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Cathodoluminescence of HPHT type IIa diamond with boron concentration up to 0.03 ppm

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A study was carried out of a single-crystal multi-sector plate of type IIb HPHT diamond with a minimum boron level detectable by IR absorption spectra. In the growth sectors {111} and {110}, the boron concentration was 0.03 and 0.01 ppm. In the growth sectors {100}, {113}, {115}, the boron concentration is lower than the detection limit by absorption spectra. In the cathodoluminescence spectra of all sectors at a temperature of 77 K, broad structureless bands with maxima at 2.3 and 3.3 eV were revealed. The band with a maximum at 2.3 eV has two components with decay times in the ranges of $5-14\,\mu$s and $0.2-2\,\mu$s, respectively, differing in different growth sectors. The decay time of the band with a maximum of 3.3 eV is less than 100 ns. A difference in the intensity of luminescence of the sectors upon excitation by light of 220 nm and cathodoluminescence was revealed. The intensity of photoluminescence is minimal in the {110} and {115} sectors, and the cathodoluminescence of the {110} sector is the most intense. Comparison with previous studies showed that with a decrease in the boron concentration in HPHT diamond, the intensity and decay time of CL decrease.

Keywords: IR spectroscopy, growth sector, luminescence properties, lifetimes.

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Introduction

Type IIb diamond is a semiconductor with a band gap of 5.5 eV and an acceptor level of 0.37 eV of the boron atom that replaces carbon. As the boron concentration increases, an impurity band is formed with a lower boundary of about 0.12 eV [1]. A type IIa diamond has the electro-optical characteristics of a dielectric. The properties of diamond as a dielectric are obtained on a reproducible basis only in CVD diamonds grown from high-purity gases. Boron and other impurities in such crystals are at a level of less than 1 ppb. At the moment, there is a problem of determining the boundary value in case of a transition of the diamond to type IIa from types Ia, Ib, IIb. In the gemological literature, the value 1 ppm is often used for natural and synthetic diamonds, below which the diamond belongs to type IIa. It is also convenient to use it because the IR spectroscopy method no longer detects an impurity of nitrogen below this value, for natural diamonds this is the main parameter. However, this method is several orders of magnitude more sensitive for determining the concentration of boron impurities. The issue of classifying diamonds to one type or another has become even more relevant in the mass production of HPHT diamonds, since boron and nitrogen impurities are present in almost all HPHT diamonds at the level of tens to hundreds of ppb (depending on the purity of the catalyst metal). Such diamonds belong to type IIa according to the physical classification and color characteristics, however, an admixture of boron in such concentrations can still give it the characteristics of a semiconductor.

Natural and synthetic diamonds contain many defective impurity centers in their structure, which are active in the luminescence [2–5]. The luminescence of HPHT diamonds with boron admixture has been repeatedly studied, and its recombination nature (recombination of electrons and holes on donor-acceptor (DA) pairs) is now recognized. The model of the luminescence center proposed in Ref. [2,6,7] discusses a nitrogen dimer as the donor and a substitutional boron atom as the acceptor. It is shown that the luminescent characteristics of the band should depend on the concentration of the doping impurity in diamonds (boron and nitrogen), however, systematic studies are complicated by the difficulty of controlling the defect-impurity composition. A new variant of the origin of this

glow was proposed in Ref. [8] based on the study of the phosphorescence of HPHT diamonds: greenish-blue glow is associated with the addition of boron and iron, orange glow is associated with the addition of boron and sodium. The explanation is given using modeling and theoretical calculations.

This study in continuation of Ref. [9–11] obtained data on the spectral and temporal characteristics of luminescence in different growth sectors of a colorless type IIa single crystal diamond grown by the HPHT method with a boron concentration of up to 0.03 ppm. Such crystals exhibit intense greenish-blue and faint orange phosphorescence in case of excitation by short-wavelength ultraviolet radiation, which is similar or similar in nature to those previously studied in type IIb diamonds.

