

Chemical composition of surface and structure of defects in diamond single crystals produced from detonation nanodiamonds

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We present the results from our investigation of the structure and composition of microcrystalline diamonds obtained by sintering at high pressures and at high temperatures of detonation nanodiamond particles. Using XPS, XAS and photoluminescence spectroscopy, we found that the surface's chemical composition and a defects structure of microcrystalline diamonds significantly differ from the initial detonation nanodiamonds. This indicates the essential transformation of structure and composition of initial detonation nanodiamonds particles during the formation of single crystals at high pressure and temperature.

Keywords: detonation nanodiamond, HPHT sintering, single crystal, XPS and XAS spectroscopy, photoluminescence, defects.

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1. Introduction

The possibility of growing bulk single crystals from detonation nanodiamond (DND) particles by oriented attachment in the presence of alcohols or/and hydrocarbons was predicted and experimentally demonstrated by our group in previous works [1–3]. It is assumed that diamond single crystals of size between 500 nm and 15 μm are formed directly from 4 – 5 nm sized diamond nanoparticles under conditions of high pressure and high temperature (HPHT) ($P \approx 7$ GPa, $T \approx 1300 - 1700$ °C). One of the most promising applications of synthesized diamond microcrystals is related to the formation of luminescent impurity centers inside diamond lattice from their own system of defects originating during crystal growth. The distinction of composition and structure of lattices defects in sintered microcrystals and initial DND particles was found for the first time by ESR [4, 5]. The goal of present work is studying transformation of composition and structure of defects of DND resulting from forming microcrystals by HPHT sintering, as well as estimating the possibility of obtaining of the luminescence centers (nitrogen-vacancy) in microcrystals obtained by sintering of DND particles.

2. Experimental details

Samples of highly purified deagglomerated DND were obtained in accordance with the procedure described in [6, 7]. Samples of diamond single crystals of size between 500 nm and 2 μm were prepared by HPHT sintering of DND at the pressure of ~ 7 GPa and the temperature of ~ 1550 °C for 8 – 15 s in the presence of hydrocarbons (hexane). Initial DND particles for spectral measurements were deposited to the surface of silicon substrates by aerosolization. The thickness of layer was about 100 nm. Microcrystals obtained by sintering of DND, were dented into the surface of copper substrates. The thicknesses of obtained layers were approximately 50 μm.

For transformation of the structure of defects in the initial DND and in the synthesized diamond microcrystals, we applied ion irradiation and annealing. We used ions of nitrogen (N^+) with energy $E = 227$ keV and doze $D = 2.5 \cdot 10^{15}$ cm⁻². The annealing was carried out at temperature $T = 750$ °C in a vacuum chamber ($P = 10^{-8}$ Torr) for 1 h.

X-ray photoelectron (XPS) and CK edge X-ray absorption (XAS) spectra were measured at the Russian–German beamline of electron storage ring BESSY-II (Helmholtz-Zentrum Berlin) using the beam line ultra-high vacuum (UHV) experimental station [8]. The XPS spectra were acquired at fixed photon energies using hemispherical analyzer SPECS Phoibos 150 operated in constant-pass-energy mode. The CK edge XAS spectra were measured in the mode of total electron yield (TEY) by recording a value of the sample drain current as a function of the energy of the incident photons.

Photoluminescence (PL) studies were performed at room temperature using spectrometer Ocean Optics Maya2000 Pro with spectral range 200 – 1100 nm and resolution 0.45 nm. The excitation wavelength was 532 nm.

3. Results and discussion

Typical SEM image of microdiamond particles produced by HPHT sintering of DNDs is presented in Fig. 1a. Respective survey XPS spectra of initial DND and synthesized diamond microcrystals are presented in Fig. 1b.

