

OPTICS AND SPECTROSCOPY

SPECTRAL AND KINETIC CHARACTERISTICS OF THE PULSED CATHODOLUMINESCENCE OF A NATURAL IIA-TYPE DIAMOND

E. I. Lipatov,¹ V. M. Lisitsyn,² V. I. Oleshko,² and V. F. Tarasenko¹

UDC 535.37

Emission spectra and decay kinetics of pulsed cathodoluminescence of a natural Iia-type diamond sample are investigated in the spectral range 340–680 nm. The luminescence of the vibronic N3-system and band A are observed. The N3-system is dominant on a nanosecond scale and has a 415.2-nm zero-phonon line with phonon replicas in the range 430–460 nm. The decay time for the N3 system is found to be 30–50 ns. Structureless band A is observed on a millisecond scale; it has a maximum at 460 nm and a decay time of 8.5–8.8 ms.

INTRODUCTION

The defect structure of diamond determines its jewelry quality and carries information on the geological history of the sample. The luminescent analysis [1, 2] is one of the main methods of investigating the structure and composition of diamond defects. Many papers are devoted to the study of the cathode, photo-, and x-ray luminescence of diamonds (for example, see [3–10]). It has been established that the spectrum envelope depends on the impurity content, sample prehistory, and excitation conditions. Tens of bands of various luminescence centers were observed.

In the last few years, the luminescence of the diamond excited by pulsed electron beams and laser radiation has been studied with time resolution [11–13].

The present paper studies the emission spectra and decay kinetics of the pulsed cathodoluminescence (PCL) of a natural Iia-type diamond excited by a high-current electron beam.

EXPERIMENTAL

The examined Iia-type diamond sample had a thickness of 0.25 mm and an area of $\sim 20 \text{ mm}^2$ (Fig. 1). The intrinsic absorption band edge in the absorption spectrum of the sample was observed at $\sim 226 \text{ nm}$, and the absorption monotonically decreased toward longer wavelengths. The natural Iia-type diamond samples contained no more than 10^{18} cm^3 of nitrogen [1].

The sample was excited by the pulsed electron beam with 10-ns duration at half-maximum and waveform shown in Fig. 2 (curve 1). The energy per pulse did not exceed 0.1 J/cm^2 . A maximum of the electron energy distribution was at 250 keV. The maximal electron energy reached 360 keV.

The emission kinetics was measured in the time interval from 10^{-8} to $5 \cdot 10^{-2}$ s. Measurements were carried out in the spectral range 300–700 nm with a step of 5 nm and in the range 414–417 nm with a step of 0.2 nm. The emission spectrum was reconstructed from measured emission waveforms at a fixed time after the onset of the light pulse. The emission kinetics in the above-indicated time interval was measured separately for nano- and millisecond scales.

The possible effect of the luminescence change with increasing number of excitation pulses was controlled by check measurements, and the sample periodically had “a rest” without irradiation at room temperature. The emission spectra

¹High-Current Electronics Institute of the Siberian Branch of the Russian Academy of Sciences, e-mail: lipatov@loi.hcei.tsc.ru; ²Tomsk Polytechnic University. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 1, pp. 53–57, January, 2007. Original article submitted May 18, 2006.

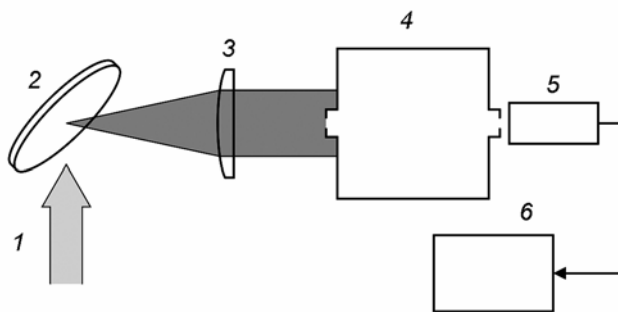


Fig. 1. Block-diagram of the experimental setup comprising electron beam 1, sample 2, optical system 3, monochromator 4, photomultiplier 5, and oscilloscope 6.

