

# Spectral-Kinetic Features of Pulsed Cathodoluminescence of I<sub>IIa</sub> Type Natural Diamond

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**Abstract** – Pulsed cathodoluminescence spectra and decay kinetics of a natural diamond of I<sub>IIa</sub> type in the 340–680 nm spectral range were investigated. The emission of vibronic N<sub>3</sub> system and band-A was observed. The N<sub>3</sub> system was dominant in a nanosecond scale, had a zero-phonon line at 415.2 nm and phonon replicas in the 430–460 nm range. The decay time of N<sub>3</sub> system was 30–50 ns. Structureless band-A was observed in a millisecond scale, had a maximum at 460 nm and the decay time of 8.5–8.8 ms.

## 1. Introduction

The structure of defects in a diamond determines its jewellery quality and contains information about geological history of sample. The luminescence analysis is one of the main methods of structure and defect composition in diamonds studying [1,2]. There were published many papers about cathodo-, photo- and X-ray luminescence of diamonds [3–10]. It was found that a spectrum envelope depends on defect content, prehistory of a sample and excitation conditions. Tens of bands and systems of different centers were observed.

During the last years luminescent studies of diamonds with time resolution under the action of e-beams and laser pulses were carried out [11–13].

The present paper has the aim studying of emission spectra and decay kinetics of pulsed cathodoluminescence (PCL) of a I<sub>IIa</sub>-type natural diamond under the action of high current e-beam.

## 2. Experimental

The studying sample of I<sub>IIa</sub> type has thickness of 0.25 mm and diameter of 5 mm. Its absorption spectrum showed the fundamental edge at the 226 nm and a monotonous decreasing to long-wavelength area. Such behavior of absorption is explained due to a low (for diamonds) density of nitrogen impurities – less than  $10^{18} \text{ cm}^{-3}$  [1].

The PCL excited under the action of high-current pulsed electron beam of ~ 10 ns duration (see. Fig. 1, curve 1). The energy density on the sample was  $0.1 \text{ J/cm}^2$  per pulse. The maximum of energy distribution of electrons was at ~ 250 keV. The maximal electron energy was up to 360 keV.

The PCL kinetics were measured in a wide time scale from  $10^{-8}$  up to  $5 \cdot 10^{-2}$  s (in a nanosecond scale and a microsecond scale, separately). Measurements

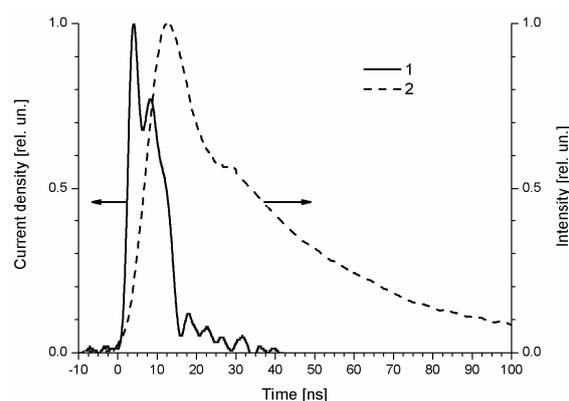


Fig. 1. An e-beam current pulse used for PCL excitation (1). A typical PCL emission pulse of the I<sub>IIa</sub>-type diamond (2).

were carried out in the 300–700 nm spectral range with the 5 nm step, but with 0.2 nm step in the 414–417 range. PCL emission spectra were reconstructed from obtained traces at a fixed time from pulse beginner.

Spectral measurements were performed using MDR-23 monochromator, FEU-118 and FEU-97 photoelectronic multipliers. PCL traces were saved using TDS-2022 digital scope. The time resolution was not worse than 10 ns. Reconstructed PCL spectra were corrected using a spectral response of our apparatus. The inaccuracy of measured emission intensity was less than 5%.

An e-beam fallen down on the sample under the  $45^\circ$  angle, but emission measurements were carried out under the normal angle to an e-beam. PCL spectra and decay kinetics was measured at room temperature in a vacuum chamber at residual gas pressure of  $\sim 10^{-4}$  torr.