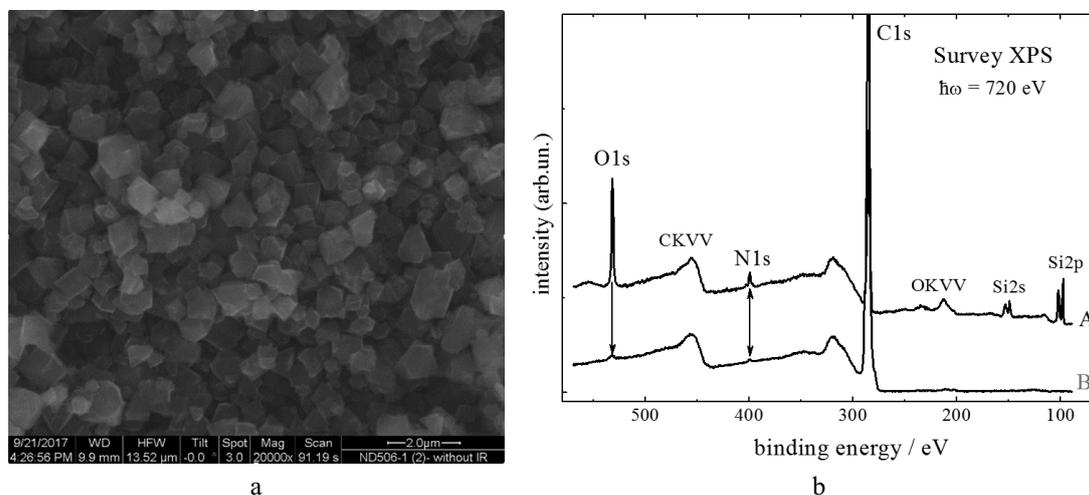


FIG. 1. a) SEM images of synthesized diamond microcrystals obtained by sintering of DND under HPHT conditions. Scale ruler – 2 μm . The average crystal size is 1 μm . b) Survey XPS spectra of DND (curve A) and of synthesized diamond microcrystals (curve B) recorded at the energy of monochromatic synchrotron radiation equals to 720 eV

Figure 1a, confirms the above-mentioned size range for synthesized diamond microcrystals and gives proof for their single crystal nature. Fig. 1b expectedly shows that initial DND and synthesized diamond microcrystals have almost the same chemical composition, which includes three elements: carbon, oxygen and nitrogen. However, the obtained XPS spectra clearly show that unlike initial DNDs, the chemical composition of synthesized diamond microcrystals does not contain any discernible traces of nitrogen (N1s core level peak (BE \sim 401 eV) is completely absent in the XPS spectra of synthesized diamond microcrystals). Thus, we may assume that process of HPHT sintering of DND is accompanied by stringent removal of nitrogen from the near surface layers of the produced diamond single crystals.

Figure 2 presents CK edge XAS spectra of the same diamond particles measured, respectively, on the untreated samples (spectra 1), on the samples first irradiated by nitrogen ions with the energy of 227 keV and the dose of $2.6 \cdot 10^{15}$ ions/cm² (spectra 2) and then on the same samples annealed during 1 h at the temperature of 750 °C under high vacuum (spectra 3).

Analysis of XAS spectra clearly shows that besides removal of nitrogen, DND sintering is also accompanied by essential transformation of their bulk electronic structure and of their surface chemistry. Proof for this is shown by a number of new spectral features which were absent in the XAS of initial DNDs (spectrum 1A), but they appear in respective spectra (spectrum 1B) of synthesized diamond microcrystals. These are the following post-edge ($h\nu > 289$ eV) features: a very narrow (\sim 0.3 eV) peak of C1s core exciton at \sim 289.3 eV, broad bulk σ^* -resonances at \sim 290.8, \sim 295.3 and distinctive shoulder at \sim 303.3 eV. All of these features are commonly considered signs of high structural perfection of diamond [9, 10] and point that HPHT sintering converts DNDs into single crystal diamonds whose bulk electronic structure and degree of structural perfection are very similar to quality synthetic diamonds.

The prominent distinction in the shape of pre-edge regions ($h\nu < 289$ eV) points out the difference in the surface chemistry of initial DNDs and synthesized diamond microcrystals. It could be related to the strong functionalization of synthesized diamond microcrystals surface by C–H groups revealing itself in high intensity of $\sigma^*(\text{C–H})$ -resonance at \sim 287.3 eV [9, 10].

The other XAS spectra also presented in Fig. 2 (spectra 2 and 3) show that irradiation of nano- and micro-sized diamonds by nitrogen ions with energy of 227 keV and dose of $2.6 \cdot 10^{15}$ ions/cm² can produce just only moderate and reversible transformation of their bulk electronic structure. The noticeable decrease of C1s core exciton (\sim 289.3 eV) gives evidence for the respective decrease of microdiamonds structural perfection. Some increase in the intensity of $\pi^*(\text{C=C})$ resonances (\sim 285.1 eV) and corresponding decrease in the intensity of σ^* -resonances we regard as the formation of the surface layer of sp²-coordinated carbons.

