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Luminescent Characteristics of Needle-Like Single Crystal Diamonds

Sergey A. Malykhin,* Jonathan Houard, Rinat R. Ismagilov, Anton S. Orekhov, Angela Vella, and Alexander N. Obraztsov

Luminescent properties of needle-like single crystal diamonds are investigated in a wide range of wavelength. The luminescent spectra with zero phonon lines centered at 389, 442, 468, 534, 563, 575, and 738 nm are detected using excitation by photons and electrons. Obtained photo- and cathodo-luminescent (PL and CL) spectra indicate presence in the single-crystal diamond needles of nitrogen- and silicon-vacancy centers as well as substitutional or/and interstitials related to these atomic impurities. The dependencies of PL intensities of the 575 and 738 nm lines (related, correspondingly, to nitrogen- and silicon-vacancy centers) on excitation wavelength are determined. Time-resolved measurements are performed for the 575 nm PL line. The luminescence decay behavior for this line demonstrates the presence of recombination processes with characteristic times of about 28 ns (on 200 ns time scale) and 2.8 ns (on 20 ns time scale).

1. Introduction

Diamond is an amazing material that combines record hardness and thermal conductivity, biocompatibility, optical transparency, and other properties attractive for numerous applications.^[1,2] Development of methods for synthesis of diamond with high-pressure–high-temperature (HPHT)^[3] and chemical vapor

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deposition (CVD) techniques^[4] provides expansion of industrial usage of diamond.^[5] Crystalline qualities of synthetic diamonds (which may be better than the best natural diamonds at present time^[6]) are critical for many applications as well as properties of particular structural defects. This stimulates investigations of structural peculiarities and defects in diamond. Many of these defects attract attention because of their optical and luminescent properties. More than 500 types of the color-centers are known in diamond.^[7] Luminescent characteristics of some of them allow consideration of diamond as promising material for different optical and quantum optical applications.^[8,9]

Important advantage of CVD techniques consists in ability to produce diamond crystallites of needle-like shape^[10,11] which

may be usable for some applications. In particular diamond needles are considered for creation of optical probes and sensors. These applications require comprehensive investigation and deeper understanding of the luminescent properties of particular color-centers in this type of diamond material. In this work, we perform study of the diamond needle-like single crystals to reveal their photo- and cathode-luminescent characteristics in a wide range of wavelength, never explored before for this kind of samples. Results of preliminary investigations of these properties have been reported in Refs. [12,13]. Here we present results of our studies of the diamond needle-like single crystals aimed to further revealing peculiarities of their photo- and cathode-luminescent characteristics.

2. Experimental Details

2.1. Materials

The needle-like single crystal diamonds (SCD) were obtained by combination of the CVD and selective oxidation techniques.^[10] Home built direct current plasma enhanced CVD allowed creation of the carbon films composed of the pyramid shaped needle-like single crystal diamonds surrounded by a matrix of graphite, nanodiamond, and amorphous carbon. The films were grown on silicon wafer substrate. A selective oxidation at 650° C in air atmosphere for about 24 h was applied to remove the low-ordered and graphitic part of CVD film and, thus, to obtain the

pyramid-shaped diamond crystals in form of powdered material. This powder was used to prepare ethanol-based suspension containing SCD needles. The well-separated diamond crystallites were deposited on the substrates (e.g., on silicon wafers) by subsequent precipitation and drying the drops of the suspension. Detailed description of used methods and facilities are presented elsewhere.^[14]

2.2. Cathodoluminescent Measurements

The cathodoluminescent (CL) investigations were made using specially prepared samples of SCD. Individual diamond crystallites in these samples were disposed on silicon substrates and fixed by local Pt deposition to prevent their uncontrollable moving by electrostatic forces appeared due to charging of dielectric particles by electron beam. The localization and Pt deposition were made with use of Versa 3D dualbeam (FEI) facility equipped by micromanipulators. The samples with different orientation of the diamond crystallites were prepared for these CL investigations. Scanning electron microscope (SEM) images of some of the samples and simplified scheme of their positioning are presented in **Figure 1**. It is worth noting that the bottom part of the needle in **Figure 1(b)** is not fixed on the right side, but it has not got any effects on further investigations. Surface purity of the samples was analyzed by energy-dispersive X-ray spectroscopy (EDS) using INCA EDS analyzer attached to JEOL 7001F scanning electron microscope. Obtained EDS maps did not indicate any detectable impurities on the facets of the SCD samples which were investigated.

