

# Electronic structure of diamond/graphite composite nanoparticles

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**Abstract.** The electronic structure of samples produced by nanodiamond annealing has been examined using ultra-soft X-ray emission and X-ray absorption spectroscopy. Analysis of spectra of diamond/graphite composites showed that carbon atoms constituting the nanoparticles are at least in three states: diamond-like state, graphitic-like state and interface carbon, characterized by high electron localization. Comparison between theoretical spectra of the models and experimental spectra suggested the latter states correspond to three-coordinated carbon atoms from diamond surface.

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## 1 Introduction

Diamond/graphite composites involve two forms of carbon, which are dramatically different in properties. A specificity of electron interactions at the interface can initiate unusual electrical, magnetic and optical features of material [1]. One of the most effective methods for production of diamond/graphite composite nanoparticles is an annealing of nanodiamonds (ND) in a high vacuum [2]. Precise temperature control makes it is possible to vary number of graphitic shells peeling from the diamond core. Graphitic covering was shown to change significantly the electronic properties of ND particles, particularly, their electric conductivity [3] and field electron emission characteristics [4].

The complete picture of electronic structure of a substance can be derived from measurement of X-ray emission and X-ray absorption spectra. The former spectrum arises as a result of electron transitions from occupied valence states to a previously created core hole, while the latter spectrum is formed due to transitions of the core electrons to unoccupied states. As the transitions are governed by the dipole selection rules, X-ray emission and X-ray absorption spectra probe the  $C2p$  partial density of states in the valence and conduction band of a specimen. Recently, X-ray emission spectroscopic examination of onion-like carbon produced at the intermediate stage of ND annealing has found an enhancement of density of

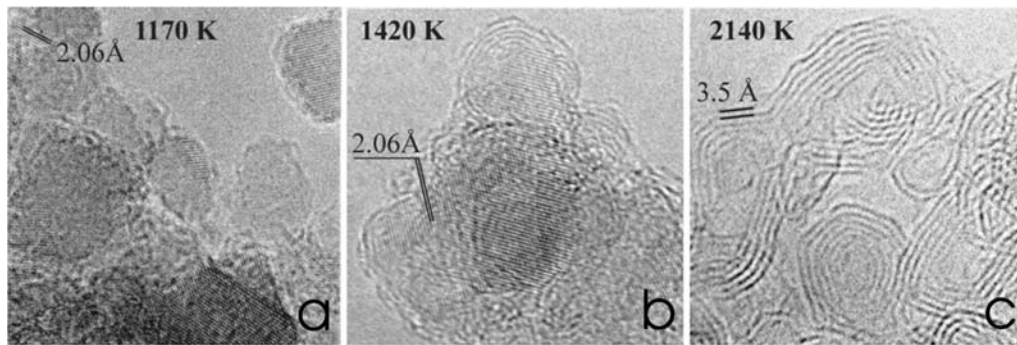
high energy states that was attributed to two-coordinated carbon atoms at vacancy boundaries [5]. X-ray spectra are rather characteristic for individual compounds, such as diamond or graphite, and they should be a superposition of electronic states of different kinds of carbon atoms constituting the composite particle. Subtraction of intensity attributed to the graphite and diamond components from a composite spectrum could supply information about electronic state of the interface.

In the present work we use X-ray emission and X-ray absorption spectroscopy for investigation of electronic structure of diamond/graphite composite nanoparticles produced in the result of ND annealing at moderate temperatures.

## 2 Experimental

The ND particles with average size of  $\sim 5.0$  nm were prepared by an explosive method [6] and then annealed in high-vacuum chamber ( $\sim 10^{-6}$  torr) at fixed temperatures (1170, 1420, 2140 K) during 0.5 h. The micrographs of the products were obtained with a JEM-4000EX transmission electron microscope (TEM). Annealing of ND at 1170 K removes the most of oxygenated functionalities from the sample retaining the particle structure unchanged. Actually, the distance between the interference fringes being equal to  $2.06 \text{ \AA}$  corresponds to the (111) diamond spacing (Fig. 1a). Increase of annealing temperature up

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**Fig. 1.** Transmission electron micrographs of nanodiamond particles heated at 1170 K (a), 1420 K (b), and 2140 K (c) in vacuum ( $\sim 10^{-6}$  torr).

to 1420 K causes development of graphitic shells over the diamond core (Fig. 1b). The measurements of the true density of this sample revealed the diamond weight fraction is equal to 0.82 [7]. Thus, the particles produced are diamond/graphite nanocomposites (NC). The transformation of ND particles is completed at 2140 K with formation of hollow nanopolyhedrons (NP) consisted of 3–10 graphitic layers (Fig. 1c).

