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Laser-induced luminescent centers in diamond: influence of exposure and duration of short laser pulses

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The optical properties of point luminescent centers formed in the volume IaA-type natural diamond under the action of ultrashort laser pulses in the visible range (515 nm) with durations of 0.3−2.4 ps were investigated. The analysis using confocal Raman spectroscopy demonstrates the formation of nitrogen vacancy centers (NV) and there are no graphitization traces in processing areas. The luminescence amplitude of NV centers depends linearly on the exposure time at different durations of ultrashort laser pulses.

Keywords: ultrashort laser pulses, luminescence, luminescent centers in diamond, NV centers.

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Introduction

Point defects in dielectrics and crystals, including diamond, formed under the action of ultrashort laser pulses, find applications in the field of quantum technologies, optical memory and „invisible“ laser micromarking, which is carried out without visible damage to the sample [1–7]. One of the best studied optical defects in diamonds is negatively charged nitrogen vacancy center (NV) with zero-phonon line (ZPL) ~ 638 nm [4]. At the same time, the registration of single NV centers was first reported more than 20 years ago [5].

The method of direct laser beam writing in dielectrics by ultrashort laser pulses has shown itself well for writing various structures in diamonds, including single NV centers [6,7]. To detect optically active impurities and laser-induced defects in diamonds, photoluminescence is actively used, which also makes it possible to analyze the nature of the electron-phonon interaction in a crystal during the formation of point defects [8–12]. Single NV centers can be detected using confocal microscopy, and it is efficient to use laser sources with a wavelength of ~ 514 nm [8] to excite their luminescence.

This work presents the results of laser beam writing by ultrashort pulses with wavelength of 515 nm and durations of 0.3-2.4 ps of point luminescent centers in the volume of natural diamond at various exposures of 30−360 s with a repetition rate of laser pulses of 100 kHz, which corresponds to the number of pulses per point $N = (3-36) \cdot 10^6$. The formed arrays were visualized and analyzed using scanning confocal Raman spectroscopy, and the dependence of the luminescence yield of point centers on exposure was studied for various laser pulse durations.

Experimental part

The second harmonic radiation (SH, $\lambda_{las} = 515$ nm) of Satsuma femtosecond ytterbium fiber laser (by Amplitude Systems) with the maximum pulse energy (excluding losses in the optical scheme) $E_{max} = 3.6\,\mu$J in TEM_{00} mode and repetition rate 100 kHz was used to process the diamond. The pulse duration was varied in the range 0.3−2.4 ps using a built-in compressor. Laser radiation was focused to a depth of $\sim 200\,\mu$m by micro-objective (OB1, Fig. 1) with the numerical aperture NA = 0.25, while the spot size in air in the focal plane was $R_{1/e} \approx 2.2 \pm 0.2\,\mu$m. The sample was fixed on a three-coordinate motorized Standa platform (MS, Fig. 1) with a minimum movement step of 150 nm.

IaA-type diamond sample represents the colorless transparent cube with side ~ 4 mm. For preliminary characterization, the transmission spectra were measured in the visible (200−1100 nm) wavelength range using the SF-2000 spectrophotometer. The absorption spectrum shown in Fig. 2 shows the presence of N3 centers [4,8] in our sample.

Visualization and analysis of the luminescence spectra of point defects formed by ultrashort pulses in the volume of diamond was carried out using 3D scanning confocal Raman microscope Confotec MR350 with a continuous pump laser 532 nm and cooled CCD array as a detector. The spectra were recorded using the 600 st/mm grating, which made it possible to obtain a resolution of $\sim 5\,\text{cm}^{-1}$.