The CL measurements were performed using GATAN MONO CL3 attachment to JEOL JSM7001F scanning electron microscope at room temperature (300 K) and with cooling down to temperature of about 81 K. The electron beam accelerating voltage was varied from 3 to 30 kV and the beam current was changed from 500 pA to 150 nA. The electron beam was focused in the area less than 10 nm in diameter as it was estimated from sample contrast on the SEM images obtained in secondary electrons mode. The diffraction grating with 1200 lines per mm (sensitivity maximum on 500 nm wavelength) was used in spectrometer for CL spectra detection. The optimal values of signal to noise ratio and spectral resolution were achieved at 15 kV voltage and 80 nA current of the electron beam. These parameters of the electron beam were used for detection of all CL spectra presented in this work.

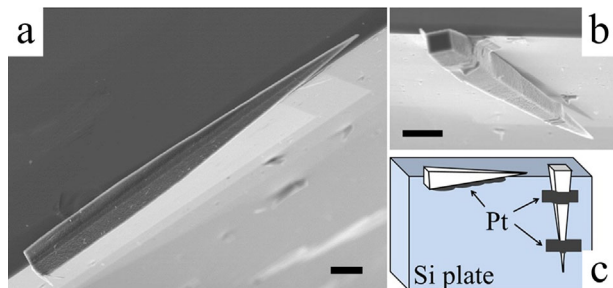


Figure 1. SEM images (a and b) and schematic representation (c) of the samples prepared for CL investigations. Scale bars correspond to 10 μm .

2.3. Photoluminescent Measurements

The needle-like single crystal diamonds were also investigated with photoluminescence (PL) technique. A simplified optical scheme of used facility assembled on optical table is presented in **Figure 2**. A titanium-sapphire tunable pulsed laser (Chameleon Ultra from Coherent) with wavelength varied from 690 to 1080 nm and 80 MHz frequency was used as a source of excitation irradiation. A pulse picker was used to reduce the laser retention rate at 4 MHz. Laser irradiation was passed through the second and third harmonic generation block (SHG/THG in **Figure 2**). To pick out needed wavelength from the generated set of laser radiation color filter was used (excitation filter in **Figure 2**). Selected laser beam, after passing through the 50/50 ultraviolet beam splitter (BS UV 50/50 in **Figure 2**) and reflective objective, irradiated the sample. The PL radiation emitted by the sample was collected by the same reflective objective and directed to the imaging camera (if optical image of the sample is required) or to the spectrometer analyzing collected light radiation. An additional optical filter (imaging filter in **Figure 2**) was installed before the spectrometer to remove intensive scattered radiation of the laser beam or its harmonics. A streak camera (model C5680 from Hamamatsu with slow sweep and an ultimate timing resolution of about 20–30 ps) situated after the spectrometer also was used for decay time determinations.

The PL investigations were performed under room temperature (300 K) and with cooling down to 24 K and to 4 K temperatures. Wavelength of excitation radiation was varied from 260 to 515 nm. Power of the irradiation beam measured before reflective objective was varied from 50 to 800 μW . PL spectra were obtained by focusing laser beam at different areas along an individual needle-like diamond crystal.