1. Sample

A colorless multisectoral diamond wafer $4 \times 4 \times 0.5$ mm of type IIa HPHT diamond, has been studied. The crystals were synthesized in SK-850 high-pressure cubic press in a temperature range of 1450–1550°C, at a pressure of 5.5 GPa. Fe–Co alloy with the addition of nitrogen and boron getters was used as a catalyst metal. The wafer is cut by laser perpendicular to the direction $\langle 100 \rangle$ from the central part of a single crystal of HPHT diamond, close to type IIa. Next, the wafer was mechanically polished using a polishing disc. The crystal morphology was dominated by the facets {111} and {100}, while simple shapes were less developed {110}, {113}, {115}. The sample was grown without deliberate doping with boron, boron is present in diamond, probably due to the presence of low concentrations in the catalyst metal. There were 4 seeds in the high-pressure cell, oriented with a face {100}.

2. Research methods

The boron impurity content was estimated using IR absorption spectra. Absorption spectra were recorded using Bruker Vertex-70 spectrometer with a Hyperion 1000 microscope in the range of 600–6000 cm^{-1} with a resolution of 2 cm^{-1}, averaged over 32 scans with the size of the recording area $100 \times 100\,\mu$m.

The boron concentration was determined using a known relationship [12–16]:

$$[B](\text{ppm}) = (5.53 \times 10^{-4}) \times I_{2802}\,(\text{cm}^{-2}), \qquad (1)$$

where I_{2802} is the integral absorption coefficient of the band with a maximum of about 2800 cm^{-1}.

The sectoral structure of the diamond plate was visualized using Diamond Inspector tester with excitation by an excimer lamp at a wavelength of 220 nm. The maximum possible excitation density is estimated to be no more than 1 W/m^2. Cathodoluminescence (CL) spectra were recorded using CAMEBAX electron probe microanalyzer (Cameca, France) with an optical microscope and combined with a proprietary cathodoluminescence station [17]. The device based on CAMEBAX microanalyzer makes it possible to obtain optical images of a sample in reflected light, measure the luminescence decay and flaring up times at a CL station with a time resolution of 100 ns and record the spectra of cathodoluminescent (CL) emission with a spatial resolution of 1 μm. The CL spectra were obtained with an accelerating voltage of 15 kV, current of 20 nA absorbed by the sample and an electron beam diameter of 3 μm at 77 K. The excitation density is about 300 W/m^2.

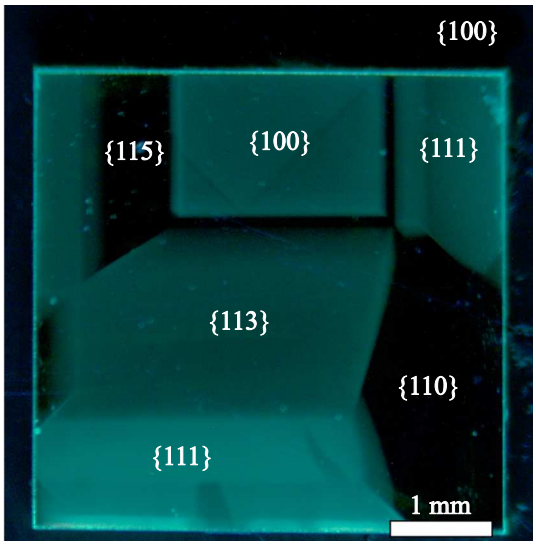

Figure 1. Photoluminescent microscopy image of the sectorial internal structure of a diamond wafer (with excitation at $\lambda = 220$ nm).

Table 1. Concentration of boron and nitrogen in different diamond sectors

Sector	B, ppm (2802 cm^{-1})	N, ppm (not detected)
{111}	0.03±0.01	< 0.5
{110}	0.01–0.005	< 0.5
{113}	(< 0.005) not detected	< 0.5
{115}	(< 0.005) not detected	< 0.5
{100}	(< 0.005) not detected	< 0.5

3. Results and discussion

3.1. Luminescent microscopy

Fig. 1 shows the images of the sample obtained by photoluminescence microscopy. The images show a contrast typical for HPHT-diamonds. The morphology of the crystal and the arrangement of growth pyramids of facets of simple shapes helped to identify the growth sectors {100}, {110}, {113}, {115}, {111}.

