ATOMIC CLUSTERS

Specific Features of the Structure of Detonation Nanodiamonds from Results of Electron Microscopy Investigations

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Abstract—The experimental results of a comprehensive investigation of the structure of detonation synthesis nanodiamonds by electron microscopy methods have been presented. The morphology of diamond nanoparticles has been investigated and the microdiffraction patterns have been analyzed. The method of characteristic fast electron energy loss spectroscopy in transmission electron microscopy has been used. The local density of structural components of a nanodiamond (diamond core and fullerene-like shell) has been obtained. The shape of the shell surrounding the nanocrystal has been determined using model calculations. A hypothesis explaining the charging of the nanodiamond surface has been proposed.

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1. INTRODUCTION

The detonation synthesis of nanodiamonds has been performed under nonequilibrium conditions at high pressures (~20 GPa) and temperatures (~3000 K) in the region of the existence of the stable diamond phase. The nucleation and growth of this phase proceed during very short periods of time or, more precisely, for several fractions of a microsecond [1]. The diamond nanocrystals formed in the course of these processes have a crystal lattice predominantly belonging to the cubic system [2, 3]. The surface of diamond nanocrystals exhibits unusual properties: namely, it is covered with a carbon-containing shell that consists predominantly of carbon atoms in the sp^2 -hybridization state [4-7]. Information about the structure and properties of carbon-containing shells on the surface of diamond nanocrystals is important for understanding the processes of interaction of nanodiamond particles both among themselves and with other substances. Furthermore, the space between the diamond nanocrystals is filled with graphite-like and/or amorphous carbon, which, then, is almost completely removed during physicochemical treatment after the synthesis [8].

The widespread use of diamond powders and suspensions [9, 10] requires continuous improvement of the synthesis procedures, post-processing techniques, and current control methods [11]. Electron microscopy investigations of nanodiamonds are of the utmost importance for solving these problems.

The purpose of this study was to examine the specific features revealed in the structure of the core and shell of a diamond nanocluster directly in an electron microscope using three complementary methods. First, in order to investigate the morphology of diamond nanoparticles, we analyzed the electron microscopy images of nanoobjects; second, we examined the microdiffraction patterns; and, third, we used characteristic fast electron energy loss spectroscopy (EELS). In this paper, we present two types of fragments of the EELS spectra. If the electron energy loss (Δ) is relatively small, i.e., $\Delta < 100$ eV, interband plasmons are predominantly excited in the carbon materials [12]. If the electron energy loss is in the range 280 eV < Δ < 380 eV, the C 1s core electrons are excited into the conduction band of the material, which allows direct observation of the density of unoccupied electronic states.

We also used additional methods, namely, soft X-ray absorption [13] and Raman spectroscopy. These methods are widely accepted and allow comparison of the electron microscopy data with the results obtained by other methods.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

All measurements were performed on standard powder samples ("Alit" and "Tekhnolog") obtained by the detonation synthesis in the liquid phase [1, 3]. The main characteristics of the samples are as follows: the





Fig. 1. (a) TEM image of a nanodiamond powder. (b) A fragment of high-resolution TEM image. *AA* is the scanning line in the measurement of the characteristic electron energy loss spectra.

pycnometric density is $3.0-3.3 \text{ g/cm}^3$, the surface area is $400-500 \text{ m}^2/\text{g}$, the average size of aggregates is 120-140 nm, the temperature of the onset of oxidation in air is 350° C, and the particle charge is negative.

The investigations were performed using high-resolution transmission electron microscopy (HR-TEM) with a JEOL JEM 2000 FX II electron microscope. The maximum spatial resolution used in the formation of TEM images was 0.2 nm. In addition to the direct observation of the morphology of nanocrystals, the samples were examined using the microdiffraction and EELS methods. The EELS spectra were measured with a resolution of ~1 eV and an electron energy of ~200 keV.

The near edge X-ray absorption fine structure (NEXAFS) spectra of the "Tekhnolog" detonation nanodiamond sample were investigated at the Rus-

sian–German beamline of extraction and monochromatization of synchrotron radiation from the electron storage ring BESSY II (Berlin, Germany). The NEX-AFS spectra were obtained by recording the total electron yield of the external X-ray photoemission effect in the mode of measurement of the leakage current from the sample by varying the energy of incident photons in the range 280–350 eV. The technique used in these measurements was described in more details in [12].

