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High temperature light emitting diamond pin diode based on nitrogen-vacancy luminescence centers

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A diamond light-emitting $p-i-n$-diode has been fabricated from a nitrogen-doped synthetic single crystal diamond (n-type conductivity) grown at high pressure and temperature, and thin layers grown by homoepitaxial growth from the gas phase: i-layer of low-doped diamond with nitrogen-vacancy optically active centers and a highly boron-doped layer (p-type conductivity). Volt-ampere characteristics and electroluminescence spectra were studied for the first time at temperatures in the range 300−680°C. The emission spectrum at $T = 450^\circ$C has a maximum in the region of 590−610 nm and is similar to the electroluminescence spectra of nitrogen-vacancy centers previously observed at room temperature in diamond $p-i-n$-diodes with n-layers doped with phosphorus. The intensity of the emission increases in proportion to the electrical power of the diode current.

Keywords: nitrogen-doped diamond, diamond pin diode, volt-ampere characteristics, electroluminescence, high temperatures.

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Light-emitting diamond $p-i-n$-diodes based on nitrogen-vacancy (NV) optically active centers are being developed as sources of single photons with electrical pumping [1–4]. The possibility of production of femtosecond high-power diamond lasers is also being examined [5,6]. Diamond doped with boron and phosphorus is commonly used as a p-type and n-type material, respectively, in such diodes [1–4]. An i-layer then contains optically active NV-centers and an insignificant number of individual nitrogen substitution atoms (C-centers) and, in certain cases, phosphorus atoms [4]. A mixed structure of the n-type layer was used in [3]: to raise the electron emission efficiency, additional structures were fabricated on top of a nitrogen-doped layer from diamond heavily doped with phosphorus. Just as phosphorus, nitrogen in the form of individual atoms at substitution sites is a donor doping element for diamond. We have already demonstrated the possibility of fabrication of n-type Schottky diodes based on diamond doped with nitrogen [7]. The ionization potential of nitrogen in diamond is much higher than the one of phosphorus: 1.7 eV [8,9] and 0.57 eV [10], respectively. In view of this, the concentration of free electrons in diamond doped with nitrogen is very low at room temperature. At concentrations of C-centers falling within the $10^{18}-10^{19}\,\mathrm{cm}^{-3}$ range, electron conduction over delocalized states in diamond is observed either under illumination [8,9] or under heating above 300°C [7,8]. The effect of superinjection of carriers into the i-region, which should induce an increase in electroluminescence efficiency at higher voltages, was also predicted [11].

The aim of the present study is to examine the effect of heating to 680°C on the volt–ampere characteristics and electroluminescence spectra of a vertical diamond $p-i-n$-diode with a n-type layer doped with nitrogen.

Test samples (Fig. 1) were fabricated on substrates made from type Ib diamond, which was grown by the temperature gradient high-pressure high-temperature (TG-HPHT) method [12,13], doped with nitrogen. The concentration of nitrogen in the form of C-centers was $2.4 \cdot 10^{19}\,\mathrm{cm}^{-3}$. A layer of diamond $6\,\mu$m in thickness with a low concentration of NV-centers (i-layer) and a layer $7\,\mu$m in thickness doped with boron to a concentration of $\sim 1 \cdot 10^{20}\,\mathrm{cm}^{-3}$ (p^+-layer) were grown consecutively using the method of homoepitaxial growth from the gas phase (CVD method) [13] on these substrates ($3.5 \times 3.5 \times 0.3$ mm in size). Following CVD growth, square plates approximately $3.0 \times 3.0 \times 0.3$ mm in size were cut with a laser from the obtained three-layer crystalline structures. One of the side faces of these plates was polished to enhance optical radiation output, enable monitoring of the electroluminescence region with an optical microscope, and analyze emission spectra. A solid ohmic Ti−Pt contact 2.5×2.5 mm in size was fabricated on the HPHT substrate side by magnetron sputtering through a contact mask, and four contacts 1.0×1.0 mm in size were formed on the side of the boron-doped CVD layer. Prior to the fabrication of metallic contacts, samples were annealed in air at a temperature of 680°C in order to remove the graphitized surface layer, which was produced in the process of laser cutting, and possible surface contamination.

