Technical Physics, 2025, Vol. 70, No. 3

07

Electroluminescence of diamond NV-centers at temperatures 450 °C–680 °C

© S.G. Buga,[1,2] N.V. Kornilov,[1] M.S. Kuznetsov,[1] N.V. Luparev,[1] D.D. Prikhodko,[1,2] S.A. Tarelkin,[1]
T.E. Drozdova,[1] S.I. Zholudev,[1] S.A. Nosukhin,[1] V.D. Blank[1,2]

[1] Scientific Research Center „Kurchatov Institute“–TISNUM,
108840 Moscow, Russia
[2] Moscow Institute of Physics and Technology,
141701 Dolgoprudny, Moscow Region, Russia
e-mail: buga@tisnum.ru

Received October 3, 2024
Revised October 28, 2024
Accepted December 3, 2024

Electroluminescence spectra of a diamond light-emitting $p{-}i{-}n$-diode based on a nitrogen-doped synthetic single crystal of diamond (*n*-type of conductance), grown by high pressure and temperature growth method, and thin, grown by method of homoepitaxial growth from a gas phase, i-layer of diamond with nitrogen concentration $10^{14}-10^{15}\,\mathrm{cm}^{-3}$ with nitrogen-vacancy and silicon-vacancy optically active centers, and a layer heavily doped with boron (*p*-type of conductance), were studied. To increase the concentration of luminescence centers, the diode was irradiated with an electron beam with energy of 3 MeV at dose $5 \cdot 10^{17}\,\mathrm{cm}^{-2}$ with subsequent annealing at $T = 800\,^\circ\mathrm{C}$ in vacuum for 2 h. Electroluminescence spectra were measured at temperatures in the range of 450 °C–680 °C both before and after irradiation with electrons. Before irradiation with electrons, the maximum of the electroluminescence band was observed in the area of wavelengths 610–680 nm, depending on temperature, voltage and current of diode, and after irradiation with electrons and annealing — at wavelength of 680 nm at $T = 575\,^\circ\mathrm{C}-600\,^\circ\mathrm{C}$. Maximum integral brightness of emission of nitrogen-vacancy centers $\sim 10^{12}$ photon/s was observed at $T = 575\,^\circ\mathrm{C}$ after irradiation with electrons and annealing.

Keywords: nitrogen-doped diamond, NV-centers, diamond $p{-}i{-}n$-diode, electroluminescence, high temperatures.

DOI: 10.61011/TP.2025.03.60853.297-24

Introduction

Light-emitting diamond $p{-}i{-}n$=diodes based on nitrogen-vacancy (NV) optically active centers are being developed as electrically controlled sources of single photons with electrical pumping [1–11]. Diamond doped with boron is commonly used as a *p*-type material in such diodes, and as *n* — diamond doped with phosphorus [2–10]. 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 [10]. Just as phosphorus, nitrogen in the form of isolated atoms at substitution sites is a donor doping element for diamond. We demonstrated the possibility of fabrication of *n*-type Schottky diodes based on diamond doped with nitrogen [12]. Energy of nitrogen ionization in diamond is substantially higher than that of phosphorus: this value is 1.33–1.63 eV depending on nitrogen concentration [13], whereas for phosphorus the ionization energy is much lower: as concentration of phosphorus atoms increases, it decreases from 0.57 to 0.37 eV [14,15]. 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 [16,17] or under heating above 300 °C [13,16].