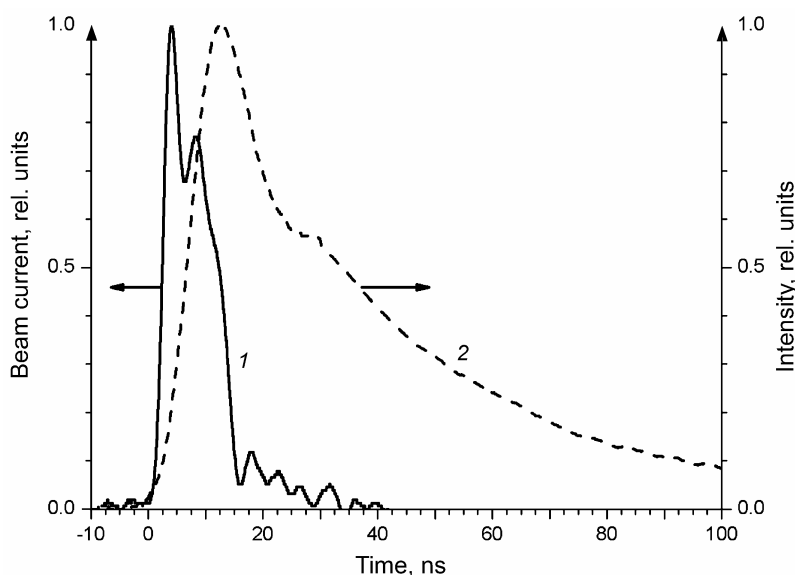


Fig. 2. Electron beam waveform (curve 1) and pulsed cathodoluminescence of the IIa-type natural diamond (curve 2).

were measured with an MDR-23 monochromator and FÉU-118 and FÉU-97 photomultipliers. Pulses of luminescent radiation were registered by a TDS-2022 oscilloscope and averaged over four pulses. The typical waveform of the luminescence pulse is shown by curve 2 in Fig. 2. The measured spectra were corrected for the effect of the spectral response of our setup. The time resolution of the setup was no worse than 10 ns. The error in measuring the emission intensity was less than 5%.

During measurements, the electron beam was incident at an angle of 45° to the sample surface, and the emission from the irradiated sample surface was registered in the direction normal to the electron beam (see Fig. 1). The emission spectra and decay kinetics were measured at room temperature in a vacuum chamber at a residual gas pressure of 10^{-4} Torr. The vacuum chamber is not shown in Fig. 1. The emission was extracted from the chamber through a quartz plate.

RESULTS AND DISCUSSION

Figure 3 shows the reconstructed emission spectra. The spectra reconstructed from light signals measured at times $t = 12$ and 90 ns after the onset of the pulse have complex structure (see curves 1 and 2 in Fig. 3). A wide band with

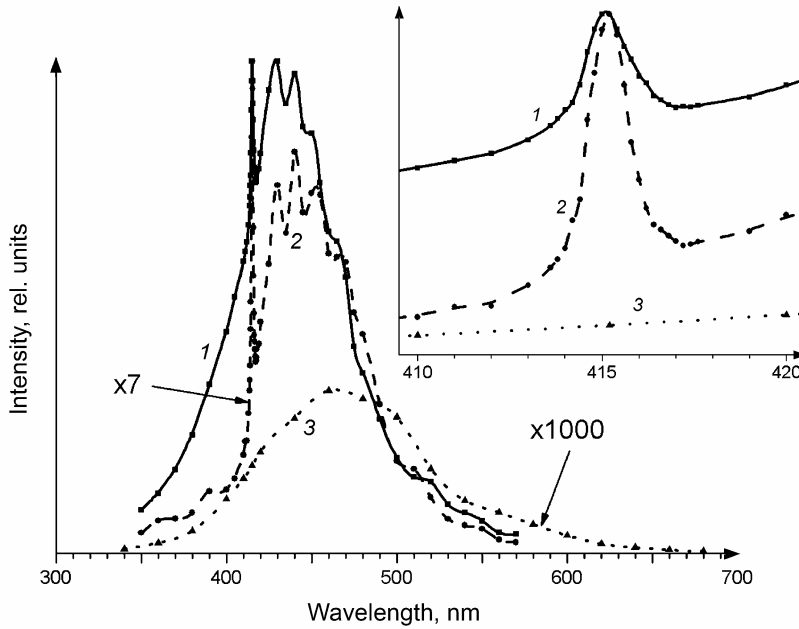


Fig. 3. Pulsed cathodoluminescence spectra of the natural IIA-type diamond excited by the electron beam and reconstructed 12 ns (curve 1), 90 ns (curve 2), and 2 ms after the onset of the pulse (curve 3). Magnified pulsed cathodoluminescence spectra in the spectral range 410–420 nm are shown in the insert.