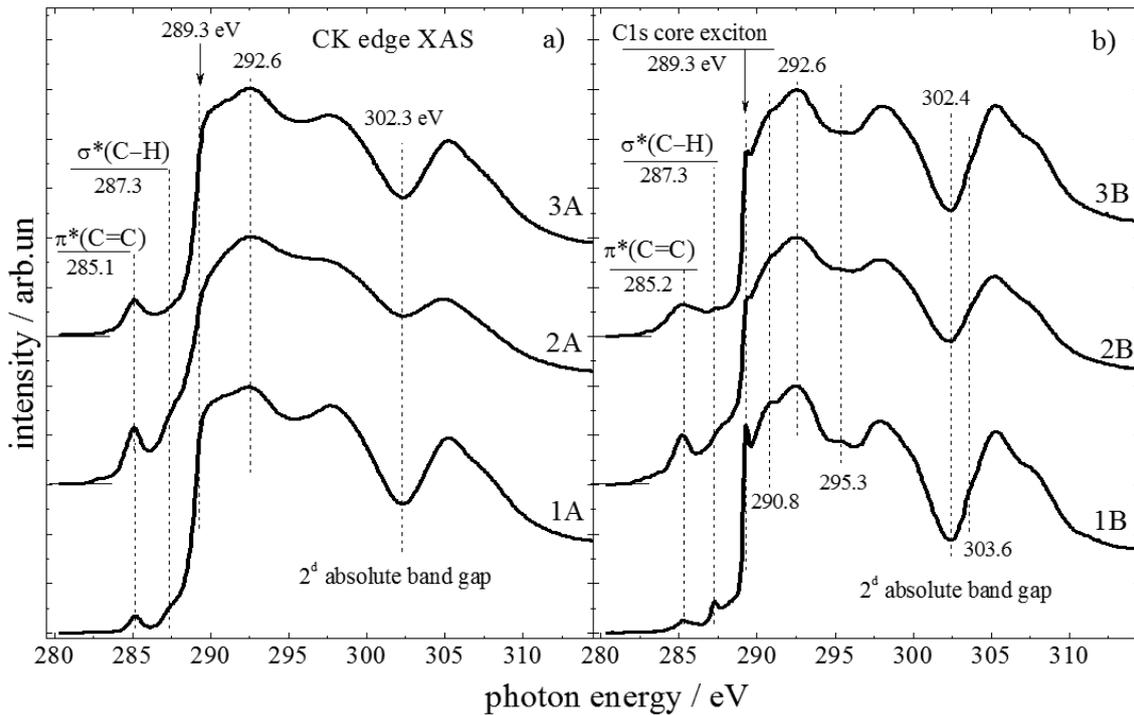


FIG. 2. CK edge XAS spectra of the samples prepared from deagglomerated DND (panel a) and synthesized diamond microcrystals (panel b). Spectra 1A, 1B correspond to the untreated diamond samples. Spectra 2A, 2B – to the same samples irradiated by nitrogen ions with energy of 227 keV and dose of $2.6 \cdot 10^{15}$ ions/cm². Spectra 3A, 3B – the irradiated samples after their 1-hour annealing in high vacuum conditions at 750 °C

Comparison of spectra 2 and 3 shows that 1-hour annealing at 750 °C provides only partial restoration of the bulk structural perfection but inevitably results in an irreversible increase in the surface graphitization degree both for nano- and microdiamond particles.

Figure 3a presents typical PL spectra of the initial powder of DND (spectrum 1A) and of a high-quality type Ib single crystal diamond plate that was fabricated commercially by Element6 using HPHT growth and initially contained 200 ppm of *N*. The sample was irradiated with 3 – 5 MeV neutrons at the temperatures close to room temperature to a total dose of 10^{18} cm⁻², then annealed at the temperature $T = 800$ °C for 2 h in the presence of a forming gas (H₂) in order to achieve a high density of NV⁻ centers (Fig. 3a, spectrum 2A). The spectrum 1A featured by wide band of photoluminescence with maximum at wavelength 570 nm and the spectrum 2A featured by wide band of photoluminescence with maximum at wavelength 680 nm.