3. Results and Discussion

The advanced experimental techniques used in this study allow obtaining much more details about CL and PL spectra in comparison with our preliminary investigations reported in Refs. [12,13]. These details include spectral characteristics of the luminescence, dependence of the spectral lines on temperature and excitation wavelength, their decay time dependence, and phonon vibronic bands characteristics. In the preliminary investigation, we have established that luminescent characteristics of SCD indicate on nitrogen and silicon impurities contaminations.^[12,13] While the nitrogen-related color centers are distributed more or less homogeneously in the crystallites,

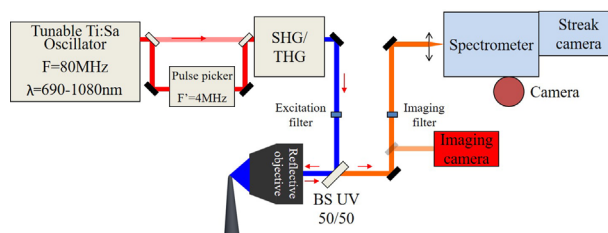


Figure 2. Scheme of the PL setup used for investigation of the diamond needles (see description in text).

the silicon centers are concentrated predominantly at their apexes. The CL and PL investigations were performed in different areas of SCD (near the apex, in the middle, and near the base). The same luminescence lines in all of these points were observed. In this study, we focused mostly on the analysis of crystallite luminescent properties on the whole. The spectra discussed in this work were observed near the middle of the SCD and are used here as the most representative for the whole crystallite while spectra variations along the needles are discussed in other our works.^[12,13]

3.1. Main Luminescence Lines

The luminescent spectra were obtained in wavelength range of 225–900 nm with CL technique and (depending on the excitation wavelength) in the range of 260–880 nm for PL. The spectra in the range of 350–800 nm are presented in **Figures 3 and 4**.

Typical CL spectra measured in the middle part of SCD at room temperature and with cooling down to 81 K are presented in Figure 3. Figure 4 presents the PL spectra obtained at room temperature and at cryogenic temperature (24 K). At low temperatures, luminescence intensity increases, the width of the lines and, especially, the width of the broad bands related to structural defects in diamond reduces markedly. Overall signal-to-noise ratio is increased with temperature decrease that allows appearance of more details in the spectra.

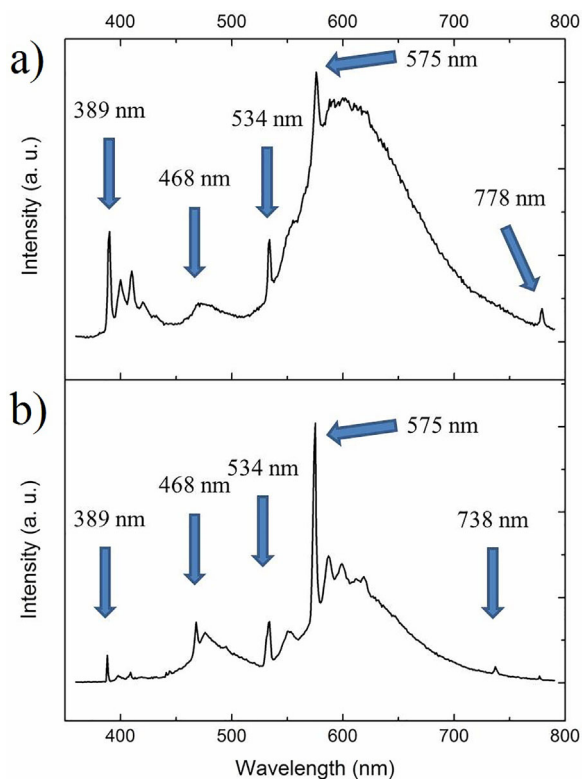


Figure 3. Typical cathodoluminescent spectra obtained at 300 K (a) and at 81 K (b). Energy of irradiated electrons is 15 keV, beam current is 80 nA.