The Raman spectra were measured at room temperature. The measurements were carried out using a "Senterra" confocal Raman microscope spectrometer operating at a laser wavelength of 532 nm with a spectral resolution of $1-3 \text{ cm}^{-1}$ and a spatial resolution of $1 \mu m$. Only the Stokes component of the scattering in the wave number range 1000–2000 cm⁻¹ was measured. All the measurements were performed at a constant laser power.

3. DESCRIPTION OF THE RESULTS

3.1. Morphology of Diamond Nanocrystals

Figure 1 shows the TEM images of the nanodiamond powder for two magnifications. In the TEM image obtained with a magnification that makes it possible to examine a sufficiently large number of nanoparticles (Fig. 1a), it is revealed that the diamond nanocrystals have different sizes. These nanocrystals are combined into agglomerates. In the TEM image obtained with a high resolution (Fig. 1b), we can see that the shape of nanocrystals is close to cubic. Figure 1b shows two adjacent nanocrystals with cube side sizes of ~4 and ~7 nm. Layers of carbon atoms are well distinguishable. A thin shell on the surface is also clearly seen. The AA line in Fig. 1a approximately corresponds to the scanning line in the measurement of the EELS spectra. A total of six EELS spectra were obtained along this line (for details, see below).

Thus, the direct observation has revealed the cubic shape of the nanocrystals, the size distribution of the nanocrystals, and their agglomeration.

3.2. Microdiffraction of Nanocrystals

The microdiffraction pattern of a typical agglomerate consisting of diamond nanocrystals is shown in Fig. 2a. The most intense diffraction reflection D_1 1 represents the coherent scattering from the diagonal (111) planes of the diamond. Figure 2b shows a magnified fragment of the diffraction ring caused by the scattering from the (111) planes. The broadening of this diffraction reflection r_1-r_2 is associated with the small sizes of nanoclusters, as well as with the variations in the interplanar distances. The evaluation of the interplanar distances $d_{111} \approx 0.20-0.22$ nm. It should be noted that, in a large diamond single crystal, the corresponding distance is equal to 0.206 nm [14]. This

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Fig. 2. (a) Microdiffraction pattern of a typical agglomerate consisting of diamond nanocrystals. (b) Fragment of the diffraction reflection (111). D_1 , D_2 , and D_3 are the electron microdiffraction maxima; and r_1 and r_2 are the inner and outer radii of the diffraction ring (111), respectively.

experimental fact is quite consistent with the results of the calculations presented in [15]. The authors determined the local structure of diamond nanoclusters and demonstrated that there is a significant increase in the interatomic distances in nanoclusters as compared to the large diamond crystal.

3.3. Electron Energy Loss Spectra

Figure 3 shows two EELS spectra for the case where the electron energy loss lies in the range $0 < \Delta <$ 70 eV. Spectrum I was measured near the center of one of the diamond nanocrystals, whereas spectrum II was obtained near the edge of one of the diamond nanocrystals. The experimental EELS spectra were subjected to the following methodological treatment. The

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Fig. 3. EELS spectra of diamond nanocrystals: (I) from the central part of one of the diamond nanocrystals and (II) from the edge of one of the diamond nanocrystals.

scale of the abscissa axis was changed so that the energy was reckoned from the energy corresponding to the maximum of the intensity of elastically scattered electrons: $\Delta = 0$. The scale of the ordinate axis was reduced so that the maxima of the intensities of inelastically scattered electrons at $\Delta = 0$ coincided.

The two EELS spectra shown in Fig. 3 are characterized by two main maxima of the energy losses, namely, *A* and *B*. However, the relative intensity of the second maximum (*B*) in spectrum II is significantly lower. In addition to the two main maxima, spectrum I of the nanodiamond exhibits a broad shoulder *C* in the high energy loss range. In spectrum II of the nanodiamond, such a shoulder is not observed. Note also that, in both spectra, there is no π -plasmon maximum.