Earlier it was found that the integral intensity of radiation of ultraviolet diamond $p{-}i{-}n$-diodes increases 3 times when heated from 25 to 200 °C [18,19]. It is known [20] that the intensity of photoluminescence (PL) of negatively charged nitrogen-vacancy complexes ((NV^-)-centers) in diamond at $T = 700\,\mathrm{K}$ decreases approximately down to 15 % compared to the value at $T = 300\,\mathrm{K}$, and further decrease occurs more slowly in agreement with the known theoretical dependence. Besides, the maximum of intensity of the PL phonon wing spectrum of (NV^-)-centers shifts from 710 nm at $T = 300\,\mathrm{K}$ to 750 nm at $T = 573\,\mathrm{K}$. However, the maximum of the spectrum of cathodoluminscescence (CL) phonon wing of (NV^-)-centers shifts from 670 to 700 nm as temperature increases from 293 to 776 K [21]. CL spectrum intensity in this case decreased down to $\sim 10\,\%$ at $T = 776\,\mathrm{K}$. This paper studied the specimen of diamond containing high concentration of substituting nitrogen $\sim 10^{19}\,\mathrm{cm}^{-3}$ and NV-centers mostly in the negative charge state with concentration $\sim 10^{18}\,\mathrm{cm}^{-3}$. Besides, [21] shows that the intensity of zero-phonon line (ZPL) in (NV^-)-centers decreases much stronger with the temperature growth compared to the ZPL line (NV^0)-centers. At $T > 393\,\mathrm{K}$ the ZPL lines of both centers have become indiscernible on the background of a broad band of luminescence phonon wing.

Shift of ZPL lines in (NV^-) and (NV^0)-centers with growth of temperature from 77 to 300 K was studied in [22]. In the range of 250−300 K the shift $\Delta E/\Delta T$ was around -0.002 eV. Based on this value, we approximated the shift value at $T = 723$ K by -0.017 eV, and at $T = 923$ K — by -0.027 eV, that for ZPL in (NV^0)-centers means a shift relative to $\lambda = 575$ nm (at $T = 300$ K) to a long-wavelength area by ~ 4 and ~ 7 nm accordingly.

In case of silicon-vacancy (SiV^-)-centers in diamond it was found that ZPL intensity decreases by 50 % with temperature rise from 300 to 500 K and reduces down to 20 % at $T = 873$ K [23] at the expense of increased probability of nonradiative recombination.

In the temperature range up to 950 K we observed approximately the linear dependence of electroluminescence (EL) intensity in (NV^0)-centers at wavelength of 625 nm from the consumed electrical capacity of the diode in the range of up to 330 mW [11].

NV-centers in diamond are studied actively for use in various quantum optical-electronic devices, in particular, as single-photon sources for the systems of space quantum communications [24,25], and in lasers on NV-centers [26,27].

NV-centers are present in various charge states: neutral (NV^0), negatively charged (NV^-) and positively charged (NV^+) [4,42–49]. (NV^0) and (NV^-)-states are primary. Depending on the intensity and wavelength of the exciting radiation in the luminescence spectra, various ratios of band intensities are observed, related to (NV^0)- and (NV^-)-centers [46], and at recombination of holes and electrons in case of electric current passage in diamond $p-i-n$-diodes EL of (NV^0)-centers is mainly observed [1,2,9,11]. Quantitative ratio of (NV^0)- and (NV^-)-centers depends on the position of Fermi level [3,4,42–49], and, in case of additional light doping of i-layer with phosphorus, with increase of voltage on $p-i-n$-diode in the open state from 30 to 50 V, together with (NV^0)-centers, EL spectra of (NV^-)-centers are observed with the maximum at wavelengths 675 nm, due to a wide wing of phonon repetitions in ZPL of luminescence 637 nm [10].

Previously we manufactured and studied for the first time the light-emitting diamond $p-i-n$-diodes on NV optically active centers without using a phosphorus-doped layer [11]. The layer with n-type of conductance was a single-crystal substrate made of diamond grown by high pressure high temperature method (HPHT) with concentration of C-centers $2.4 \cdot 10^{19}\,\mathrm{cm}^{-3}$. Such concentration of the doping admixture of nitrogen provides for the least specific electrical resistance and good quality of Ti/Pt contacts with linear current-voltage characteristic in a wide range of temperatures of up to 680 °C [13,28]. Thin layers of lightly doped diamond were grown on such substrates with nitrogen-vacancy optically active centers (i-layer), and diamond heavily doped with boron (p-layer). IV characteristics and spectra of electroluminescence were studied in the range of 300 °C−680 °C. The radiation spectrum at $T = 450\,^\circ$C is characterized by the maximum at the wavelength ~ 610 nm and differs from EL spectra in (NV^0)-centers observed previously at room temperature in diamond $p-i-n$-diodes with n-layers doped with phosphorus [1,2,9,10] by somewhat larger half-width and shift of around $\sim 20-25$ nm to the long-wavelength area, which is also specific for cathodoluminscescence spectra of (NV^-)-centers [21], and for PL [20], but by a higher value. The radiation intensity increased proportionately to the electric power of the diode current. The maximum value of the diode current was 15 mA at voltage 21.6 V and temperature 680 °C. Current density at the same time was $0.2\,\mathrm{A/cm^2}$. Density of LED current with a specially made n^+-emitter from diamond doped with phosphorus [9], exceeded $10^3\,\mathrm{A/cm^2}$ even at room temperature. Intensity of radiation of individual NV-centers in such diode was estimated as $\sim 6 \cdot 10^5$ photon/s.