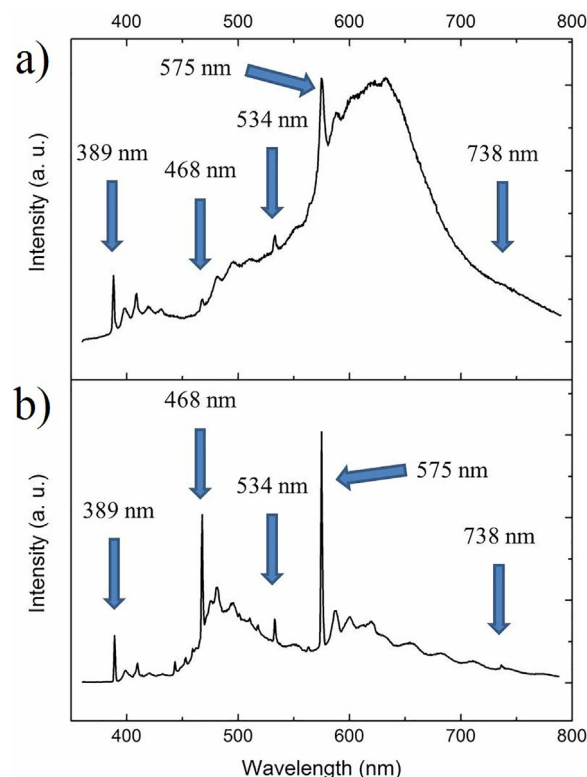


Figure 4. Typical photoluminescent spectra: (a) spectrum measured at sample temperature of 300 K and with wavelength of excitation radiation of 300 nm; (b) spectrum measured at sample temperature of 24 K and with wavelength of excitation radiation of 260 nm.

The most intensive sharp lines distinguished in the spectra are centered at 389, 442, 468, 534, 563, 575, and 738 nm. The line at 778 nm presenting in the CL spectra is a second order diffraction of 389 nm line. The spectral shape of low temperature PL spectrum in 650–730 nm wavelength range is due to transmission characteristics of the imaging optical filter. Previous investigations^[15–17] allow assignment of observed luminescent line at 389 nm (3.188 eV) to a zero phonon line (ZPL) of nitrogen-related centers in diamond. Intensity of this 389 nm line was changed significantly during CL signal accumulation for electron beam accelerating voltage above few kV.^[7] It may explain variation of relative intensity of this line in the spectra shown in Figures 3 and 4. The intensity of similar 389 nm line have been increased strongly after diamond annealing at temperature from 600 to 800 °C.^[7] Such annealing may occur during oxidation of the CVD diamond film at 650 °C. The nitrogen-related centers proposed for this line may include: defects that contains interstitial nitrogen atoms^[18]; pseudomolecules C-N formed by single substitutional nitrogen atom shifted along the $\langle 111 \rangle$ axis^[7] or C2N^[19]; defects containing substitutional nitrogen atom bound to interstitial carbon atoms.^[20]

The 442 nm (2.807 eV) line obtained at 24 K with excitation wavelength of 260 nm has been assigned also to nitrogen impurities and represents a ZPL observed in the PL spectra.^[7] Moreover this line can be observed in low temperature CL

spectra but it is too weak for detailed analysis. The line is not visible in PL and CL spectra measured at room temperature probably due to large background noise. In accord with previous investigations, the luminescent centers responsible for appearance of 442 nm line can contain interstitial carbon atoms.^[7]

The 468 nm (2.651 eV) line has been observed in high-quality single-crystal CVD diamond films. This line has been assigned to the centers containing nitrogen and interstitial atoms.^[7,17] However, in some reports this type of centers was associated also with silicon impurities that appeared in CVD diamond grown on Si substrates.^[15,19] Clarification of this contradictory assignments requires high-temperature annealing of diamond in vacuum which was unavailable for us in this work. Obtained spectra demonstrate different shape of 468 nm line because of vibronic bands which will be discussed in the next section. Intensity of 468 nm line shows a significant increase in both CL and PL spectra at low temperatures. On the whole 468 nm line demonstrates greater relative intensity in photo-luminescence in comparison with cathode-luminescence.