Figure 4 shows two spectra of different nature for samples of nanodiamonds. The first spectrum, which is designated as ND-EELS, corresponds to the electron energy losses under excitation of the C 1s core level when the electron beam is positioned at the center of one of the nanocrystals. The second spectrum (ND-NEXAFS) corresponds to the photon absorption in the spectral range 280-320 eV for a nanodiamond powder. For comparison, the dashed line in Fig. 4 shows the HOPG-NEXAFS spectrum of graphite (HOPG stands for highly oriented pyrolytic graphite). In order to compare the spectra of different nature, the energy scale was renormalized: the origin was taken as the position of the maximum of the π prepeak (at a photon energy of 284.9 eV). This local maximum was reliably observed in the spectra of nanodiamonds and graphite [16]. It is associated with the increased density of free π^* -electronic states.



Fig. 4. Comparison of the electronic states in the conduction band of nanodiamonds (ND) for two spectra of different nature. The ND-EELS spectrum corresponds to the characteristic electron energy losses under excitation of the 1s core level of carbon. The ND-NEXAFS spectrum corresponds to the measurements of the photon absorption under excitation of the C 1s core level. For comparison, the dashed line shows the photon absorption spectrum measured under excitation of the C 1s level of graphite (HOPG-NEXAFS). The spectra are brought into coincidence in the position of the π^* -absorption peak. The energy corresponding to this peak is taken as zero. (*1–4*) Features of the density of states for the conduction band of the diamond single crystal (see Table 1).

The main features (maxima and shoulder) observed in the two spectra of different nature for nanodiamond samples are in satisfactory agreement. The vertical arrows in Fig. 4 indicate the positions of the maxima of the density of states in the conduction band for the diamond single crystal according to the data reported in [14, 17, 18]. The energies corresponding to the maximum densities of states in the conduction band are numbered 1-4. The parenthetic values presented in Table 1 are the energies at the high-symmetry points Γ , X, and L in the Brillouin zone. The numerals 1-4 in

Table 1. Energies in electron-volts (in parentheses) at the high-symmetry points Γ , *X*, and *L* of the band spectrum of the diamond according to the data obtained by different authors (the energy is reckoned from the valence band top)

Arrow numbers in Fig. 4.	[14]	[17]	[18]
1	$\Gamma_{15}(6.6), X_1(6)$	$\Gamma_{15}(5.6)$	$\Gamma_{15}(6.4), X_1(4.5)$
2	$L_3(8.6), L_1(8.7)$	_	—
3	_	$\Gamma_2(14-15)$	$\Gamma_2(14.9), X_3(16.7)$
4	_	$L_2(20)$	



Fig. 5. EELS spectra of the diamond nanocrystal in the conduction band of the nanodiamond: (I) from the center of the nanocrystal and (II) from the edge of the nanocrystal. The vertical arrow indicates the π^* -states with the energy taken as zero.

Table 1 correspond to the numbers of the arrows in Fig. 4. In all cases, the zero-energy value is chosen as the energy of the triply degenerate state Γ_{25} . This electronic state at the center of the Brillouin zone corresponds to the top of the valence band in the diamond crystal. Arrows *I* correspond to the electronic states near the bottom of the conduction band in the diamond crystal.

The two dominant maxima observed at zero energy and an energy of ~8 eV in the HOPG-NEXAFS spectrum (Fig. 4) correspond to the free π^* -electronic states in the vicinity of the points *M* and *T* of the Brillouin zone, respectively. Unfortunately, the specific features of the electron density of states of graphite almost completely coincide with the corresponding features observed for the diamond; consequently, from a comparison of these spectra, it is difficult to identify the possible presence of the "graphite-like phase" in the spectrum of the nanodiamond.

Two electron energy loss spectra obtained under excitation of the C 1s core level upon scanning in the electron microscope are compared in Fig. 5. The electron energy loss in this case was varied in the range from 280 to 380 eV. However, in the construction of these spectra, the origin was taken as the position of the maximum of the π^* -prepeak, as in the spectra shown in Fig. 4. Just as in Fig. 3, spectrum I corresponds to the measurements in the vicinity of the central part of one of the nanocrystals, and spectrum II, to the measurements in the vicinity of the edge of the

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nanocrystal. The chosen wide range of energy losses Δ allows observation of two additional characteristic features in the electron energy loss spectra: the first maximum is observed at an energy 39–41 eV above the π^* -states, whereas the second maximum is located at an energy 60–90 eV above the specified mark (shaded).

