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Laser-induced luminescence of boron-doped synthetic diamond at various laser pulse durations

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Excitation of type IIb synthetic diamond by ultrashort laser pulses in the visible range causes broadband luminescence in the UV visible range; the observed luminescence band can be attributed to the A band characteristic of diamonds. The photoluminescence spectra were obtained at different laser pulse durations (0.3−6.2 ps) depending on the pulse energy. A nonlinear dependence of the luminescence yield on the intensity of ultrashort pulses is established.

Keywords: broadband luminescence, boron doped diamond, two-photon luminescence, A-band.

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Introduction

Diamond is a unique material, whose exceptional properties allow it to be used more and more widely in science and technology, from the manufacture of durable processing tools to quantum technologies [1–4]. More than 100 optically active centers [5] have been registered in diamond, some of which draw of particular interest [6,7]. Some of these centers are present in as-grown diamonds, in addition, regardless of their origin, additional centers can be formed due to irradiation or ion implantation [8].

Photoluminescence is the most sensitive methodology for detecting optically active centers in crystalline diamond. For this reason, photoluminescence becomes the key process that allows new functionality to be implemented on this platform.

Type IIb boron doped diamonds (BDDs) are of particular interest for optoelectronic applications. The BDD itself is a *p*--type semiconductor. Due to a number of properties, such as a large band gap, high carrier mobility, high thermal conductivity, as well as the ability to withstand extreme conditions, it is used for near-Earth and deep space research, nuclear power plants, electrochemistry [9–11].

It is also worth noting the work [12], in which the broadband luminescence of natural diamond, excited by ultrashort laser pulses in the visible range, was studied. The observed luminescence was associated with the presence of point imperfections nitrogen and free vacancies, including those generated under the action of femtosecond laser radiation in the volume of diamond. In this work, the photoexcitation of broadband luminescence in synthetic nitrogenless IIb-type boron doped diamond at wavelength of 515 nm depending on the intensity of laser radiation at femtosecond and picosecond pulse durations was studied.

Experimental part

As a sample in this work, we used blue synthetic (HPHT) IIb-type boron doped diamond. The sample was a thin wafer with thickness $\sim 300\,\mu$m, size $\sim 4 \times 4$ mm. Wafer with (001) crystal-lattice orientation contains mainly growth sectors {100}, {111}. On centre was located the region $\sim 1 \times 1$ mm of the growth sector {100}, along the edges was the region of the sector of growth {111} (Fig. 1).

The diamond was previously characterized in the transmission mode using the Bruker Vertex 70v IR Fourier -spectrometer in the range of $2-25\,\mu$m. In the transmission spectrum (Fig. 2) absorption bands are observed at 2440−4070 nm ($4095\,\text{cm}^{-1}-2457\,\text{cm}^{-1}$), dips in this region are characteristic of IIb-type diamond and are caused by the presence of boron impurity. The boron concentration was estimated from the absorption band at $2800\,\text{cm}^{-1}$ (3570 nm) and amounted to $\sim 10^{17}\,\text{cm}^{-3}$ and $\sim 3 \cdot 10^{17}\,\text{cm}^{-3}$ in sectors {100} and {111} respectively. The central region of the wafer contained a smaller number of imperfections; therefore, in the course of further work, photoluminescence was excited in the {100} sector.

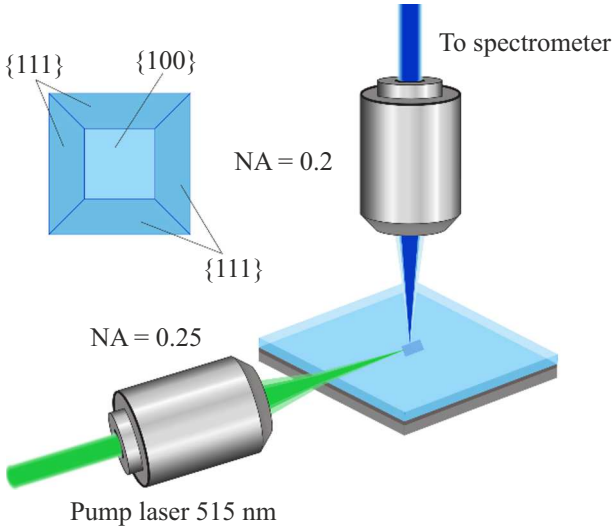

Figure 1. Experimental scheme. Blue rectangle is the photoexcitation region, the radiation from which is collected in the spectrometer. The inset shows the schematic layout of the main growth sectors (top view).