Experimental results and discussion

Visualization of luminescent centers

In our work, point defects in the form of a matrix with variable energy (60−600 nJ) and exposure time (30−360 s) were formed at a depth of $\sim 200\,\mu$m in the volume of

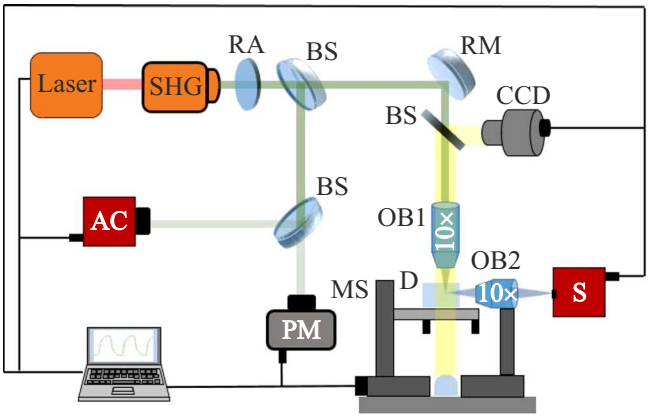

Figure 1. Scheme of the stand for laser beam writing and registration of luminescence in diamonds: Laser is ytterbium fiber laser 1030 nm; SHG is second harmonic generator 515 nm; RA is diffraction attenuator; BS is beam splitters; RM is- reflective mirror; PM is power meter; AC is autocorrelator; MS is three-axis motorized platform Standa; S is spectrometer Avesta ASP-150; CCD is CCD camera; OB1 is pumping object lens NA = 0.25 10×; OB2 is UV observation lens NA = 0.1 10×; D is diamond; PC is control computer.

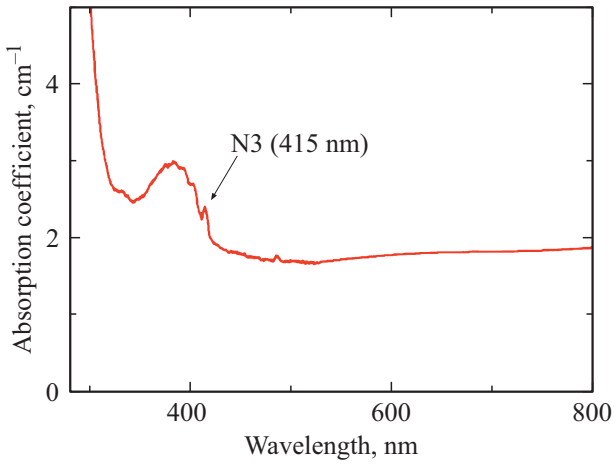

Figure 2. Absorption spectrum of diamond in the wavelength range 280–800 nm.

diamond under by the action of laser pulses with wavelength of 515 nm, durations of 300 fs, 1.0 ps, and 2.4 ps, with repetition rate of 100 kHz. The processing area was first analyzed using optical microscopy for damage to the diamond structure during writing. Figure 3 shows images of the surface and volume of diamond after irradiation with laser pulses with wavelength of 515 nm and a duration of 1 ps. No traces of graphitization were found by optical methods.

Then, using scanning Raman spectroscopy with pumping of 532 nm, 2D fluorescent images of the formed defects were obtained (Fig. 4). To do this, areas $\sim 150 \times 150\,\mu$m were scanned with the step $\sim 3\,\mu$m. It can be seen that

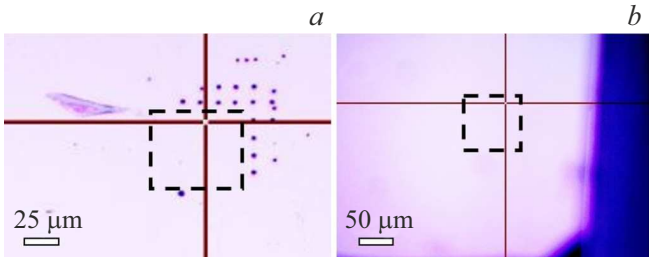

Figure 3. Optical images of the surface (*a*) and volume (*b*) of diamond after treatment with laser pulses with wavelength of 515 nm, duration 1 ps. The black dashed line indicates the area in which the matrix of point defects was recorded.

the modified regions differ significantly in luminescence brightness from the rough diamond and have a good contrast.

Spectroscopy

Further, let us turn to the consideration of the spectral features of the formed matrices. Figure 5, *a* shows a comparative luminescence spectrum of rough diamond (red curve) and a point defect formed at a pulse energy of 450 nJ, duration of 300 fs, and exposure time of 360 s ($36 \cdot 10^6$ pulses to a point). It can be seen that in the range 600–680 nm the luminescence after processing increases several times. The main Raman line of diamond 1331 cm^{-1} [4] is also present, which corresponds to the ~ 572 nm line in the luminescence spectrum at 532 nm pumping. Figure 5, *b*–*d* shows the difference spectra minus the averaged background for different exposure times and pulse energies ~ 300 nJ.