a maximum in the spectral range 430–450 nm was observed. A narrow zero-phonon line (ZPL) was observed on the short-wavelength band shoulder at 415.2 nm together with its possible phonon replicas in the spectral range 430–460 nm caused by the vibronic N3-system. We note that peaks in the spectral range 420–470 nm had amplitudes higher than the pulse-to-pulse electron beam instability and measurement error. The ZPL width at half-maximum was 1.1–1.2 nm for both spectra.

The emission intensity measured at $t = 12$ and 90 ns after the onset of the light pulse differed by ~ 7 times. For convenience of comparison, the spectra shown in Fig. 3 were normalized.

The spectra in the spectral range 350–570 nm differ mainly by their short-wavelength parts. The normalized intensity measured at $t = 90$ ns in the spectral range 350–450 nm was much less than the corresponding value measured at $t = 12$ ns.

In the spectrum measured 2 ms after the onset of the pulse, the ZPL and its phonon replicas of the N3-system were absent (curve 3 in Fig. 3). The maximum was shifted toward 460–470 nm. The normalized emission intensity in the spectral range 300–450 nm decreased, while it increased at wavelengths exceeding 500 nm. This wide structureless luminescence band of natural diamonds is conventionally called band A. In [1–3, 11, 13] the band-A maximum of the natural diamond emission spectra was observed in the spectral range from 400 to 480 nm.

Investigations into the decay kinetics of emission demonstrated the presence of two characteristic components. Waveforms on the nano- and millisecond scales at the wavelength $\lambda = 460$ nm are shown in Fig. 4a and b, respectively. As can be seen from Fig. 4, the emission kinetics is characterized by at least two clearly different exponential functions on the nano- and millisecond scales. For the nanosecond scale, the characteristic emission decay time was 41 ns. The emission intensity decreased by approximately 3 orders of magnitude 2 ms after the onset of the light pulse. The decay time on the millisecond scale was 8.6 ms (Fig. 4b).

Thus, the bands in the PCL spectrum of the given sample on the nanosecond and millisecond scales have essentially different decay times and hence refer to different luminescence centers.

In [11] it was demonstrated that the integral PCL spectra of natural diamonds at room temperature represented wide structureless band A. When the integral spectra were recorded within 1 ms after the onset of the pulse, band A was weak and the N3-system was manifested. The photoluminescence of a synthetic diamond with nitrogen impurity subject to high-pressure high-temperature annealing was studied in [12]. The luminescence excited by a pulse of laser radiation with