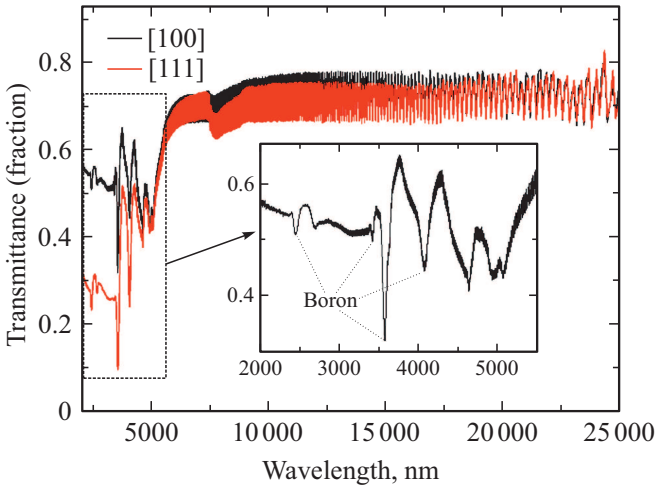

Figure 2. The transmission spectra of boronated diamond in the range $2-25\,\mu$m for the corresponding growth sectors (indicated in the figure); the absorption dips characteristic of boron are shown.

Next, the luminescence and combinational scattering spectra were measured using the Confotec MR350 confocal Raman laser scanning microscope with pumping wavelength of 532 nm. Figure 3 clearly shows the Raman line of diamond with peak at wavelength of 572 nm, the optical phonon in this case is equal to 1331 cm^{-1}, and the energy is 0.16 eV. Also in Fig. 3 one can see the second order of the combinational scattering and weak luminescence in the red region.

Next, to excite the luminescence, the second harmonic radiation ($\lambda_{las} = 515$ nm) of the Satsuma fiber ytterbium laser (by Amplitude Systemes) with variable pulse duration and maximum pulse energy $E_{max} = 3.3\,\mu$J in TEM$wasused_{00}$.

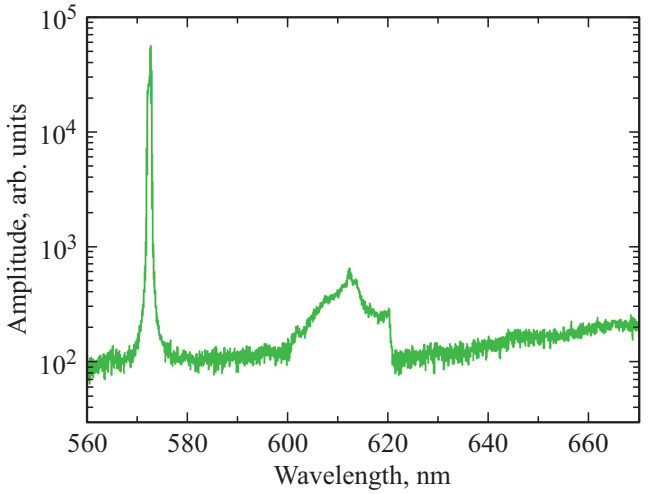

Figure 3. Luminescence spectrum for sector {100} at pumping wavelength 532 nm.

The laser radiation was focused to the center of the diamond wafer ($\sim 150\,\mu$m under the surface) by the microscope objective with numerical aperture NA = 0.25 (Fig. 1). The resulting photoluminescence was focused onto the slit of an Andor Shamrock 303i ICCD-spectrometer using a LOMO UV objective lens with NA = 0.2 in the direction orthogonal to the propagation of pumping-radiation of laser. The sample was placed on motorized three-axis Standa platform with minimum motion step of 150 nm.

The photoluminescence signal was measured in a wide wavelength range (300–800 nm) by pulses with duration of 0.3, 1.3, 6.2 ps at variable energy of 2–400 nJ and pulse-repetition rate of 100 kHz. To avoid damage to the detector by intense pumping, the region 460–530 nm was not recorded.