The brightness of LED radiation on optically active centers depends not only on current in the open state, but on concentration of such centers, in this case — NV-centers. Besides, the modern injection LEDs and lasers use the superinjection effect in heterostructures [29,30], due to which the concentration of free charge carriers in the i-area may exceed their concentration in doped layers by several orders and therefore provide for high intensity (brightness) upon their recombination. The same effect is predicted for homostructures based on wide band-gap semiconductors [6–8], which include diamond too. Accordingly, the brightness of diamond LEDs may be substantially increased by increasing the concentration of NV-centers in i-layer, and also upon provision of the conditions for superinjection of free electrons, concentration of which in the diamond is usually much lower than the concentration of holes at comparable concentrations of donors and acceptors due to substantially higher energy of ionization of donors (atoms of phosphorus, nitrogen) compared to acceptors (boron atoms).

Concentration of NV-centers spontaneously formed in diamond grown by CVD method without addition of nitrogen, is very low. Except for the case of implantation of nitrogen atoms into diamond [10,31,32], the concentration of NV-centers is usually much lower than the concentration of nitrogen atoms. To increase the concentration of NV-centers in the diamonds doped with nitrogen, the methods of irradiation with ions [33–38] or electrons [20,39–45] are used to create vacancy defects, and further annealing at temperature above 600 °C to form nitrogen-vacancy complexes. For example, at concentration of C-centers $\sim 2 \cdot 10^{17}\,\mathrm{cm}^{-3}$ irradiation with a flow of electrons with energy of 3 MeV and dose of $4 \cdot 10^{17}\,\mathrm{cm}^{-2}$ with subsequent annealing caused formation of ~ 12 ppb ($2 \cdot 10^{15}\,\mathrm{cm}^{-3}$) ($NV^-$)-centers [39]. It is important that irradiation with high energy electrons provides for formation of vacancy defects in the entire volume of the diamond crystal, while when irradiated with ions, the thickness of the layer,