It is noticeable that with increasing exposure, the luminescence of point defects increases and has a maximum in the region ~ 640 nm. This maximum is apparently associated with the formation of negatively charged NV centers [4,9], but in our case the ~ 638 nm [4] ZPL characteristic of them is not observed. It is also worth noting that the highest luminescence amplitude is characteristic of centers formed at a laser radiation duration of 1.0 ps.

Next, we studied the dependence of the luminescence yield (in terms of the amplitude maximum) of the formed point centers at various laser pulse durations. On the whole, for all energies of laser radiation, the dependences have a similar character. Figure 6 shows graphs of the luminescence yield (by the amplitude maximum) for energies of 150 and 300 nJ as a function of the number of pulses. It can be seen that in both cases the dependence has a linear character.

Conclusion

The laser-induced formation of point luminescent centers in IaA-type natural diamond under the action of

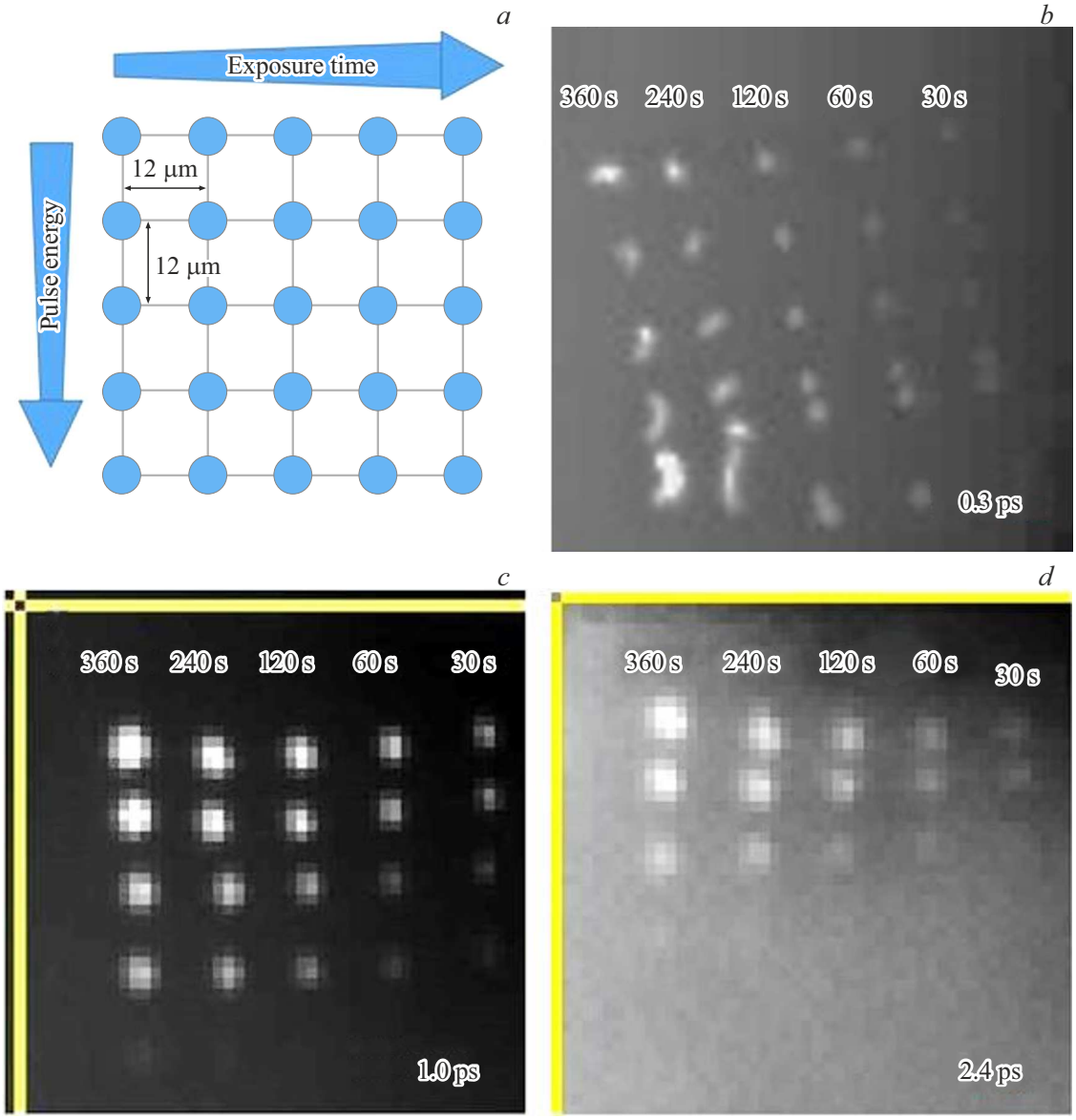

Figure 4. Images of luminescent centers in natural diamond obtained by scanning Raman spectroscopy with pumping of 532 nm and formed by ultrashort laser pulses with wavelength of 515 nm at a depth of $\sim 200\,\mu$m with repetition rate of 100 kHz at various exposures (shown in the figure) and energies in the range of 60−600 nJ. *a* is the scheme for recording point centers; *b* is the matrix formed with duration 300 fs; *c* is the matrix formed at duration 1.0 ps; *d* is the matrix formed at duration 2.4 ps.

ultrashort pulses with a wavelength of 515 nm, durations of 0.3-2.4 ps at various exposures of laser radiation $N = (3-36) \cdot 10^6$ impulses to a point, was studied. It has been established that negatively charged NV centers are formed under the action of laser radiation, the luminescence of which is most important when formed by laser pulses with a duration of 1 ps. The luminescence yield of point defects (NV) to a maximum of ~ 640 nm for different durations of laser radiation, depending on the exposure at pumping energies up to 600 nJ, has a linear character. Laser beam writing of luminescent marks seems to be a promising method for micro-marking diamonds due to the absence of visible damage (graphitization) in the area of laser radiation.

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Conflict of interest

The authors declare that they have no conflict of interest.