X-ray emission spectra of the ND, NC and NP samples were recorded with laboratory X-ray spectrometer using a crystal-analyzer of ammonium biphthalate ( $\text{NH}_4\text{AP}$ ). The procedure was described elsewhere [8]. The samples were deposited on copper supports and cooled down to liquid nitrogen temperature in the vacuum chamber of the X-ray tube operating with copper anode ( $U = 6$  kV,  $I = 0.5$  A). The nonlinear reflection efficiency of  $\text{NH}_4\text{AP}$  crystal-analyzer allows the reliable measurement of the  $\text{K}\alpha$  emission of carbon in the energy region of 285–275 eV. Determination of the X-ray band energy was accurate to  $\pm 0.15$  eV with spectral resolution of  $\sim 0.5$  eV. Carbon K-edge X-ray absorption spectra (XAS) of the samples were measured using the Berlin synchrotron radiation facility at the Russian-German laboratory in BESSY-II. The XAS data were acquired in the total yield of electrons mode and normalized to the primary photon current from a gold-covered grid, which was recorded simultaneously. The energy resolution of incident radiation was about 0.06 eV.

### 3 Calculation

Three carbon models were used for interpretation of the experimental data. Diamond fragment has a tetrahedron shape with (111) faces, graphite fragment belongs to the  $D_{6h}$  point group of symmetry. The carbon-carbon bonds were assumed to be 1.54 and 1.42 Å long in the diamond and graphite respectively. The dangling bonds at the fragments boundary were saturated by hydrogen atoms yielding the  $\text{C}_{89}\text{H}_{60}$  and  $\text{C}_{96}\text{H}_{24}$  composition for the diamond and graphite models. The third model was obtained with elimination of hydrogen atoms from one of the faces of diamond fragment. Position of the naked carbon atoms was relaxed by the molecular mechanic MM+ force field. The optimized values of distance and valence angle for surface atoms constituted 1.53 Å and  $112.8^\circ$ .

The carbon models were calculated within the density functional theory (DFT). The three-parameter hybrid functional of Becke [9] and the Lee-Yang-Parr correlation functional [10] (B3LYP method) with 6-31G\* basis set included in the *Jaquar* program package [11] were utilized. The theoretical spectra were plotted on the basis of ground state calculation of the models. The energy of X-ray transition was equal to the difference between outer  $j$ th level and core  $i$ th level:

$$E_{ji} = \varepsilon_j - \varepsilon_i. \quad (1)$$

Taking into account localization of carbon 1s orbitals, the intensities of a spectrum were computed assuming that X-ray transition occurs within the same atom A:

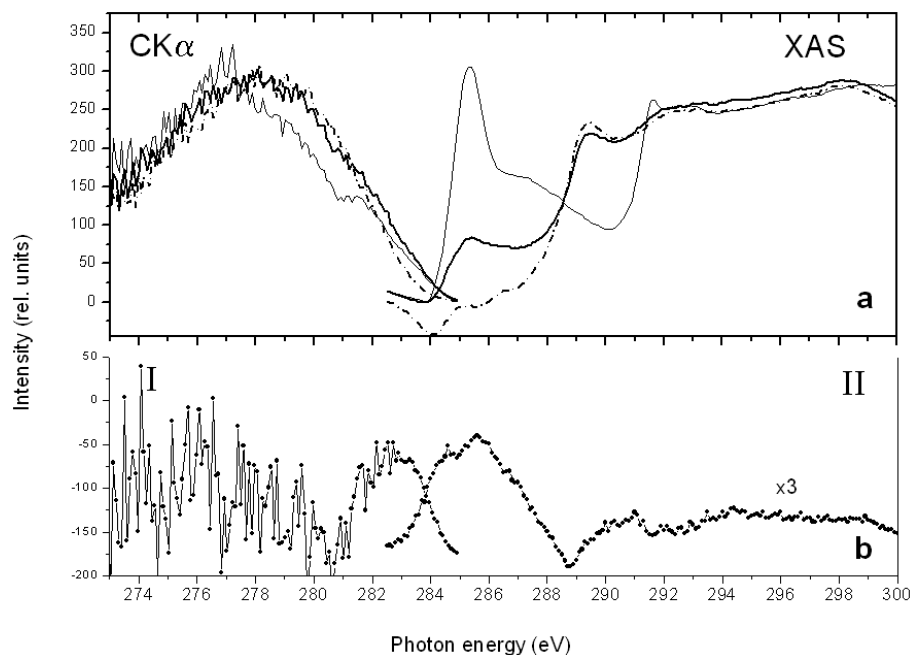
$$I_{ji} = \sum_A \sum_m \sum_n |C_{im}^A C_{jn}^A|^2, \quad (2)$$