## 3. Results and discussion

PCL emission spectra of the diamond sample were shown in Fig. 2. Two of them were reconstructed at  $t = 12$  and  $90$  ns after a pulse beginner (curve 1 and 2 in Fig. 2, respectively) and had a non-elementary structure. These spectra demonstrated a wide band with maximum at 430–450 nm, but had a narrow zero-phonon line (ZPL) at 415.2 nm of vibronic N<sub>3</sub> system. Possibly, the local maxima in the 420–470 nm range were phonon replicas of the ZPL 415.2 nm. These local maxima had amplitudes higher than a pulse-to-pulse e-beam instability or an experimental inaccuracy. The width at half-maximum of ZPL was 1.1–1.2 nm for both cases.

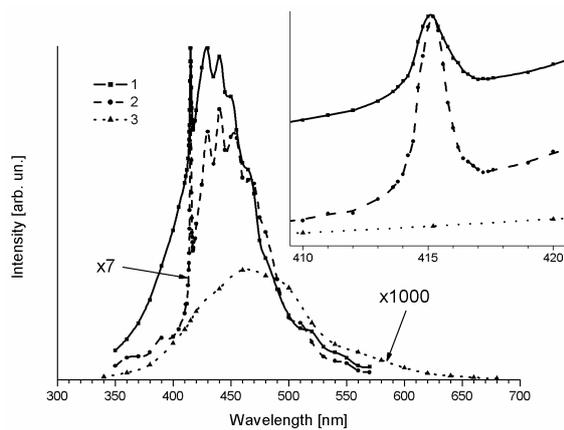


Fig. 2. PCL emission spectra of the IIa-type natural diamond under the action of e-beam, which were reconstructed at  $t = 12$  ns after a pulse beginner (1), at  $t = 90$  ns (2), and at  $t = 2$  ms (3). On insert – magnified PCL spectra in the 410-420 nm range.

It should be noted that in the 350–450 nm range a normalized intensity of PCL emission at  $t = 12$  ns was significantly lower than at  $t = 90$  ns.

The reconstructed PCL spectrum at  $t = 2$  ms had not any ZPL or its phonon replicas (Fig. 2, curve 3), but demonstrated a wide structureless band with a maximum displaced to 460–470 nm. In the 300–450 nm range a normalized intensity of PCL emission was decreased in comparison with spectra in a nanosecond scale. But for wavelength higher than 500 nm a normalized intensity was increased. Same wide structureless luminescence band was accepted to name as band-A. Numerous papers reported that maximum of band-A locates from 400 up to 480 nm [1–3,11,13].

The PCL decay kinetics of the sample showed two different components. Traces of PCL emission in nano- and millisecond scales at  $\lambda = 460$  nm shown on Fig. 3 (a) and (b), respectively. It is obvious that the PCL decay kinetics consisted of at least two different exponential functions in nano- and millisecond scales.

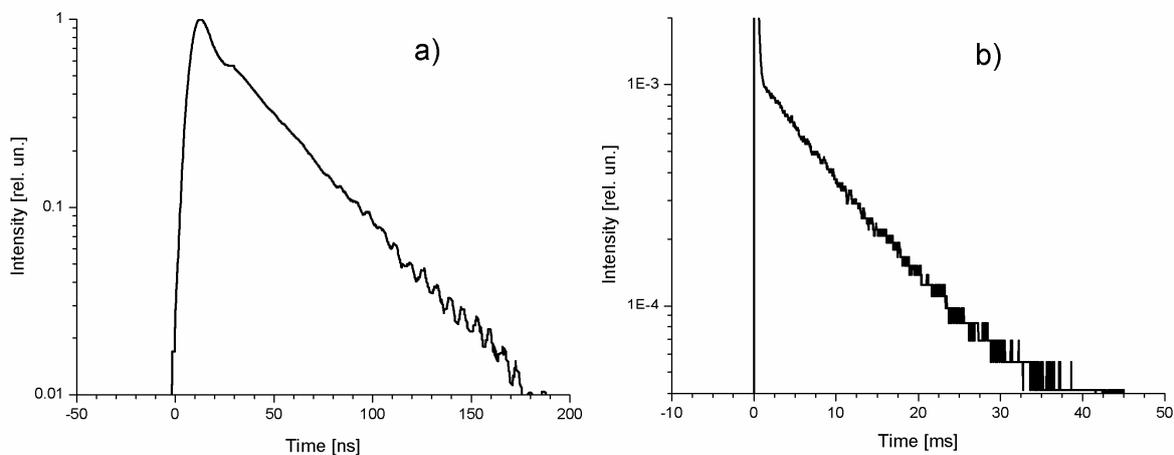


Fig. 3. PCL kinetics of the IIa-type natural diamond at  $\lambda = 460$  nm in a nanoseconds (a) and a milliseconds (b).