The 534 nm (2.322 eV) line is supposed to be associated with the centers containing nitrogen atoms or nitrogen-vacancy complexes in its structure.^[15] Usually the line is observed as a part of ZPL doublet containing also 531 nm line. But in perfect homoepitaxial CVD diamond films, this line has been observed as a single ZPL line instead.^[7] Only single line can be resolved in all spectra obtained in our work (see Figure 3 and 4). This may be considered as an evidence of the high-quality single crystal structure of the needle-like diamonds in consistency with previously reported results.^[21] The 534 nm line is better resolved in CL spectra. It may be due to less intensity of the vibronic bands of 468 nm line that results to less intensive background.

The 563 nm line can be detected in PL and sometimes in CL spectra but this line is weaker in comparison with the nearest 575 nm band. Moreover other lines in this spectral range relate to different defects in diamond.^[7]

The 575 nm (2.156 eV) line in the luminescence spectra corresponds to the nitrogen-vacancy centers in uncharged state (NV⁰).^[22] The properties and structural features of NV⁰ are investigated in details (see e.g., Ref. [23]). Intensity of vibronic bands associated with 575 nm line is significantly reduced and the zero phonon line becomes much more pronounced at low temperatures (see Figure 3 and 4).

The decay time of 575 nm line was investigated with excitation by pulsed laser radiation at 370 nm. **Figure 5(a)** shows detected

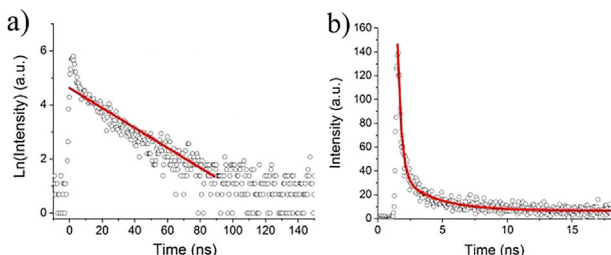


Figure 5. Time dependences of photoluminescent 575 nm line decay on long (a) and short (b) time scale. Excitation wavelength is 370 nm, beam power is 400 μ W. Red lines correspond to exponential decay adjustments in semi-logarithmic (a) and linear scale (b).

time dependence of PL intensity after pulse irradiation on long time scale of 200 ns. The decay time of neutral nitrogen-vacancy color centers luminescence calculated from this data is about 28 ± 1 ns. This value is in agreement with previously reported values of about 29–32 ns for the decay time of 575 nm line.^[7,24] However, our measurements indicate that in short time scale (20 ns) a fast decay of luminescence intensity with characteristics time of 2.8 ± 0.3 ns also occurs (see Figure 5(b)). Similar characteristics decay time has been previously observed in diamonds.^[25]

The 738 nm (1.681 eV) line has been assigned to another well-known color center in diamond related to silicon impurities (so called silicon or silicon-vacancy (SiV) color center).^[26] Investigations of this center in recent year have been mostly stimulated by its potential usage in quantum optical devices.^[27] Atomic structure of SiV center has been supposed as interstitial silicon atom between two substitutional vacancies.^[28] The center is known to exist in neutral and negative charge states. The line at 738 nm corresponds to its negatively charged state. Only single ZPL line may be resolved in CL and PL spectra obtained in our work.

The intensities of the lines at 575 and 738 nm were found to be dependent on wavelength of excitation radiation. The dependencies obtained for the ratios of PL line amplitude to base signal are shown in **Figure 6**. For the 738 nm line, the relative intensity increases linearly with the laser wavelength, suggesting that excitation of these centers with longer wavelength (around 500 nm) is preferable.^[7] The linear intensity dependence is in consistency with PL excitation spectra reported in previous studies.^[29] In contrast, the 575 nm line shows a non-monotonic (parabolic) variation of excitation efficiency, which increases of a factor three from 400 to 500 nm. Similar strong dependencies of 575 nm line on excitation wavelength has been explained by