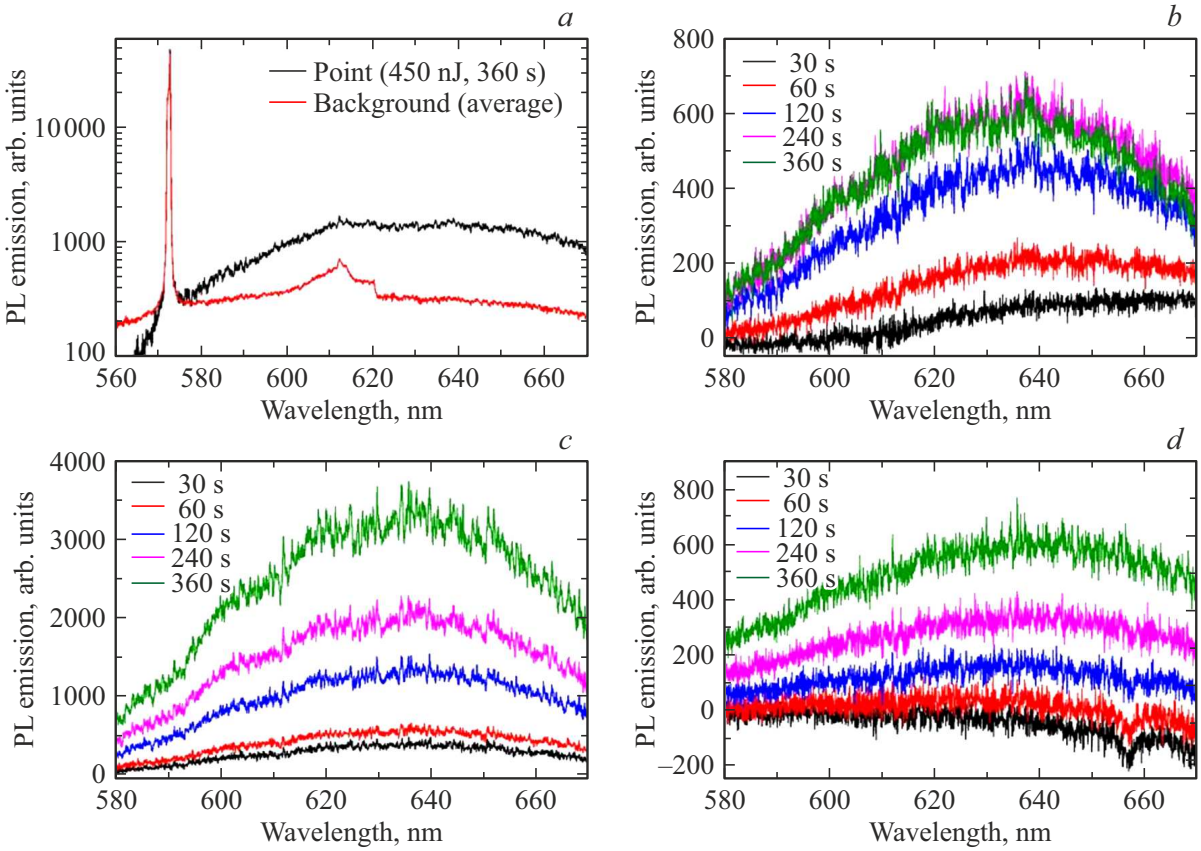

Figure 5. Luminescence spectra of point defects in natural diamond for different exposures and energies in a 300 nJ pulse when pumping by laser with wavelength of 532 nm. *a* is luminescence spectrum of unmodified diamond and label (450 nJ, 300 fs, 360 s); *b* is luminescence of point defects minus the background for various exposures of laser radiation (30, 60, 120, 240, 360 s) and pulse duration 300 fs; *c* is luminescence of point defects minus the background for various exposures