There are no significant differences in spectra I and II for an energy loss of less than 30 eV. Only the intensities of the maxima differ from each other. For example, the maximum of π^* -states at zero energy in spectrum II is significantly higher than that in spectrum I taken from the central part of the nanocrystal. However, there are significant differences in these spectra for higher energy losses. In particular, the shaded broad feature of spectrum I does not manifest itself in spectrum II.

The EELS investigations have demonstrated that the electronic properties of the core of the diamond nanocrystal differ significantly from those of its periphery.

3.4. Raman Spectrum

A typical Raman spectrum for the nanodiamond sample in the wave number range 1000–1700 cm⁻¹ is shown in Fig. 6. This spectrum has a complex shape and consists of at least four components. The dominant maximum centered at the wave number $v_A =$ 1326 cm⁻¹ corresponds to the diamond phase. In the diamond single crystal, this maximum is observed at the wave number of 1332 cm⁻¹ and has a small width at half-maximum $\delta_A \approx 5-10$ cm⁻¹ [19]. A somewhat smaller value of v_A is due to the small size of the crystal and large interlayer distances [20]. The value $\delta_A =$ 28.7 cm⁻¹ (Table 2) also indicates the small size of the scattering region.

The overall shape of the Raman spectrum shown in Fig. 6 differs significantly from the shape of the Raman spectrum of a microcrystalline diamond produced by the chemical decomposition of hydrocarbons on a substrate [21]. The Raman spectrum is decomposed into four Gaussians (lines a-d). The parameters and assignment of the Gaussians are presented in Table 2.



Fig. 6. Experimental Raman spectrum for the nanodiamond sample (thick solid curve). (a-d) Gaussians and (Σ) sum of the Gaussians.

Maximum *d* is characterized by the wave number corresponding to the longitudinal stretching vibrations of hexagons. The obtained value substantially exceeds the corresponding value in graphite and graphite-like materials: 1580 cm^{-1} [26]. This effect is presumably caused by the strong deformation of the hexagons that form the surface nanoclusters [27].

4. DISCUSSION OF THE RESULTS

4.1. Local Density

The results of the electron microscopy investigations presented above allowed us to concretize and refine the structure of the nanocore and shell of the detonation diamond nanocrystals. First of all, we discuss the results of the EELS investigations performed directly in the electron microscope. The plasmon loss spectra are shown in Fig. 3. In our opinion, the appearance of the double maximum A-B in the EELS spectra is associated with the presence of the shell on the surface of detonation synthesis diamond nanoc-

Table 2. Parameters of the decomposition of the Raman spectrum of nanodiamonds into the Gaussian components a-d (in the last column, the assignment of the components is given according to [22, 23])

Notation of the Gaussian	Position of the maximum, cm^{-1}	Full width at half-maxi- mum, cm ⁻¹	Nature of the Gaussian
а	1275	187.4	Chains with radicals*
b	1326	28.7	Diamond
С	1545	124.3	Chains
d	1620	52	Deformed hexagons and chains

Note: The presence of radicals of the hydroxyl type (C–OH), the carbonyl groups (COOH), and the carboxyl groups (CO) on the surface is confirmed by the results obtained from the study of the photoelectron spectra of the C 1s states [24] and by Raman spectroscopy [25].

rystals. Maximum A corresponds to the characteristic energy losses in this shell and is observed at an energy loss of $\sim 21.0 - 21.8$ eV. This is a manifestation of the $\pi + \sigma$ -plasmons [12, 28]. Maximum *B* corresponds to the characteristic energy losses in the diamond moiety of the sample. This maximum is observed at an energy loss $\Delta \approx 32.5$ eV and is caused by the excitation of the σ -plasmons [12]. A detailed description of the nature of the aforementioned maxima is presented in [28]. Plasmons represent an important tool for the identification of allotropic forms of carbon, including those obtained under substantially nonequilibrium conditions. The plasmon self-energy E_p is sensitive to the density ρ of the material (see, for example, [28]). The well-known relationship between the plasmon energy E_p and the density ρ of the material [29] can be rearranged to the form which is quite acceptable for the interband σ - and π + σ -plasmons:

$$E_p^2 = \frac{\hbar^2 e^2 N_{\text{eff}}}{m_a m^* \varepsilon_0 \varepsilon_m} \rho.$$
(1)