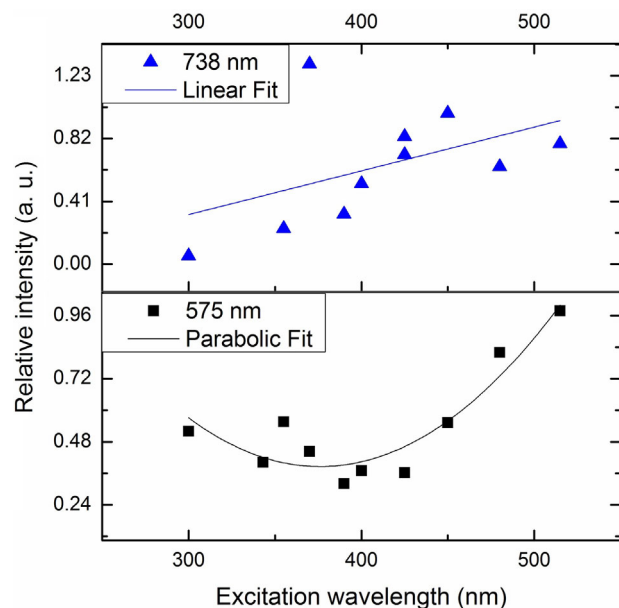


Figure 6. Photoluminescent intensity dependence for 575 and 738 nm on excitation wavelength measured for the area located near the apex of diamond needle.

increasing of absorption efficiency in the range near 415 nm (3 eV).^[30]

3.2. Vibronic Bands

Besides of the ZPL lines the luminescent spectra of SCD contains pronounced phonon replications (or vibronic) bands for most of the color centers. **Figure 7** presents dependencies of the spectra in vicinity of the ZPL lines with phonon replications on the phonon energy. The phonon energies were calculated from wavelength in luminescent spectra (similar to that shown in Figures 3 and 4) considering phonon energy equal to zero for the wavelength of corresponding ZPL lines. The spectra presented in Figure 7 were normalized on intensity of corresponding ZPL lines and shifted in vertical direction for clarity.

The most of the vibronic bands detected in spectra shown in Figure 7 are in well consistency with previous investigations. The observed vibronic bands of 389 nm ZPL line are appeared in PL and CL spectra at 80 ± 6 , 159 ± 6 , and 236 ± 6 meV that corresponds to electron transitions with local vibrational modes associated with 75 meV transverse acoustic (TA) phonon^[31] and 165 meV longitudinal optical (LO) phonon.^[7] Interaction of 389 nm transition with both of these phonons can explain appearance of 236 ± 6 meV feature in the spectra.^[7] The observed vibronic bands of 442 nm line (Figure 7(b)) correspond to phonon energies of 58 ± 4 and 96 ± 4 meV.

Four phonon bands can be resolved for 468 nm line in its side band (Figure 7(c)). Predominant interaction with 76 ± 4 meV phonon (similar to that described in Ref. [7]) corresponds to the bands observed at 148 ± 5 and 220 ± 4 meV for two- and three-phonon processes, respectively. However, the line corresponding