Experimental results and discussion

The spectra in Fig. 4 demonstrate the broad luminescence band for all durations above and below the pumping wavelength in the wavelength range 350–650 nm. Clear cut peak at wavelength of 555 nm corresponds to the Raman line (optical phonon $\sim 1331\,cm^{-1}$). The band with a maximum at 555 nm corresponds to single-photon Raman scattering of light by sp3 vibrations of the diamond lattice. In Fig. 4, *b, c*, corresponding to durations 1.3 and 6.2 ps, a ~ 537 nm peak is distinguishable on the red shoulder of the luminescence band. On the blue shoulder of the luminescence band for all durations, a peak at ~ 432 nm is clearly discernible, close to there is a narrow peak at ~ 434 nm. For more accurate interpretation of these peaks, it is necessary to see the full luminescence spectrum with the central region 460–530 nm, which seems to be impossible in our work. For more accurate interpretation of these peaks, it is necessary to register the total luminescence spectrum with the central region

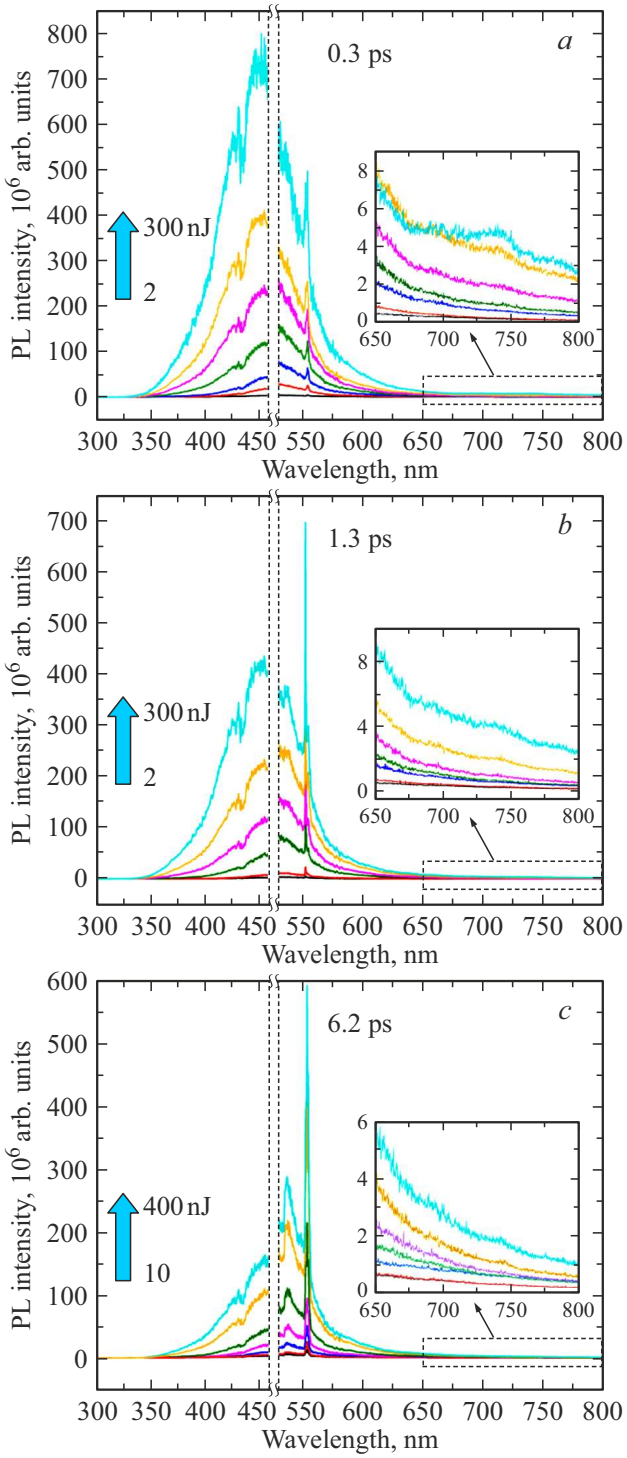

Figure 4. General view of the photoluminescence spectra of boronated diamond excited at a wavelength of 515 nm for pulse durations of 0.3 (*a*), 1.3 (*b*), 6.2 ps (it c) and pulse repetition rate 100 kHz. The inset shows an enlarged region of red luminescence. The spectra were sewed together taking into account the exposure during registration.

of 460−530 nm, which seems to be impossible in our work.