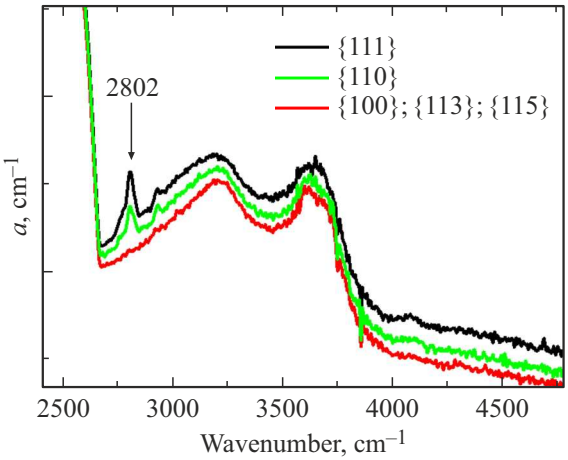

Figure 2. IR absorption spectra of growth sectors {111}, {110}, {100}, ({311}, {115}) of HPHT diamond in the spectral region with the boron absorption band of 2802 cm^{-1}.

3.2. Impurity composition and IR absorption spectra

Fig. 2 shows the IR absorption spectra recorded in different growth sectors of the diamond wafer. The band 2802 cm^{-1} is observed on the spectra, which characterizes the presence of boron admixture in the crystal [13]. The intensity of this band is sufficient to calculate the concentration only in the sectors {111} and {110}.

Boron-doped diamonds were studied in Ref. [9–11] which were synthesized using the same pressing equipment as the sample studied in this article. Nitrogen and other impurities of boron were not detected in the sample in this study like in the previous ones, the detection limit. The calculation of the boron concentration in the sectors {111} and {110} by IR spectra is provided in Table 1.

It can be seen from the obtained data that the presence of boron impurity cannot be detected by IR spectroscopy in the sectors {100}, {113}, {115} of a multisectoral sample from a single crystal of HPHT diamond with a wafer thickness of 0.5 mm: its concentration is less than 5 ppb.

3.3. CL-studies

The CL spectra of the identified growth sectors of the diamond wafer are shown in Fig. 3. The shape of the CL spectra of each sector corresponds to a superposition of wide bands with maxima around 2.3 and 3.0 eV.

Diamond wafers synthesized under similar conditions, but with a boron doping level of up to 15 [10] and 60 ppm [11] were studied in previous papers. 2.3 eV band and a band with a maximum of 3.0 eV were observed in the spectra of CL wafers from Ref. [10,11]. Two broad bands with a maximum of 2.3 and 3.3 eV were detected in the spectra of the studied sample. There is an obvious shift of the maximum of the band with a higher energy — from 3.0 to 3.3 eV.

The recombination luminescence model assumes [6,18–21] that the position of the band maximum depends on the concentration of the donor and acceptor

$$E(r) = E_g - (E_{ac} - E_d) + e^2/\varepsilon r,$$

where $E(r)$ is the photon energy, E_g, E_{ac}, E_d is the band gap, the position of the acceptor and donor levels, respectively, e is the electron charge, ε is the dielectric constant, r is the distance between donor and acceptor. At the same time, the maximum shift of 3.3 eV band, depending on the sector, is within the margin of error.

The ratio of nitrogen concentration in diamond was determined as 1 : 10 : 46 : 100 for sectors, respectively, {110} : {113} : {100} : {111} in Ref. [21]. The ratio of boron concentration in diamonds was determined as 2 : 16 : 34 : 100 for sectors, respectively, {100} : {113} : {110} : {111} in Ref. [9,11]. However, these ratios vary widely depending on the growth rate, the composition of the medium, and the temperature. In general, the face {111} is the most active in capturing nitrogen and boron impurities, the face {113} is in the third position in terms of activity in capturing both nitrogen and boron impurities. The faces {110}, {100} have different activities for nitrogen and boron capture, and their roles are reversed: {110} is more active in boron capturing, while {100} is more active in nitrogen capturing. The intensity of the studied CL bands probably does not depend directly on the content of boron alone or nitrogen alone in the growth sector, but is also determined by the ratio of these elements.

The most intense CL bands 2.3 and 3.3 eV are observed in the sectors {111} and {110}, characterized by the maximum concentration of boron. The ratio of the intensities of bands 2.3 and 3.3 eV in each sector is different (Table 2), and the direct dependence of the intensity of CL on the content of boron or nitrogen is not revealed. The recorded intensity of the CL spectra does not correspond to the photoluminescence intensity distribution (PL) in case of 220 nm excitation (Fig. 1). The sectors {110} and {115} are characterized by minimal intensity in PL. The sector {115} luminesces more strongly than {311} in CL. The explanation for this effect may be that in CL, unlike photoluminescence, there may be an inversion in the luminescence intensity of sectors due to the different diffusion length of charge carriers, which affects the size of the generation region. The difference can also be explained by the fact that the pump density at CL differs by more than 100 times than when it is excited by a 220 nm lamp.

