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# Study of photo- and electroluminescence of nitrogen-related color centers in a diamond $p{-}i{-}n$ diode


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The luminescence line with a wavelength of 533 nm associated with nitrogen in diamond has been examined for the first time with combined photoexcitation and electrical excitation in a diamond-based $p{-}i{-}n$- diode. The variation of intensity of this line was compared with the change in intensities of zero-phonon lines of a nitrogen−vacancy color center in neutral and negative charge states under varying levels of current through the diode and power of the excitation laser.

**Keywords:** CVD diamond, $p{-}i{-}n$ diode, color centers, electroluminescence.

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Nitrogen−vacancy color centers (NV- centers) in diamond hold promise for application in the field of quantum data processing [1], magnetometry [2], and biological sensing [3]. Optical transitions for just two charge states of an NV- center (neutral $NV^0$ and negatively charged $NV^-$) are known at present [1]. Nevertheless, the search for new electron transitions of an NV- center continues [4]. A narrow line at a wavelength of 533 nm in the electroluminescence spectrum of diamond has been reported for the first time in our study [5]. In earlier studies, this line was observed in the cathodoluminescence spectra of diamond [6–8] and the photoluminescence spectra recorded under excitation by a laser with a wavelength shorter than 325 nm [9]. Since the intensity of this line depends on the nitrogen concentration in diamond [10], it may correspond to an electron transition of a nitrogen-related center (for example, NV, NVH, or NVN). It is very narrow and highly intense, which is advantageous for various quantum applications. It is also important to establish the nature of this line. The present study is the first to examine the dependence of intensity of the line at a wavelength of 533 nm under combined photoexcitation and electrical excitation on the level of laser power and current in a $p{-}i{-}n$- diode and compare it with similar dependences for the emission intensities of $NV^0$ and $NV^-$- centers. The first results of this research have been published as part of conference proceedings [11].

The $p{-}i{-}n$- diode diagram is shown in Fig. 1, *a*. The diode fabrication procedure was similar to that detailed in [12]. The main difference was that nitrogen was used instead of silicon to dope the inner diode region for production of NV- centers. A structure consisting of a heavily boron-doped $p^{++}$ layer 250 nm in thickness with a concentration of $[B] = 1.7 \cdot 10^{21}\,cm^{-3}$ (9605 ppm) and a nitrogen-doped layer 800 nm in thickness with a concentration of $[N] = 3 \cdot 10^{18}\,cm^{-3}$ (17 ppm) was grown on a substrate $3.5 \times 3.5 \times 0.5$ mm in size made of HPHT (high pressure high temperature) diamond. The $n^+$ region doped with phosphorus with a concentration of $2.5 \cdot 10^{20}\,cm^{-3}$ (1412 ppm) was formed by selective refilling of a rectangular groove etched in the nitrogen-doped layer. All layers of the diode structure were grown in a CVD reactor, which was discussed in detail in [13]. The impurity concentrations and layer thicknesses were measured using the SIMS (secondary ion mass spectrometry) method. Ti/Mo/Au metals were used to form ohmic contacts to the $p$ and $n$-regions of the diode.

Figure 1, *b* shows the current–voltage curve of the $p{-}i{-}n$- diode. Compared to [12], the diode opening voltage increased from 5 to 20 V. This voltage increase may be attributed to the presence of nitrogen in the $i$- region of the diode. Nitrogen is a deep donor impurity in diamond and may influence the parameters of the space charge region in the $p{-}i{-}n$- diode.

A RENISHAW inVia Reflex confocal Raman dispersive spectrometer with a laser operated at a wavelength of 514 nm was used to measure the electroluminescence and photoluminescence spectra. Luminescence from the $i$-region of the diode was excited optically and collected from the substrate side (Fig. 2, *a*). When a $50\times/0.75$ lens was used, the collection area had an approximate diameter of $1\,\mu$m; its depth of several micrometers undoubtedly exceeded the thickness of the $i$- region (800 nm).