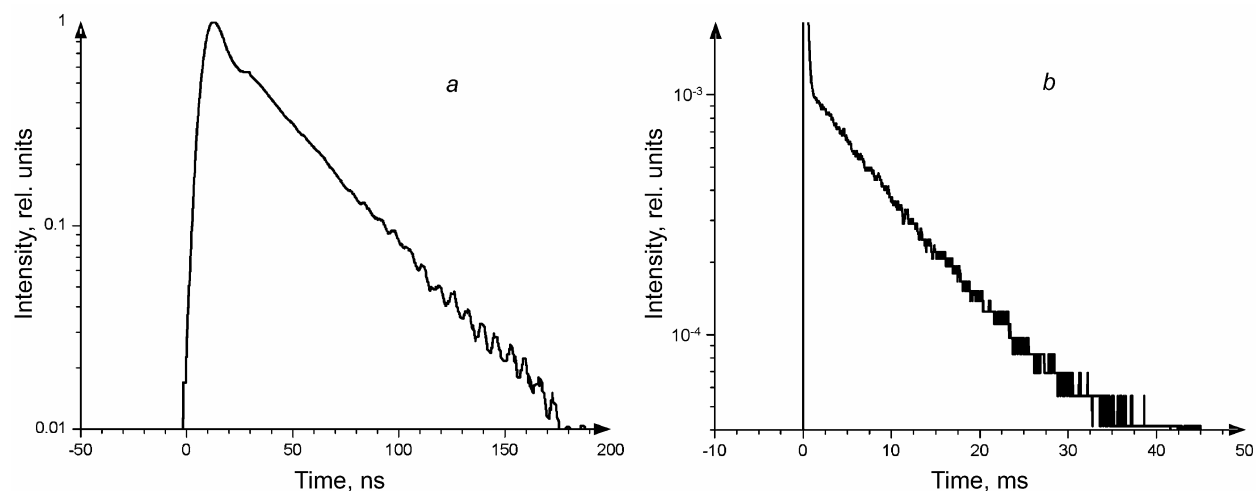


Fig. 4. Kinetics of pulsed cathodoluminescence of the natural IIa-type diamond at a wavelength of 460 nm on the nanosecond (*a*) and millisecond scales (*b*).

a wavelength of 353 nm was registered at the temperature of liquid nitrogen. The intensive N3-system was observed in the integral spectrum. However, the N3-system was not observed in the integral PCL spectrum registered with a delay of 1 μ s from the laser pulse, but weak band A with a maximum at \sim 450 nm was manifested. Thus, the N3-system had characteristic decay time on the nanosecond scale, while band A had the decay time on the millisecond scale, which is in agreement with our observations.

The diamond N3-center is formed by three substituting nitrogen atoms in the neighboring points of the lattice in the (111) plane “bonded” with a vacancy [1]. The excited energy level of the N3-center is located 0.42 eV below the bottom of the conduction band [7]. It is well known that the vibronic N3-system associated with these centers is well excited by laser radiation at a wavelength of 353 nm at the temperature of liquid nitrogen and has the decay time less than 1 μ s [12].

Unlike the N3-center, blue band A is caused by the intrinsic defects of the diamond lattice. It is suggested [8, 14] that this band is caused by the luminescence of intrinsic defects of the lattice formed by broken bonds of atoms in dislocations. Therefore, band A maximum must be localized on the energy axis close to the center of the energy band gap (at \sim 455 nm). It seems likely that luminescence bands of other optical centers (N3, H3, N_s, B_s, etc.) superimposed on band A cause the position of its maximum to change in a wide spectral range [1–3, 11, 13].

In [15] the sample luminescence was excited by an electron beam with pulse duration at half-maximum of 0.2 ns and by laser radiation (10 ns) to the fundamental diamond absorption band, and the integral spectra averaged over 100 pulses were registered. We note that electron-beam excitation and photoexcitation to the intrinsic absorption band differ only by the excitation energy density. The integral emission spectrum excited by a subnanosecond electron beam virtually coincided with the spectrum shown by curve 1 in Fig. 3. However, under excitation by laser radiation, the normalized intensity in the spectral range 450–700 nm was much higher, which can be explained by superimposed less intensive band A with long decay time. It seems likely that the N3-system is effectively excited by pulses with duration longer than 0.2 ns, while the excitation pulse duration could influence band A.

Figure 5 shows the measured PCL decay time spectra for the natural IIa-type diamond on the nano- and millisecond scales. As follows from these measurements, the decay time is 30–45 ns for the spectral range 410–550 nm on the nanosecond scale. For wavelengths shorter than 410 nm and longer than 550 nm, the emission decay time sharply decreases. A sharp increase in the decay time is observed for the ZPL of the N3-system.

The decay time on the millisecond scale for the spectral range 370–570 nm is 8.5–8.8 ms and remains virtually unchanged. Outside of this spectral range, the decay time decreases down to 7 ms. It was difficult to measure the decay kinetics of emission on the millisecond scale outside the spectral range 350–600 nm because of a low light signal amplitude.