where  $C_{im}$  and  $C_{jn}$  are the coefficients with which carbon 1s- and 2p-atomic orbitals (AOs) appear in the corresponding molecular orbitals (MOs). Calculated intensities of X-ray spectra were normalized by maximal value and broadened by convolution of the Lorentzian functions with half width at half maximum (HWHM) of 0.5 eV. To avoid the boundary effect on spectral profile only central atoms from diamond and graphite fragments and from bare (111) diamond face were involved in the calculation.

### 4 Results and discussion

Carbon K-edge emission and absorption spectra of the ND, NC, and NP samples are presented in Figure 2a. The ND  $\text{CK}\alpha$ -spectrum exhibits a broad maximum around 279 eV and XAS spectrum shows a single resonance at 289.2 eV. The spectra of ND particles are almost coincident with those of bulk diamond [12] that indicates a similar character of electron interactions in these species. The main differences consist in a broadening of maxima of the ND spectra and appearance of pre-edge features in the absorption region of 284.5–287 eV.

The spectra of NP particles have a more complex shape due to anisotropy of chemical bonding in graphite. The NP  $\text{CK}\alpha$ -spectrum exhibits main maximum around 277.5 eV and short-wave maximum at 281.6 eV, which correspond to the occupied  $\sigma$ - and  $\pi$ -states. The

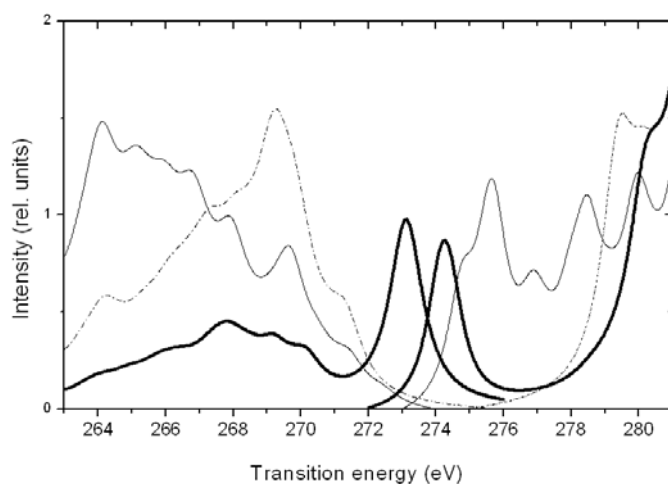


**Fig. 2.** CK $\alpha$ -spectra and CK-edge X-ray absorption spectra measured for the samples annealed at 1170 K (dot-and-dash line), 1420 K (bold solid line), and 2140 K (thin solid line) – (a). The curves I, II were obtained by subtraction of 0.82 part of ND spectrum intensity and of 0.13 part of NP spectrum intensity from the X-ray emission and absorption spectra of NC – (b).

intensity around 279.2 eV is formed by X-ray emission of both types of electrons. The CK $\alpha$ -spectrum of NP particles slightly differs from that of graphite by the location of the main maximum and the relative intensities of the marked features. The NP XAS spectrum is characterized by intense  $\pi^*$  resonance at 285.4 eV and  $\sigma^*$  resonance at 291.1 eV. Compare to the graphite spectrum these features are broadened and less sharp. The observed differences in the X-ray spectra of nanoparticles and bulk materials are likely to be caused by contribution of the surface and edge states, whose proportion becomes significant for small-size objects.