Figure 3b (curve 1B) demonstrates PL spectrum of single crystal diamonds obtained by sintering of DND. It is featured by wide band of photoluminescence between 540 and 900 nm. Bright band at the wavelength of 575 nm can be attributed to the emission of N-V⁰ defects, points to significant concentration of them in diamond microcrystals sintered from DND.

Meanwhile, synthesized diamond microcrystals subjected to ion irradiation and subsequent annealing demonstrate the prominent transformation of the PL spectrum (Fig. 3b, curve 2B) approaching to the same of perfect single crystalline diamond (Fig. 3a, curve 2A). Maximum of PL spectrum of synthesized diamond microcrystals subjected to ion irradiation on subsequent annealing is as 680 nm compare to wide band of PL as 540 nm to 900 nm of non-irradiated synthesized diamond microcrystals.

The expressed line at 638 nm points to effective formation of luminescent N-V⁻ centers during processes of ionic irradiation and subsequent annealing.

4. Conclusions

Thus, HPHT sintering of 4 – 5 nm DND particles provides effective formation of 0.5 – 2 μm sized single crystal diamonds with bulk electronic structure and structural perfection intrinsic to macroscopic high quality single crystal diamonds. Unlike initial DND, the single crystal diamonds obtained by sintering of DND contains

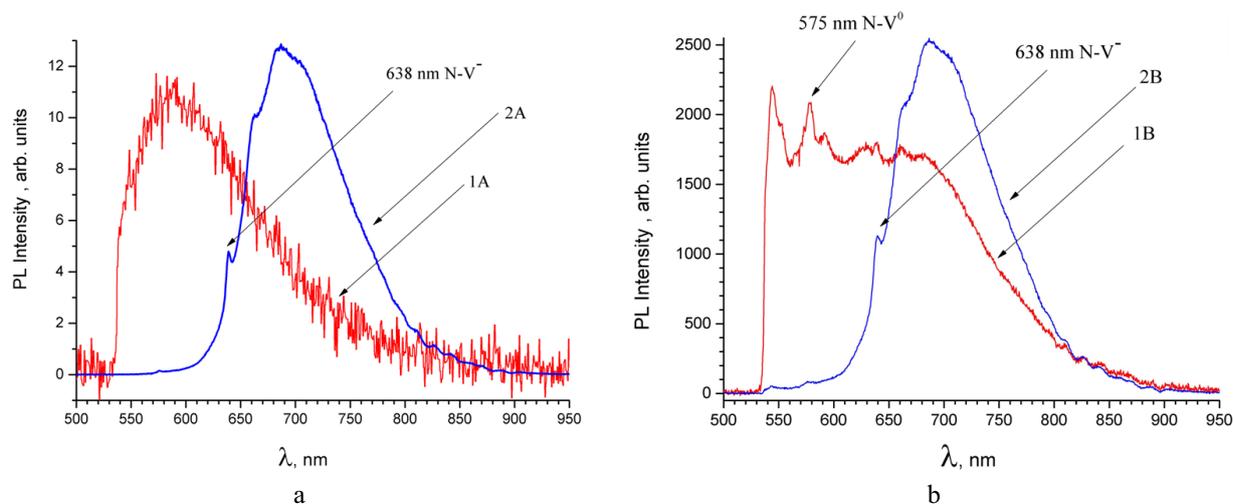


FIG. 3. a) Curve 1A – Typical PL spectra of the initial powders of DND, curve 2A – PL spectra of high-quality synthetic diamond from Element6. b) curve 1B – typical PL spectrum of diamond microcrystals obtained by sintering of DND, curve 2B – PL spectrum of the same microdiamond after ion irradiation and annealing

no nitrogen in the near surface layers. Irradiation of synthesized microcrystalline diamond by 227 keV nitrogen ions ($Q = 2.51015$ ions/cm²) and sequential 1-hour high vacuum annealing of these particles at the temperature of 750 °C results in the transformation of their PL spectra to the shape inherent to the perfect crystalline diamond with noticeable content of luminescent N–V[−] centers. These results open the way to effective technologies of production the luminescent microdiamonds for various applications.

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