \text{ at } \%$) and, to a much lesser extent, nitrogen ($< 1.3 \text{ at } \%$) are present in the carbon film. The occurrence of oxygen and nitrogen in an a-C film is associated with the adsorption from atmo-

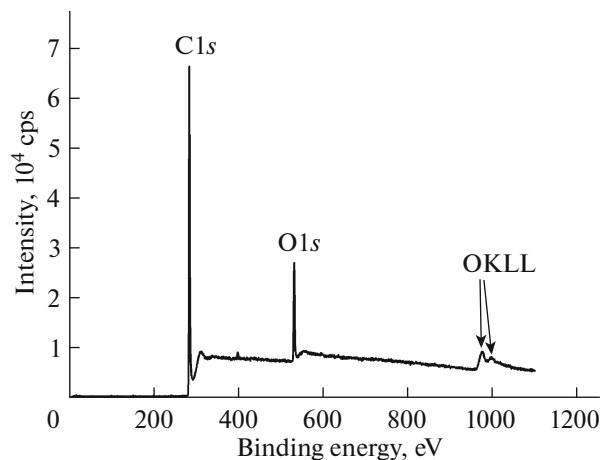


Fig. 5. XPS of an a-C film synthesized with 2.1 W/cm^2 .

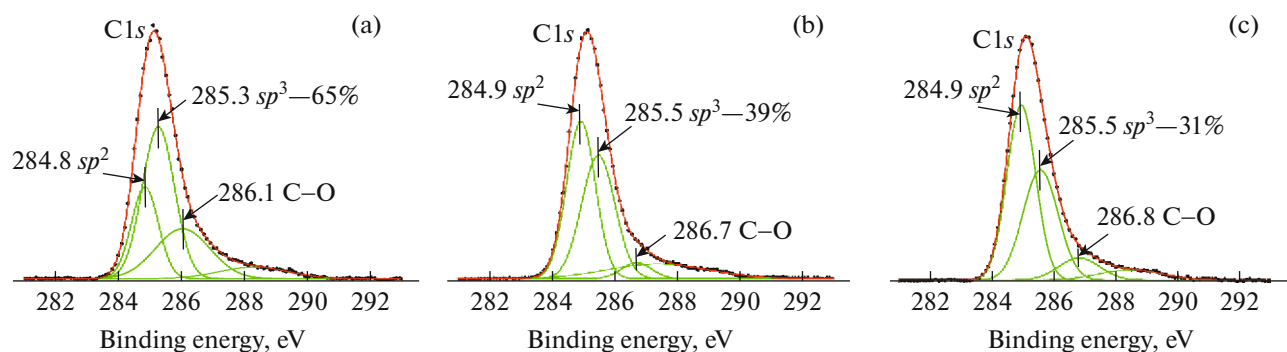


Fig. 6. XPS of a-C films synthesized at $T_{\text{sub}} = 50^{\circ}\text{C}$ and with different power densities of (a) 2.1, (b) 2.4, and (c) 2.6 W/cm^2 .

sphere. The C1s carbon peak is found in the region with an energy of about 285.2 eV and its presence is typical for all samples prepared at temperatures below 50°C .

To determine the concentration of sp^3 bonds, the C1s peak was decomposed into components (Fig. 6). The background was subtracted using the Shirley method. The position of the peak in the region of 284.9 eV corresponds to sp^2 C–C bonds, the peak at 285.25 eV corresponds to sp^3 C–C bonds, and the Gaussian peak maximums located in the region above 286 eV correspond to C–O and C–N bonds. As can be seen, the portion of sp^3 bonds decreases with an increase in the power density, whilst the portion of sp^2 bonds increases. The concentrations of the sp^2 and sp^3 C–C bonds were estimated from the areas of Gaussian peaks, taking into account the contribution of the C–O and C–N bonds. The percentages of sp^3 bonds for each value of the synthesis power density are given in Fig. 6. The increases in the concentration of sp^2 bonds with an increase in the power density level are 30, 50, and 53%, respectively. Comparing the results given in Figs. 4b and 6, one can see a definite correlation between changes in the width of optical bandgap and sp^2/sp^3 -bond ratio.

CONCLUSIONS

The use of an electromagnet in a magnetron allows one to maintain the constant E/p ratio during synthesis. The voltage and current of the DC-discharge plasma is adjusted by the magnetron magnetic field value, which makes it possible to carry out a detailed study of the effect of the thermodynamic and kinetic parameters of synthesis on the structure and properties of carbon nanoheteromorphous films. Moreover, this makes it possible to undertake a study of the effect of the gas pressure for three different values of the power density of plasma discharge on the structure formation with the same DC-discharge current, as well as to determine the influence of the structure on the width of optical bandgap. The existence of certain

relationships between the synthesis conditions, structure, and width of optical bandgap of amorphous carbon films is shown by the Raman, XPS, and optical spectroscopy methods.

Carbon films synthesized under nonequilibrium conditions have a disordered structure consisting of graphite- and diamond-like nanoclusters. The dimensions of these nanoclusters depend on the thermodynamic and kinetic parameters of synthesis and range from 6 to 12 Å. The dimensions of crystal-like particles are commensurate with the medium-range order of the structure, and a change in the dimensions of the medium-range order regions gives rise, as shown in this study, to a change in the bandgap width.

The width of optical bandgap takes a value of less than 1 eV in a-C films synthesized at 50°C with a power density of plasma discharge of 2.6 W/cm^2 . Such carbon films largely consist of a graphite-like structure. The position of the G peak in this case is determined at 1545 cm^{-1} , which indicates the formation of structures comprised of sp^3 sites, i.e., diamond-like structures. However, it is generally accepted that a-C films with E_g values greater than 1 eV should relate to diamond-like films. Thus, we see ambiguity in the characterization of the atomic structure at a synthesis temperature of 50°C .

As can be concluded from the above, the study of the structure of amorphous carbon films by the RS method is substantially complemented by the optical methods of investigation and X-ray photoelectron spectroscopy. The E_g parameter is determined by the EDOS distribution of bandgap edges, which is formed by relative concentrations of sp^2 and sp^3 sites, as is confirmed by the XPS analysis data.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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