Thus, the PCL of the natural IIa-type diamond consists of two emission types with different spectra. The first is caused by the vibronic N3-system with the ZPL at 415.2 nm which dominates on the nanosecond scale. The second is

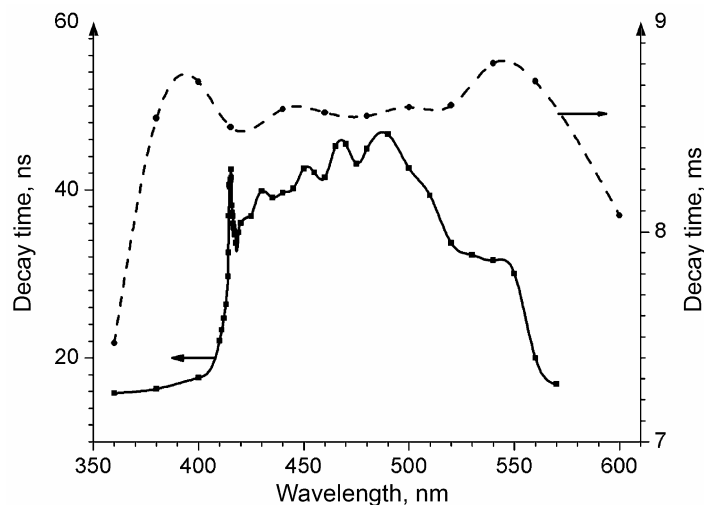


Fig. 5. Spectra of emission decay time for the natural IIa-type diamond excited by an electron beam on the nano- and millisecond scales.

structureless band A with low intensity and long decay time which contributes significantly to the integral spectra. The time variations of the spectrum shape are caused by the wavelength dependence of the characteristic emission decay time.

CONCLUSIONS

In this work, the PCL spectra and the decay kinetics of emission of the natural IIa-type diamond sample excited by the electron beam with duration of 10 ns at half-maximum have been investigated. In the visible range, the emission was caused by structural defects, including intrinsic (band A) and extrinsic (N3-system) defects. These two bands have different natures and decay times. The vibronic system of the nitrogen N3-centers with a characteristic decay time of 30–50 ns was dominant. Structureless band A caused by the intrinsic defects had a decay time of 8–9 ms. It seems likely that the band-A centers represent broken bonds near intrinsic defects of various types (for example, dislocations).

REFERENCES

1. V. B. Kvaskov, Natural Diamonds of Russia [in Russian], Polyaron, Moscow (1997).
2. J. Walker, Rep. Progr. Phys., **42**, 1607 (1979).
3. P. J. Dean, Phys. Rev., **139**, No. 2, 588 (1965).
4. V. E. Il'in and E. V. Sobolev, Zh. Prikl. Spektrosk., **7**, No. 3, 432 (1967).
5. E. F. Martynovich, L. V. Morozhnikova, and I. A. Parfianovich, Fiz. Tverd. Tela, **15**, No. 3, 927 (1973).
6. E. V. Sobolev and Yu. I. Dubov, Fiz. Tverd. Tela, **17**, No. 4, 1142 (1975).
7. E. V. Sobolev and A. P. Eliseev, Zh. Strukt. Khim., **17**, No. 5, 933 (1976).
8. J. T. Prins, Mater. Res. Innov., **1**, 243 (1998).
9. J. W. Steeds, T. J. Davis, S. J. Charles, *et al.*, Diamond Rel. Mater., **8**, 1847 (1999).
10. E. A. Vasil'ev, V. I. Ivanov-Omskii, B. S. Pomazanskii, and I. N. Bogush, Pis'ma Zh. Tekh. Fiz., **30**, No. 19, 7 (2004).
11. S. G. Mikhailov and V. I. Solomonov, Opt. Spektrosk., **80**, No. 5, 781 (1996).
12. S. C. Lawson, H. Kanda, K. Watanabe, *et al.*, Appl. Phys., **79**, No. 8, 43 (1996).

13. V. I. Solomonov and S. G. Mikhailov, Pulsed Cathodoluminescence and Its Application to an Analysis of Condensed Matter [in Russian], Publishing House of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg (2003).
14. N. Yamamoto, J. C. H. Spence, and D. Fathy, *Philos. Mag.*, **B49**, No. 6, 609 (1984).
15. E. I. Lipatov, V. F. Tarasenko, V. M. Orlovskii, and S. V. Alekseev, *Quant. Electron.*, **35**, No. 8, 745 (2005).