of laser radiation (30, 60, 120, 240, 360 s) and pulse durations 1.0 ps; *d* is luminescence of point defects minus the background for different exposures of laser radiation (30, 60, 120, 240, 360 s) and pulse duration 2.4 ps.

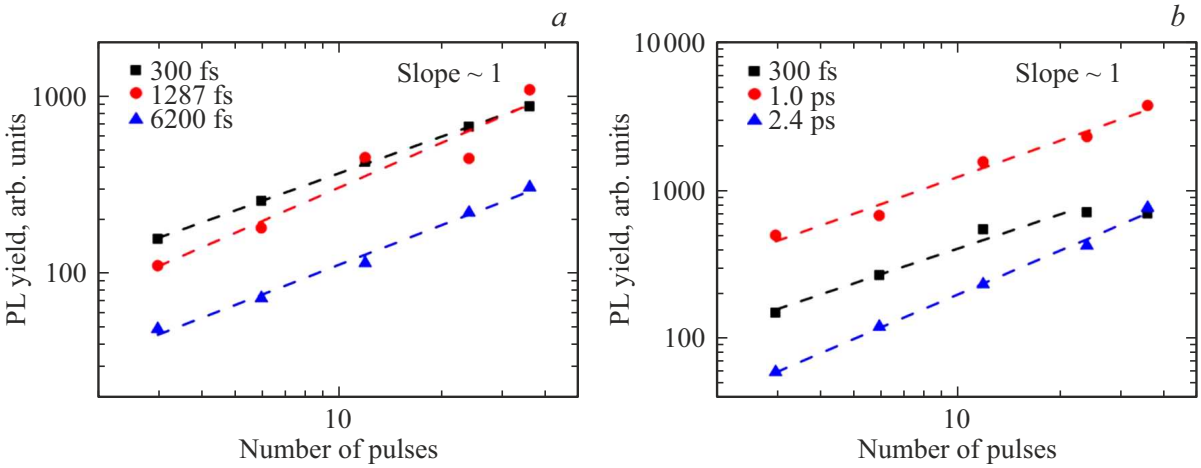

Figure 6. Luminescence yield according to the maximum amplitude of point luminescent centers in natural diamond depending on the number of laser pulses (exposure) for two energies: 150 (*a*) and 300 nJ (*b*).

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