Luminescence was observed at temperatures above 400°C when diode forward current was flowing (Fig. 1, *b*). Heating was performed in argon ambient with the use

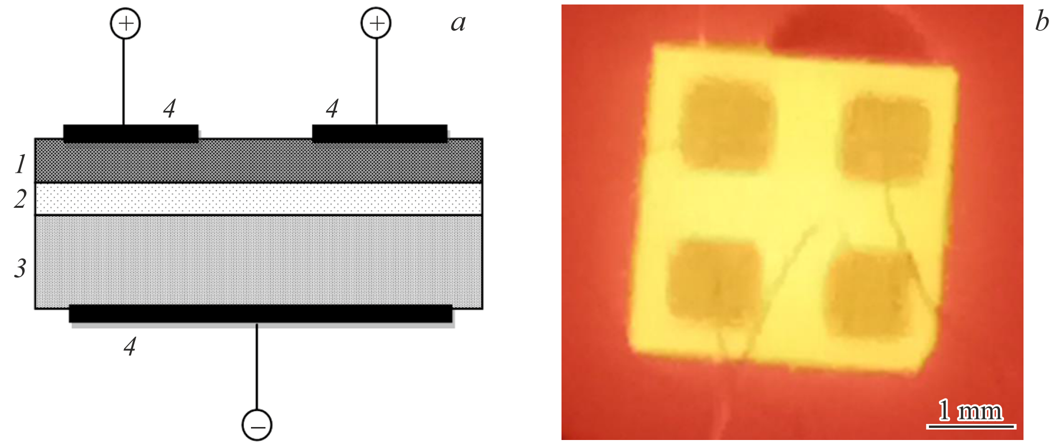

Figure 1. *a* — Diagram of a diamond $p-i-n$- diode. *1* — p^+-layer doped with boron; *2* — i-layer containing NV-centers: *3* — n-layer doped with nitrogen; *4* — ohmic Ti−Pt contacts. *b* — Electroluminescence of the diamond $p-i-n$- diode at $T = 680°$C and $I = 20$ mA.

of a vacuum-tight Linkam 1000TS heating stage with an optical window. The volt–ampere characteristics of diodes at temperatures of 300−600°C (Fig. 2, *a*) were examined with a Keithley 4200A analyzer of electrical parameters of semiconductor devices. Electroluminescence spectra were studied using a Renishaw inVia Reflex confocal Raman spectrometer with a ×50 objective and a focal spot diameter of $\sim 2\,\mu$m. In these measurements, the examined diode was positioned in the heater perpendicularly to the output optical window in such a way that the emission spectrum could be recorded from the polished end face. A bright emission region was then observed in the i-layer at the boundary with the p^+-layer. Prior to electroluminescence spectra measurements, background emission spectra of the heated diode were measured at each temperature value under zero current. These heater emission spectra were later substracted from the ones measured with the diode current switched on.

Figure 2, *a* presents the volt–ampere characteristics of the diode at 300, 400, 500, and 600°C. Diode switch-on voltage U_{on} dropped from ~ 2.0 to 1.5 V as the temperature increased within the indicated interval. The maximum current density for the conducting diode at $T = 680°$C was $j = 0.1$ A/cm^2. The resistance in this state was $R_{on} = 1.3\,\mathrm{k}\Omega$, which corresponds to the resistance of a nitrogen-doped HPHT substrate of the above-indicated size with resistivity $\rho = 4\,\mathrm{k}\Omega \cdot \mathrm{cm}$ at the given temperature [14].

At $T = 450°$C, the electroluminescence spectrum (with the heater emission spectrum subtracted from it) assumed the form of a broad band with a FWHM of ~ 150 nm and a maximum at 590−610 nm (Fig. 2, *b*). At higher temperatures and diode currents, the emission intensity increased considerably; however, the intensity of thermal radiation within the $\lambda > 700$ nm region, which was observed in spectra (Fig. 2, *d*) after subtraction of the heater spectrum, did also increase. This may be attributed to additional heating of the diode due to the current flow and the generation of thermal power, which is driven primarily by a fairly high substrate resistance. In order to prevent self-heating of the diode, one needs to perform a series of measurements of spectra in the pulsed current flow regime with a relatively low duty factor. In addition, the diode design may be refined by reducing the substrate thickness to $\sim 1\,\mu$m (e.g., by applying the lift-off process, which was used in our study [15] in fabrication of thin p-type diamond Schottky diodes) and by optimizing the concentration of C-centers in the substrate and NV-centers in the i-layer.

The spectrum in Fig. 2, *b* is consistent with room-temperature electroluminescence spectra of NV^0-centers of $p-i-n$-diodes with an n-layer doped with phosphorus [1–4]. The key difference consists in the fact that individual narrow low-intensity peaks were observed against the general background of a broad band at room temperature. These peaks are associated with phonon replicas of the zero-phonon luminescence line (ZPL) at 575 nm that overlap to form a broad band [1–4]. Figure 2, *c* presents the dependences of radiation intensity at a wavelength of 625 nm on the electrical power consumption of the diode at a temperature of 640, 660, and 680°C. It is evident that the luminescence intensity at a power level below 100 mW decreases by $\sim 10\%$ as the temperature rises. However, owing to the fact that the concentration of free electrons increases at higher temperatures, the radiation intensity grows by a factor of 1.5−2 in proportion to an increase in electrical power as it varies from 100 to 320 mW. Thus, the performance capabilities of light-emitting diamond $p-i-n$-diodes based on NV-centers within the 300−680°C temperature range were demonstrated. The parameters of these diodes may be improved further for the purpose of increasing the current density and fabricating a diamond injection laser.