In nanoseconds the characteristic decay time was 41 ns. At  $t = 2$  ms after a pulse beginner the emission intensity fallen down at the three orders of magnitude. In milliseconds the characteristic decay time was 8.6 ms.

Thus observed PCL bands have a significantly different decay time. So it is possible to conclude that they belong to different luminescence centers.

Earlier it was shown that integrated PCL spectra the most of natural diamonds demonstrate only wide structureless band-A [11]. At the same time if integrated spectrum was measured during only 1 ms after an e-beam pulse then N3 system could be observed. In [12] a laser photoluminescence of synthetic diamond was investigated. This diamond was pre-annealed at high pressure and high temperature. The integrated spectrum consisted of intensive N3 system. However the integrated PCL spectrum measured with delay of 1  $\mu$ s after a laser pulse did not show any features at 415 nm, but demonstrated only weak and wide structureless band-A with a maximum at  $\sim 450$  nm.

Hereby N3 system has a decay time in nanosecond scale, but band-A – in millisecond scale. It matches with our observations.

N3 centers in diamond represent three substitutional nitrogen atoms located in (111) neighboring points of lattice and "bounded" with a vacancy [1]. But band-A belongs to some intrinsic defects. It was supposed that these defects represent breaking bonds in dislocations and other linear defects [8,14]. So a maximum of band-A should be located near the half of energy band gap, i.e.  $\sim 455$  nm. It is possible that an imposition of other types bands of luminescence centers (N3, H3, N<sub>s</sub>, B<sub>s</sub> and so forth) on band-A resulted in changing of its maximum in a wide range [1–3,11,13].

In [15] an excitation of PCL in the sample was carried out by subnanosecond avalanche e-beam (SAEB) with duration of 0.2 ns and by laser radiation (10 ns) at wavelength in the range of diamond fundamental absorption. In the case of SAEB an

integrated PCL spectrum was practically the same like spectrum in Fig. 2, curve 1. However in the case of laser radiation an emission in the 450–700 nm range was more intensive. It can be explained in terms of imposition band-A on N3 system in an integrated spectrum.

PCL decay-time spectra of the IIa-type diamond in nanosecond and millisecond scales were shown in Fig. 4. In the 410–550 nm range the decay time in nanoseconds was 30–45 ns. For wavelength longer than 550 nm and shorter than 410 nm the decay time was decreased rapidly. There was a sharp peak in the decay-time spectrum in vicinity of ZPL 415.2 nm.

In milliseconds in the 370–570 nm range the decay time was 8.5–8.8 ms and practically unchanged. Out of this range the decay time decreased down to 7 ms

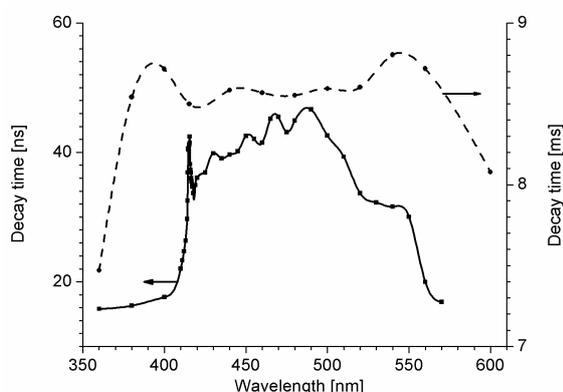


Fig. 4. PCL decay-time spectra of the IIa-type natural diamond under the e-beam excitation in nano- and millisecond scales.

and, as we supposed, lower. But a PCL signal was very weak.

Thus, the PCL of the diamond consists of two emissions with different spectra and different decay times. One of them is the N3 system with ZPL at 415.2 nm, which dominates in a nanosecond scale. Another is the long-lived structureless band-A with a weak intensity, which gives rise in integrated spectra.

#### 4. Conclusion

Studies on PCL spectra and decay kinetics of the IIa-type diamond were carried out under the action of e-beam of 10 ns duration.

The PCL bands of intrinsic (band-A) and extrinsic (N3 system) nature were observed in the visible range. These bands had different emission spectra and decay kinetics. The dominant was the vibronic N3 system with decay time of 30–50 ns. The structureless and weak band-A had decay time of 8–9 ms.

It is possible that centers of band-A represent breaking bonds in a neighbor of intrinsic defects, e.g. dislocations.

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