Broad photoluminescence band in the range 350−650 nm can be defined as A-band [5,13–15]. The spectra in Fig. 4 demonstrate a shift of the luminescence maximum to longer wavelengths as the duration of laser radiation increases at similar pulse energies. Similar effect was observed in the work [16], but for diamond CVD-films and was associated with the presence of boron in them. In type II-diamonds, the A-band can be associated with radiative recombination at dislocations [17].

The maximum of photoluminescence amplitude for the peak at 537 nm depending on the intensity of laser radiation (Fig. 5, *a*) for all three durations has the slope coefficient close to 1, which indicates the linear dependence of luminescence yield. At the same time, for the peak at 434 nm, the dependence of the photoluminescence yield on the intensity of the incident radiation, shown on double logarithmic scale (Fig. 5), is of nonlinear nature with slope coefficients just over than unity. Such a difference is probably related to the efficiency of one-twophoton excitation of luminescence depending on the intensity of the incident radiation. It is worth noting that these peaks ($\sim$ 434 and 537 nm) are noncharacteristic for photoluminescence in artificial (HPHT) diamonds IIb- [5]; the nature of their occurrence requires additional study.

Conclusion

Laser excitation of synthetic boron doped diamond ($\sim 10^{17}\,\mathrm{cm}^{-3}$) in the visible range causes luminescence of the A-band in the range 350−650 nm, which demonstrates the shift of the luminescence peak to the low-energy region with a decrease in the pumping intensity. The luminescence yield of laser radiation for all three durations has similar intensity dependences. However, the dependences of the amplitude of the luminescence peaks below and above the pumping length ($\sim$ 432 and 537 nm) on the laser radiation intensity indicate different luminescence mechanisms associated with the features of one- and two-photon excitation.

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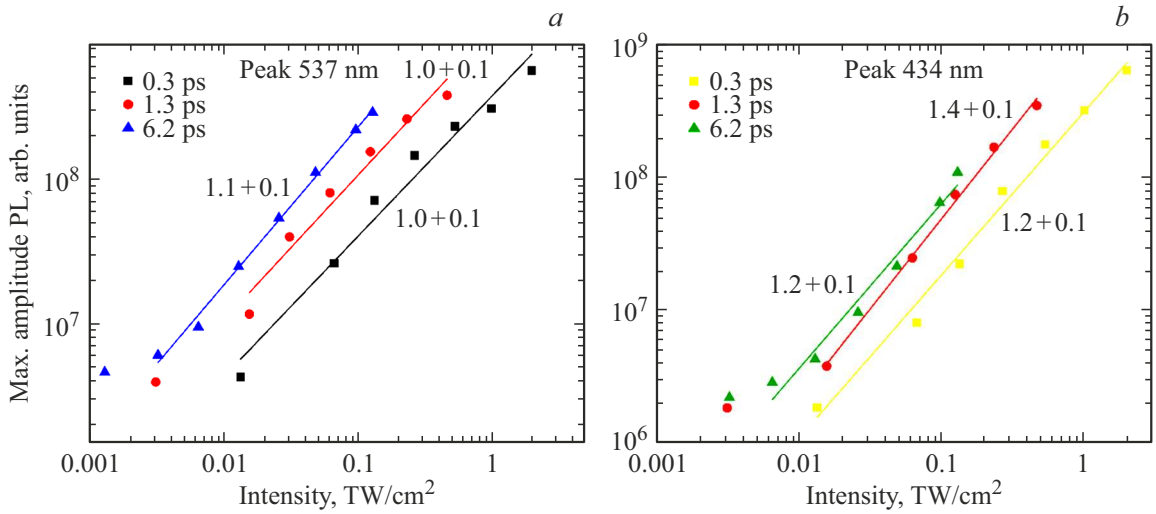

Figure 5. Dependence of the maximum PL amplitude for the peaks at 537 (*a*) and 434 nm (*b*) on the pumping intensity.

Conflict of interest

The authors declare that they have no conflict of interest.

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