Figure 2, *b* shows the spectra of electroluminescence and photoluminescence recorded from the inner region

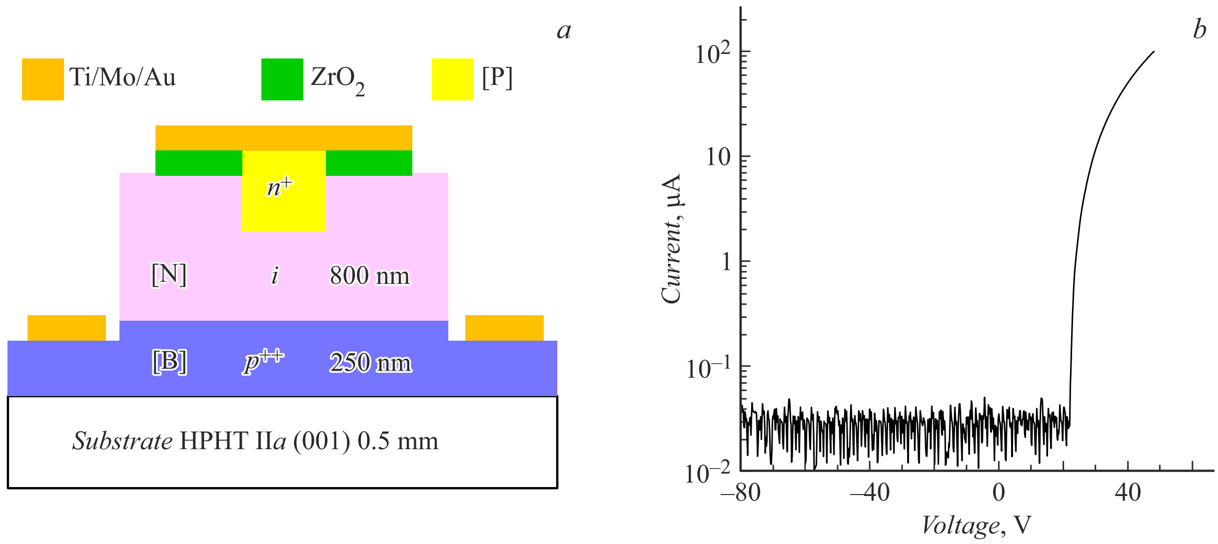


**Figure 1.** *a* — Diagram of the *p–i–n-* diode (dopant impurities are indicated in square brackets). *b* — Current–voltage curve of the *p–i–n-* diode. A color version of the figure is provided in the online version of the paper.