In formula (1), apart from the well-known universal constants (\hbar is the Planck constant, ϵ_0 is the dielectric constant, m is the electron mass, and e is the elementary charge), there are the following quantities: m_a is the carbon mass, $N_{\rm eff}$ is the effective concentration of valence electrons, and m^* is the effective mass of the valence electrons. The calculated slope of the linear dependence of the square of the plasmon energy on the density of the material at the effective concentration of valence electrons $N_{\rm eff} \approx 3$ [30] is equal to $315 \text{ eV}^2 \text{ cm}^3/\text{g}$. In the calculations, it is assumed that the effective mass m^* coincides with the mass of a free electron and the permittivity of the material is $\varepsilon_m = 1$. In this case, we can estimate the local density of carbon phases constituting the structure of the nanodiamond, because we know the values of $\Delta_B \approx E_{pB} \approx$ 32.5 eV (maximum *B* in Fig. 3, which corresponds to the diamond component) and $\Delta_A \approx E_{pA} \approx 21-21.8$ eV (maximum A). According to formula (1), we obtain the local density $\rho_D \approx 3.35 \text{ g/cm}^3$ for the diamond phase and $\rho_G \approx 1.5 \text{ g/cm}^3$ for the graphite-like phase. It is known that the densities of crystalline diamond and graphite are equal to 3.50 and 2.25 g/cm³, respectively. The above-estimated density of the diamond phase is only $\sim 4\%$ lower than the density of the massive single crystal. Taking into account that the (111) interlayer parameter of the nanodiamond crystal is 5– 7% larger than the equilibrium value (see above), the differences in the densities of these phases can be considered to be quite reasonable.

The pycnometric density of the studied nanodiamonds, according to the manufacturers, varies from 3.0 to 3.3 g/cm³. Therefore, we can estimate the relative volume content of the diamond and graphite-like components. In particular, at the lower pycnometric density of 3.0 g/cm³, the content of the diamond component in the real nanocrystal is ~60%, whereas at the higher pycnometric density of 3.3 g/cm^3 , this content reaches ~85%. Consequently, the thickness of the graphite-like component on the surface of the nanocrystal is equal to 0.70 nm in the first case, and it is equal to 0.25 nm in the second case. If one layer of the coating has a thickness of 0.335 nm (for example, as in graphene), the coating in the first case obviously consists of two layers, whereas in the second case, the coating is single-layer but not continuous. In the real material, of course, there are two cases: the thickness of the coating is smaller for the passive faces of the nanocrystal and larger for the active faces [31].

By analyzing the Raman spectra, we can refine the specific features of the structure of the shell of the nanodiamond (Table 2). The coating consists of a network of deformed hexagons, and its structure is similar to the structure of the shell consisting of fragments of large fullerenes. The coating is fixed on the surface of the diamond nanocrystal by carbon chains containing radicals. The radicals and functional groups, most likely, are joined to the carbon chain during washing of the ready synthesized material.

4.2. The Model of Surface Coating

The analysis of the high-resolution TEM images (Fig. 1b) revealed that, on the surface of nanodiamonds, there are layered dome-shaped graphene structures that resemble fragments of fullerenes. The characteristic distances between the points of attachment of the fullerene-like "cap" to the surface of the nanodiamond lie in the range $\sim 0.9-1.0$ nm, and the height of the "cap" is ~ 0.4 nm.

Figure 7 shows the schematic drawings of geometrically optimized structural models of the graphene shell covering the surface of nanodiamonds. The calculations were performed using the MM+ molecular mechanics method [32]. Fragments of graphene layers containing from 70 to 114 atoms were fixed on the (111) surface of a diamond cluster consisting of 836 carbon atoms. Figure 7a shows the structure of a model "cap" with a characteristic size of 1 nm, which is linked to the surface of the diamond cluster by six bonds. In this case, the height of the "cap," i.e., the distance from the diamond surface to the graphene layer at the layer center, is approximately equal to 0.6 nm. This distance exceeds the aforementioned experimental value. Therefore, we carried out an additional calculation of another way of fixing the graphene "cap" on the diamond face with a larger number of cross-linkings (Fig. 7b). In this case, we succeeded in achieving an almost exact match between the structural parameters of the model and the TEM images. The full geometry optimization of the surface of the diamond clusters covered with deformed graphene layers demonstrated that the cross-linkings have no appreciable effect on the parameters of the crystal structure of the diamond