A narrow line of around 2.32 eV (535 nm) and also barely discernible peaks of 2.4 eV (517 nm) and 2.29 eV (547 nm) are clearly recorded on the CL spectra for sectors {113} and {115}, against the background of 2.3 eV wide band. A defect can usually be detected in diamonds in this region of the CL spectrum H3 [22].

The values of the luminescence decay time of the bands with maxima 2.3 and 3.3 eV are provided in Table 2. It is shown in [23] that the band in the region of 3.0 eV has a decay time of the order of 10 ns. The minimum possible

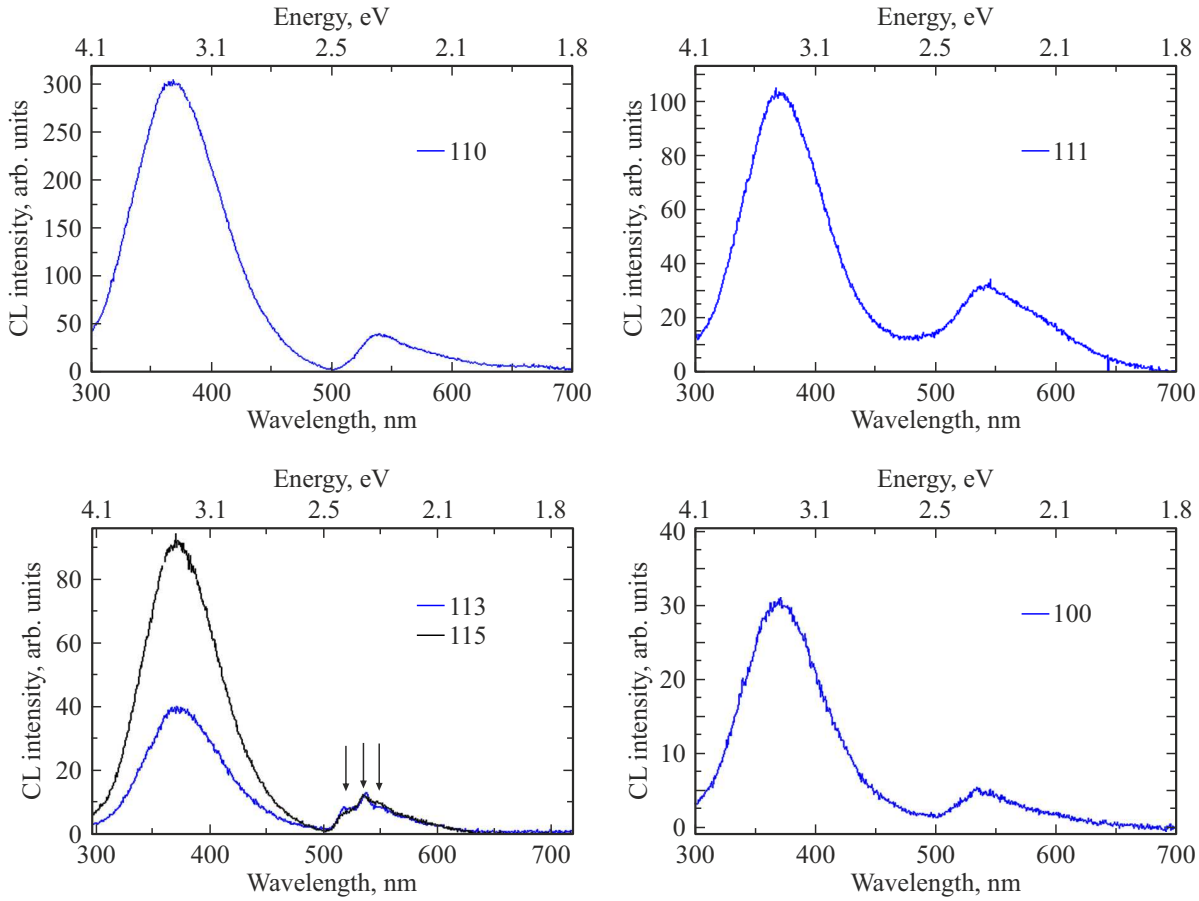

Figure 3. CL spectra of the sample at 77 K, obtained for different growth sectors of the studied sample.