The CK-edge spectra of NC particles are rather similar to those of ND sample (Fig. 2). The CK $\alpha$ -spectrum of NC particles exhibits a slight enhancement of high-energy intensity around 283 eV, the XAS spectrum indicates an appearance of  $\pi^*$ -states of graphitic component. Hence, the measured spectra are superposition of electronic state of different kinds of carbon atoms composing NC particle. To reveal the electronic state of interface we subtracted 82% intensity of the ND spectra and 13% intensity of NP spectra from the spectra of NC particles. The eliminated ND percentage corresponds to the diamond weight fraction determined from the densimetric measurements [6]. The subtracted NP portion was rated so that to avoid the negative values in resultant intensity. The obtained curves I and II (Fig. 2b) correspond to the density of occupied and unoccupied states of carbon component contained in the NC sample and being different from the diamond-like and graphitic states. The curves exhibit clearly defined maxima located close to the Fermi level. The integral intensity of the localized maximum in the absorption region is slightly larger than that in the emission region.

The mechanism of ND transformation into graphitic NP has been suggested in [13]. The diamond



**Fig. 3.** X-ray emission (left part) and absorption (right part) spectra calculated for the central atoms of diamond fragment (dot-and-dash line), graphite fragment (thin solid line), and naked atoms of the (111) diamond surface (bold solid line).

annealing was shown to proceed via the graphitization of (111) planes mainly. Developed graphitic shell covers the ND surface preserving oxidation of three-coordinated diamond atoms. To determine the energy and density of states for these atoms we compared the X-ray emission and X-ray absorption spectra calculated for the central atoms of diamond and graphite fragments and for naked atoms of the (111) diamond surface (Fig. 3). Similar to the experimental data for ND sample, the CK $\alpha$ -spectrum calculated for diamond model exhibits broad maximum with high-energy shoulder and the XAS spectrum has a single peak at 279.3 eV corresponding to the  $\sigma^*$ -states. The theoretical CK $\alpha$ -spectrum of graphite is characterized by intense maximum attributed to the  $\sigma$  occupied

states and high-energy maximum formed by emission of  $\pi$ -electrons. The relative intensity and separation of these maxima are close to the values derived from the NP sample spectrum. The maximum around 277 eV of the XAS spectrum is assigned to the  $1s \rightarrow \pi^*$  transition in graphite and its position relative to the high-energy maximum of graphite  $CK\alpha$ -spectrum well agrees with experiment.

Taking into account that the theoretical spectra have been calculated for ground states of compounds we concluded the used quantum chemical method is suitable for interpretation of X-ray spectroscopy data. The spectra plotted for naked atoms of the (111) diamond surface shows the localized maxima located close to the Fermi level. The maxima have roughly equal integral intensity and their separation by 1.4 eV well corresponds to the energy distance between maxima of the curves I, II (Fig. 2b). Hence, the electronic state derived from the  $CK$ -edge emission and absorption spectra of NC particles after elimination of diamond and graphite components should be assigned to the three-coordinated atoms of interface. The proportion of such kind of carbon was estimated from the spectra deconvolution to be about 5%. The localized maxima were revealed from analysis of corresponding MOs to be formed by electrons of dangling bonds.

In summary, the carbon K-edge emission and absorption spectra of diamond/graphite composite nanoparticles were shown to be a superposition of electronic states of two main components, diamond and graphite, and electronic state of interface between the exfoliated graphitic layers and diamond core. A specificity of the interface state is appearance of the localized electronic levels around the Fermi level. Comparison between experimental data and theoretical spectra plotted by the result of DFT calculations on the carbon models revealed the localized states correspond to naked atoms of the (111) diamond surface. Graphitic shells, covered the diamond core, protect these highly reactive atoms from oxidation. The localiza-

tion of electronic density should result in specific electronic and magnetic properties of composite nanoparticles, which could be useful for development of new types of nanoelectronic devices.

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