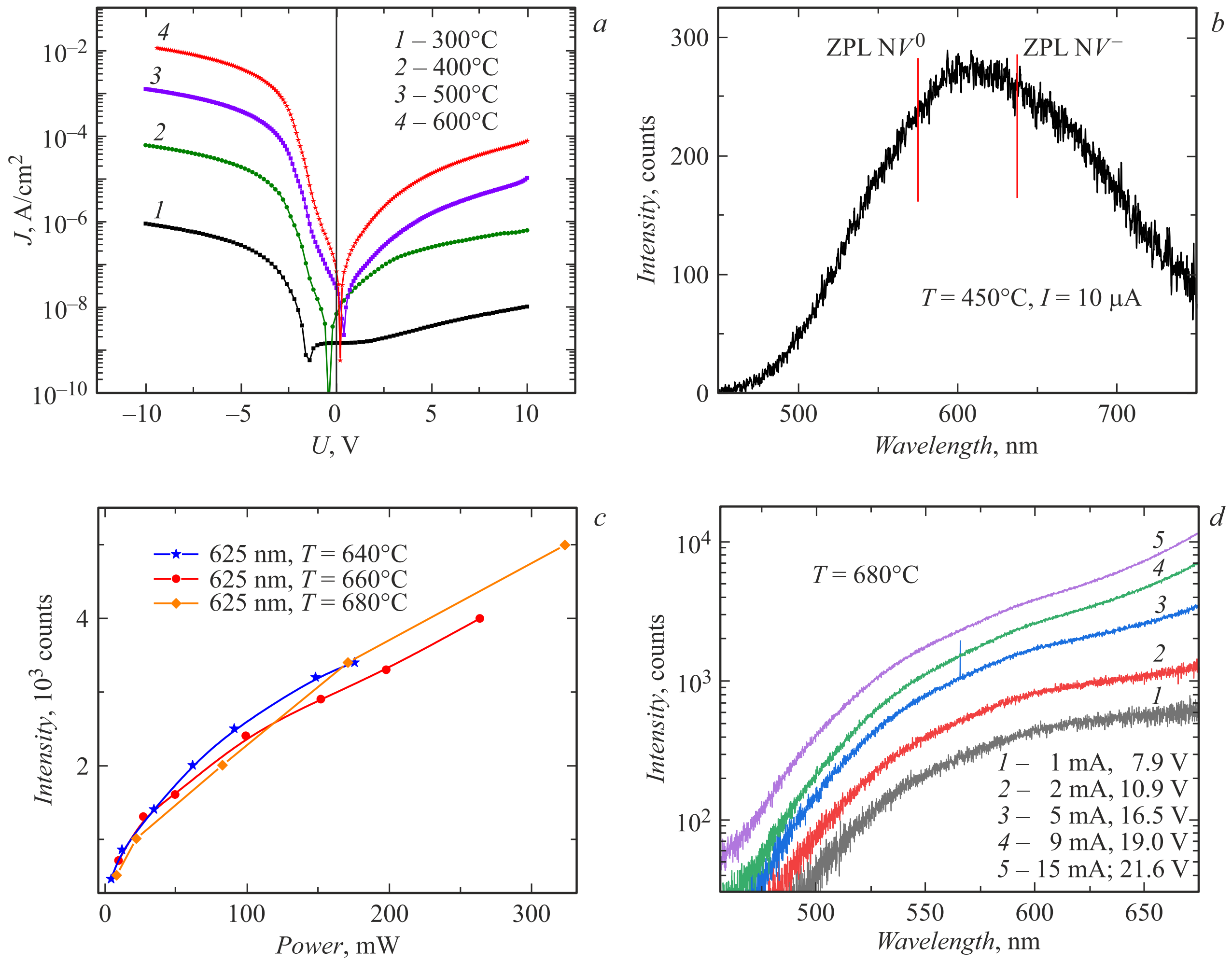

Figure 2. *a* — DC volt–ampere characteristics of the $p-i-n$- diode at $T = 300-600^\circ$C. *b* — Emission spectrum of the diode at a temperature of 450°C and a forward current of 10 μA. Vertical lines indicate the wavelengths of luminescence of zero-phonon lines of NV^0 and NV^- optical centers. *c* — Dependences of the radiation intensity at 625 nm on the electrical power consumption of the diode at a temperature of 640, 660, and 680°C. *d* — Emission spectra of the diode at a temperature of 680°C and currents falling within the 1−15 mA range.

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Conflict of interest

The authors declare that they have no conflict of interest.

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