Table 2. Luminescent characteristics of the studied luminescence bands

Sector	Ratio of band intensities	Luminescence decay time of band 2.3 eV		decay time of band luminescence3.3 eV
	$I(3.3\,\text{eV})/I(2.3\,\text{eV})$	$t1\,\mu$s	$t2\,\mu$s	$t1$ ns
{111}	3.2 ± 0.3	14 ± 2	2 ± 1	< 100
{110}	7.4 ± 0.5	6 ± 1	≤ 0.2	< 100
{113}	4.8 ± 0.5	4 ± 1	≤ 0.2	< 100
{115}	11.5 ± 0.7	6 ± 1	≤ 0.2	< 100
{100}	7.3 ± 0.5	5 ± 1	≤ 0.2	< 100

time of ~ 100 ns detected in this study by the setup was recorded in this study in the area 3.3 eV.

Fig. 4 shows the decay curves obtained in the region of 2.3 eV luminescence band. There are two components of the decay time. The first component in different growth sectors is approximated by a value from 14 to 5 μs, the second shorter component is approximated by a time from 2 to $\leq 0.2\,\mu$s. This significantly differs from the results of measurements of the decay time of the A band in natural diamonds using photo- and X-ray luminescence methods [24]. It was mentioned in Ref. [24] that the decay time is about 5–7 ms in the region of 2.3 eV band. decay times are 3 orders of magnitude shorter in our study. This can be explained by the difference of the formation of luminescence centers in synthetic diamonds and in natural diamonds, studied in the Ref. [24]. This difference can also be attributed to the excitation method, as the electron beam exceeds photoluminescent (UV) or X-ray luminescent sources in pump energy density by several orders of magnitude. It is known that the contribution to luminescence of shorter-lived states increases at high pump density, and the contribution of longer-lived states can be

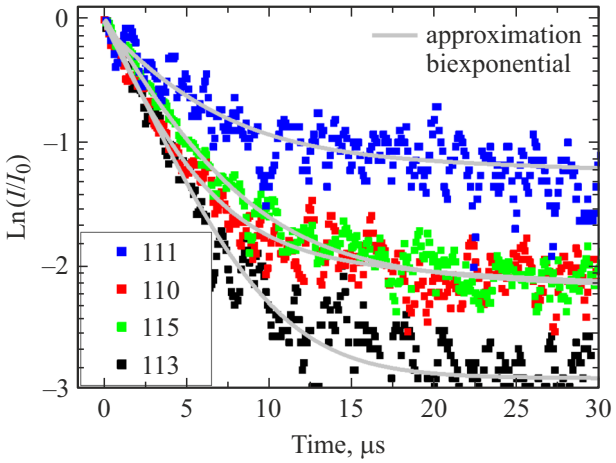

Figure 4. CL decay curves in 2.3 eV band.

at the error level. This aspect of the luminescence system's behavior requires further studies.

Thus, the CL intensity and decay time decrease with a decrease of the boron concentration in a HPHT diamond. Within the framework of the DA recombination model, the decay time should increase with a decrease of the concentration of the donor and acceptor, therefore, the results obtained provide the basis for searching for an alternative model of the CL band with a maximum of 2.3 eV.

4. Conclusions

Each growth sector in the studied HPHT diamond with a boron concentration at the IR spectroscopy detection limit is a separate material with its own luminescence parameters and impurity composition. Two CL bands with peaks of 2.3 and 3.3 eV, are observed in the CL spectra of all growth sectors. The luminescence intensity of the sectors at 220 nm does not correspond to the intensity of the CL bands. The CL intensity is maximal in the growth sectors {111} and {100} with a boron concentration of 0.03 and 0.01 ppm, respectively. 3.3 eV band is characterized by a decay time of less than 0.1 μs. 2.3 eV band has two components with decay time, which in the sector {111} is maximal with a value of 2 and 14 μs. Thus, the CL intensity and decay time decrease with a decrease of the boron concentration in HPHT diamond.

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Conflict of interest

The authors declare that they have no conflict of interest.

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