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Fig. 7. Structural models of the shell covering the surface of the nanodiamond: (a, b) different ways of fixing the graphene layer on the diamond surface and (c) fragment of the fullerene-like graphene shell with a topological defect.

cluster itself. Quite possibly, the deformed graphene layers contain topological defects, i.e., pentagons. Then, owing to the presence of such defects in the graphene layers, the dome-shaped structure of these layers can be considered as a fragment of fullerene (Fig. 7c).

The graphene shells of diamond nanocrystals observed in this study are single-layer. Similar shells observed in [7] are predominantly double-layer. The graphene shells can also contain a larger number of layers [6, 33]. The formation of graphene shells apparently occurs according to the mechanism described in [33]: the peeling of the surface layers of the diamond nanocrystal is accompanied by the transition of carbon atoms from the sp^3 -hybridization state to the sp^2 -hybridized state, which results in the formation of a graphene shell.

4.3. Surface Charge

The deformation of hexagons and chains as well as the attachment of the "cap" to the surface of the nanodiamond are responsible for the charging of the surface of the nanocrystal with respect to the nanocrystal bulk. The origin of the charging of the nanodiamond

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Wave number, arb. units

Fig. 8. Schematic representation of the electronic states near the surface of the nanodiamond: (a) energy bands in the diamond (*D*) and (b) energy bands in the shell (*G*). Designations: π and σ are the valence electronic states; π^* and σ^* are the electronic states in the conduction band; E_F is the Fermi energy; and *X*, *M*, and Γ and are the high-symmetry points in the Brillouin zone.

surface can be understood when considering the spectra shown in Figs. 4 and 5. Figure 4 actually presents the energy distribution of the density of states in the conduction band in comparison with the corresponding electronic states of graphite. The π^* maximum is located 4–5 eV lower than the states corresponding to the bottom of the conduction band in the diamond moiety of the crystal. Figure 8 shows a qualitative energy diagram of the electronic states near the nanodiamond surface with due regard for the experimental results presented in Fig. 4. The Fermi level in Fig. 8 near the surface in located in the vicinity of the edge of the free π^* -electronic states so as to be consistent with the experimental data.

According to the proposed scheme, the energy bands in the bulk of the nanodiamond (Fig. 8a) are shifted upward with respect to the energy bands on the nanodiamond surface; i.e., there occurs charge transfer from the core (*D*) to the periphery (*G*) of the nanodiamond. The surface becomes negatively charged relative to the bulk of the nanocrystal. The Fermi level in the nanodiamond core is located near the top of the valence band (Γ_{25}), and on the surface, it is located near the bottom of the π^* -subband.

5. CONCLUSIONS

This paper presents the results of the investigation of the detonation nanodiamonds directly in the elec-

tron microscope. The investigation has been performed using the methods of microdiffraction and characteristic electron energy loss spectroscopy with scanning along the diamond nanocrystal. The existing model of the structure of detonation synthesis nanodiamonds has been confirmed and refined: each nanocluster consists of the diamond core and the graphene shell. The statements of plasmonics have been used for evaluating the local density of these two components of nanodiamonds. The parameters of the graphene shell, which is similar in structure to a deformed fullerene-like "cap" linked with the diamond core by covalent bonds, have been determined from the molecular mechanics simulation using the MM+ method. The existence of functional groups on the nanodiamond surface has been confirmed taking into account additional data on Raman spectroscopy.

The analysis of the EELS spectra obtained directly in the electron microscope has revealed additional features in the electronic structure of the diamond core. In particular, it has been found that, in the electron energy loss range $0 < \Delta < 70$ eV, there is a broad shoulder with the maximum at $\Delta \approx 48-50$ eV, which is typical of the diamond component. The nature of this shoulder will be elucidated in the future.

A simple energy diagram of the contact between two carbon phases that constitute diamond nanoparticles has been proposed. This diagram explains the appearance of a negative charge on the shell [7].

The results obtained in this work can be useful for medical purposes, as well as for the design and fabrication of new composite (solid and liquid) materials containing nanodiamonds as a component.

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