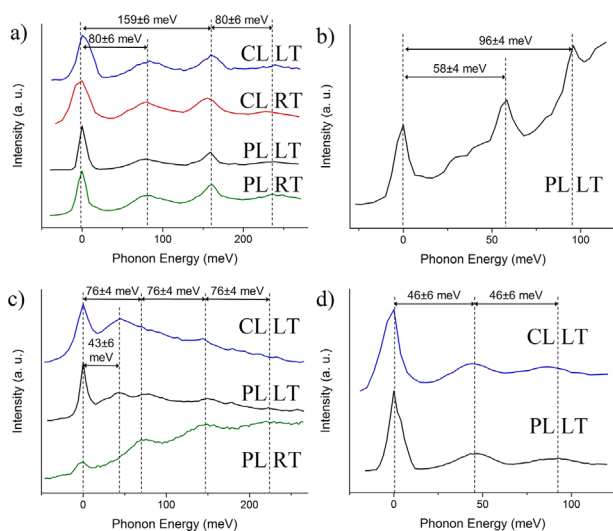


Figure 7. Vibronic bands for 389 nm (a), 442 nm (b), 468 nm (c), and 575 nm (d) centers. Blue lines (CL LT) correspond to cathodoluminescent spectra measured at 81 K, red lines (CL RT) correspond to cathodoluminescent spectra measured at room temperature, black lines (PL LT) correspond to photoluminescence spectra measured at low temperatures (24 K for (a) and (b), 4 K for (c) and (d)), green lines (PL RT) correspond to photoluminescence spectra measured at room temperature.

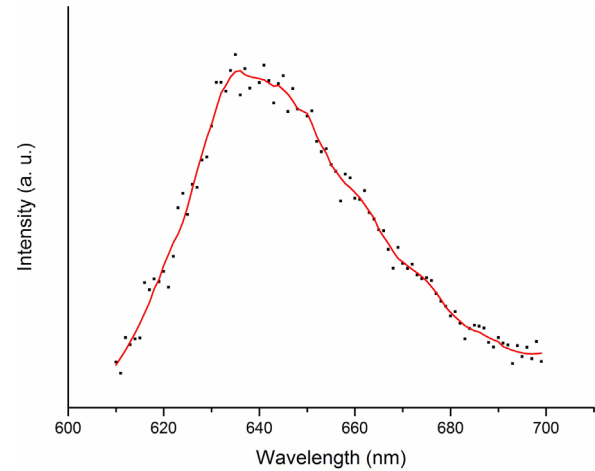


Figure 8. Spectral dependence obtained by subtraction of normalized CL spectrum from PL spectrum (shown in Figure 3(a) and 4(a), respectively) indicated by black dots. The red line corresponds to smoothed data.

to phonon with 43 ± 6 meV was also detected in some spectra for this optical center. This line can be either additional vibrational band of 442 or 468 nm lines or independent luminescence line with wavelength about 477 nm. For 534 nm line one vibrational band can be resolved. It corresponds to phonon with energy of 79 ± 8 meV that in consistency with previous researches.^[7] The phonon interactions with energies of 46 ± 6 and 90 ± 6 meV that corresponds to two-phonon process with 46 ± 6 meV can be resolved in spectral range of 575 nm line (Figure 7(d)) similar to previous reports.^[32]

Some difference between CL and PL spectra (Figures 3(a) and 4(a)) can be seen for vibronic bands of 575 nm ZPL line. The PL spectrum looks wider and more intensive around 640 nm wavelength. Subtraction of normalized CL spectrum from PL spectrum (see **Figure 8**) produces dependence with shape similar to spectrum of negatively charged nitrogen-vacancy center in diamond with 637 nm wavelength. This is in well agreement with previous reports indicating that negatively charged nitrogen-vacancy center is not detectable by CL technique.^[7]

4. Conclusion

The 389, 442, 468, 534, 563, 575, and 738 nm luminescent lines of the color centers in needle-like single crystal diamond were observed. Single zero phonon line at 534 nm, strong luminescence at 468 nm, and the vibration modes observed in the spectra demonstrate high structural quality of manufactured needle-like single diamond crystals. The presence of 389 and 468 nm luminescent lines indicates that these structures also contain interstitial and/or substitutional atoms. The luminescent lines at 389, 468, 534, and 575 nm demonstrate a nitrogen atoms content. The 738 nm line is an evidence of silicon atom impurities presence. Pronounced vibronic bands in the luminescent spectra of nitrogen-vacancy centers correspond to interactions with: 80 ± 6 and 159 ± 6 meV phonons for 389 nm line, 58 ± 4 and 96 ± 4 meV phonons for 442 nm line;

76 ± 4 meV phonons for 468 nm line; 46 ± 6 meV phonons for 575 nm line.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cathodoluminescence, chemical vapor deposition, diamond, needle-like crystals, photoluminescence

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