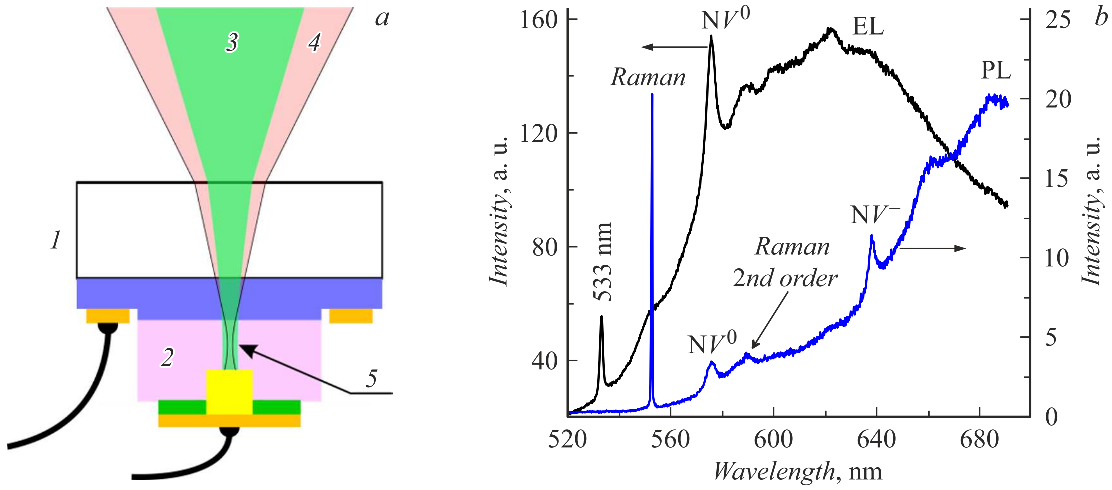


**Figure 2.** *a* — Diagram of optical measurements of luminescence in the diode. *1* — Substrate (not to scale), *2* — *i* region of the *p–i–n-* diode, *3* — laser radiation (515 nm), *4* — detected luminescence, and *5* — luminescence collection region. *b* — Electroluminescence (EL) spectra at a current of 20 $\mu$A and photoluminescence (PL) spectra at a power of 50 mW for the *p–i–n-* diode.

of the *p–i–n-* diode under separate photoexcitation and electrical excitation. The electroluminescence spectrum was obtained at a diode current of 20 $\mu$A (3.3 A/cm$^2$). The photoluminescence spectrum was measured with laser irradiation of the inner region of the diode at zero current in it. Lines corresponding to Raman scattering, zero-phonon lines at the wavelengths of 575 and 637 nm, and phonon bands corresponding to $NV^0$ and $NV^-$- centers were found in the photoluminescence spectrum. The electroluminescence spectrum featured emission from $NV^0$-centers, while emission from $NV^-$- centers was lacking. Just as in [5], a narrow line at a wavelength of 533 nm was found in the electroluminescence spectrum. Its FWHM value was 1.4 nm, while the width of the zero-phonon line of an $NV^0$-center was 4.4 nm.

The results of examination of lines with combined photoexcitation and electrical excitation of diamond in the *i-* region of the diode are presented in Fig. 3. Figure 3, *a* shows the dependences obtained at a constant laser power of 50 mW and a diode current varying from 0 to 100 $\mu$A (16.7 A/cm$^2$). As the diode current increased, the emission intensity of an $NV^0$- center increased by a factor of 8, while the intensity of an $NV^-$- center decreased by a factor of 2. The intensity of the 533 nm line started exceeding the noise level at a current of 1 $\mu$A and was directly proportional to the current value. A qualitative explanation for this behavior of intensities of $NV^0$ and $NV^-$- centers is provided by the electroluminescence model proposed in [14]:

$$\mathrm{NV}^- + h \rightarrow \mathrm{NV}^{0*},$$

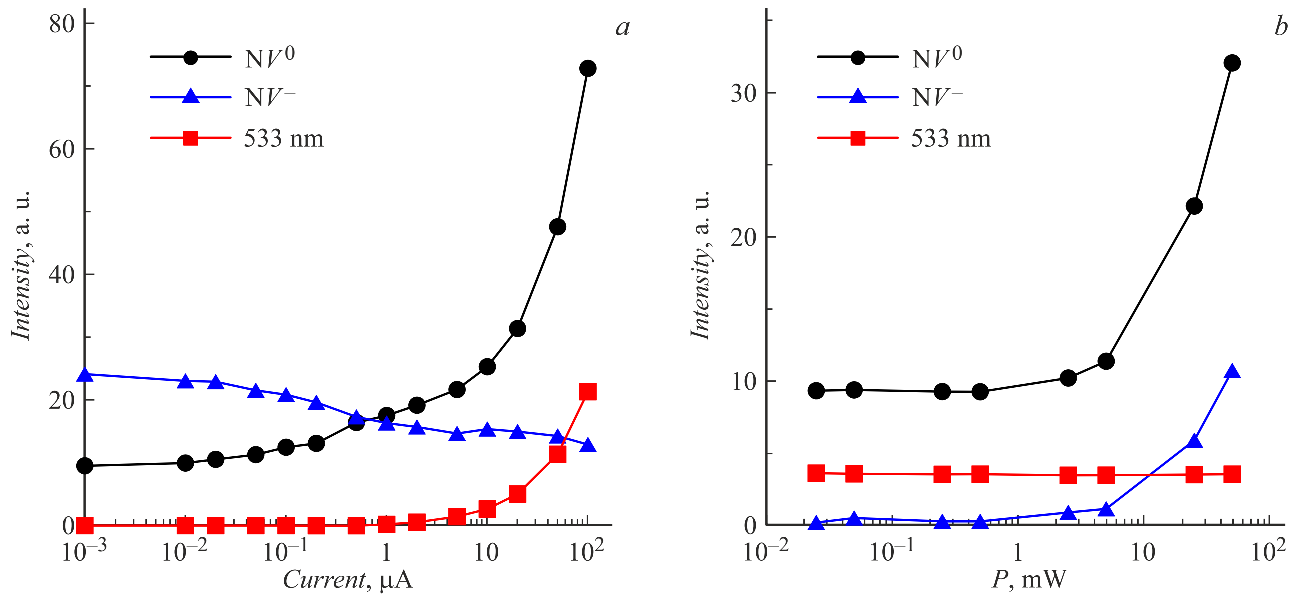


**Figure 3.** Dependences of luminescence intensity with combined photoexcitation and electrical excitation on the level of current (laser power, 50 mW; wavelength, 514 nm) (*a*) and laser power (diode current, 20 $\mu$A) (*b*).

$$NV^{0*} \rightarrow NV^0 + \hbar\omega,$$
$$NV^0 + e \rightarrow NV^-, \qquad (1)$$

where $h$ is a hole, $e$ is an electron, $\hbar$ is the Planck constant, and $\omega$ is the radiation frequency. The first equation of system (1) characterizes the process of attraction of a hole to an $NV^-$- center and its recombination. As a result, the $NV^-$- center becomes excited ($NV^{0*}$) and, having emitted a photon, goes into the ground state (the second equation of system (1)). An electron colliding with an $NV^0$- center transforms it into $NV^-$ (the third equation of system (1)). These processes are then repeated cyclically. It can be seen from the first equation of system (1) that the ensemble of $NV^-$- centers is partially involved in electroluminescence; therefore, the passage of current through the diode alters the balance of charge states, shifting it toward neutral state $NV^0$ and suppressing the intensity of $NV^-$ emission.

Figure 3, *b* shows the dependences of emission intensities on laser power at a constant current in the diode of 20 $\mu$A (3.3 A/cm$^2$). The intensity of the line at a wavelength of 533 nm is independent of laser power, while the intensities of $NV^0$ and $NV^-$- centers increase linearly with this power. No redistribution of charge states is observed; the luminescence intensity may be represented as a sum of independent intensities of photo and electrical components. The obtained results are insufficient to establish the nature of the center associated with emission at a wavelength of 533 nm. The intensity of this line depends linearly on the magnitude of diode current and does not depend on the power of laser radiation with a wavelength of 514 nm. As was already noted, photoluminescence of the center is observed only for lasers with a wavelength shorter than 325 nm. Therefore, the mechanism of its excitation differs profoundly from the mechanism of excitation of $NV^0$ and $NV^-$. It is likely that interband transitions, which become possible at a high excitation energy (3.8 eV), should necessarily be taken into account in order to devise an explanation for the mechanism of emission of the center at a wavelength of 533 nm. It appears that a study of electroluminescence at the level of single centers with the use of shorter-wavelength laser radiation (with a higher photon energy) is required to determine the nature of this center.

Thus, the line with a wavelength of 533 nm associated with nitrogen in diamond has been examined for the first time with combined photoexcitation and electrical excitation in a diamond $p$–$i$–$n$- diode. The line has a FWHM value of 1.4 nm and a fairly high intensity, which makes it promising for application in quantum applications. It was found that its intensity depends linearly on the magnitude of diode current and does not depend on the power of laser radiation with a wavelength of 514 nm. At the same time, the variation of intensities of zero-phonon lines of $NV^0$ and $NV^-$- centers with a change in diode current revealed that the processes of electrical excitation and photoexcitation were in competition, which may be explained within the existing model of electroluminescence.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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