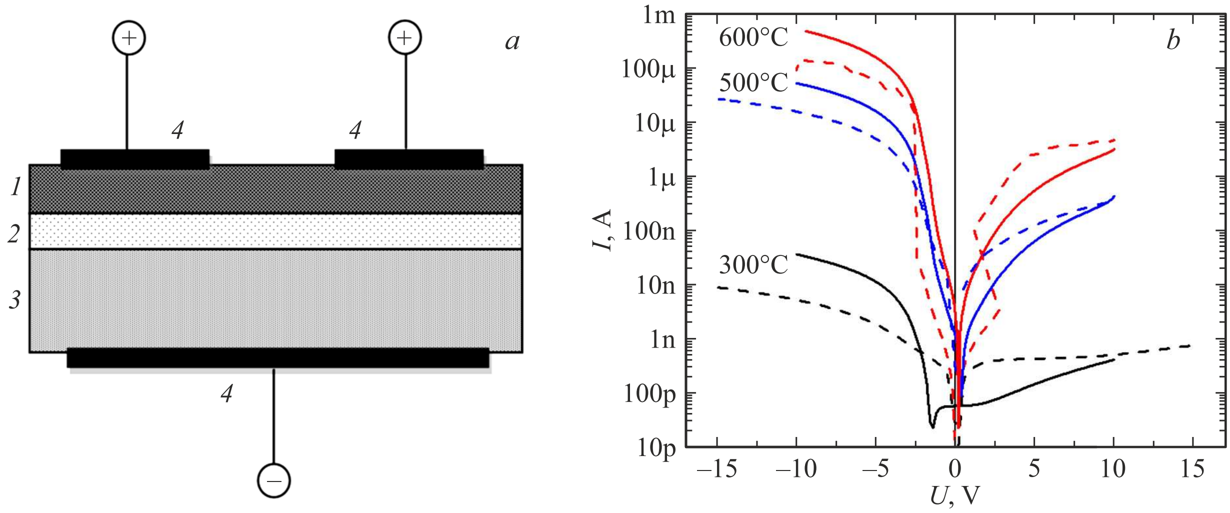

Figure 1. *a* — scheme of diamond $p{-}i{-}n$-diode: *1* — p^+-layer doped with boron; *2* — i-layer containing NV-centers: *3* — n-layer doped with nitrogen; *4* — ohmic Ti−Pt-contacts; *b* — diode IV characteristics at $T = 300$, 500 and 600 °C before irradiation with electrons (solid lines) and after irradiation and vacuum annealing (dashed lines).

where vacancies are formed, usually does not exceed one micron.

Studies in the field of development of femtosecond diamond lasers with high power at optical pumping of NV-centers in diamond [26] and continuous lasers are of substantial interest [27]. Taking into account of the theoretically predicted effect of free electron superinjection into i-area of diamond $p{-}i{-}n$-diodes [6–8], the EL studies of NV-centers in such diodes at high temperature are promising.

The purpose of this paper was to study the EL spectra of a diamond $p{-}i{-}n$-diode, similar in design [11], after irradiation with a flow of electrons with energy of 3 MeV and subsequent annealing at $T = 800\,^\circ$C to increase the concentration of NV-centers in i-layer.

1. Experimental specimens and experimental procedure

The experimental specimen of $p{-}i{-}n$-diode (fig. 1) was prepared on the substrate of nitrogen-doped single crystal of Ib-type diamond, grown by the method of temperature gradient at high pressure and temperature (TG-HPHT-method) [50,51] with nitrogen concentration in the form of C-centers $2.4 \cdot 10^{19}\,\mathrm{cm}^{-3}$. A layer of highly pure diamond with thickness of $6\,\mu$m (i-layer) and doped with boron in concentration of $\sim 1 \cdot 10^{20}\,\mathrm{cm}^{-3}$ with thickness $4\,\mu$m (p^+-layer) were grown consequently on the substrate with dimensions of $3.5 \times 3.5 \times 0.15$ mm by method of homoepitaxial growth from the gas phase (CVD-method, [51]) For CVD-growth we used Plassys BJS 150 CVD unit.

The process parameters were the following: substrate temperature — $850 \pm 15\,^\circ$C, microwave radiation power — 2.7 kW, gas mixture — H_2/CH_4 at the ratio of 24/1 and gas pressure of 180 ± 5 mbar. Growth rate of i-layer growth was $\sim 1.3\,\mu$m/h. A hydrogen purifier was used, which provides for impurity concentration of not more than 1 ppb. Methane purity was 99.9999 %. With account of the specified ratio of hydrogen and methane, the total concentration of impurities in the gas mixture does not exceed 5 ppb vs carbon. Assuming nitrogen as the main residual gas, we get the ratio $[\mathrm{N}]/[\mathrm{C}] \sim 10^{-6}$. Taking into account the coefficient of nitrogen incorporation into the diamond lattice vs carbon $\sim 10^{-3}$, we assess the minimum concentration of nitrogen in i-layer as around $10^{14}\,\mathrm{cm}^{-3}$, but with account of the possibility to etch the nitrogen-doped diamond substrate and atmosphere remains during chamber vacuumation before blowdown and filling with the working gas mixture, the upper boundary of the nitrogen concentration range in i-layer may reach the value of around $10^{15}\,\mathrm{cm}^{-3}$.

For boron doping, diborane B_2H_6 at the ratio of 48/1/0.25 was added to the gas mixture H_2/CH_4. Substrate temperature was $870 \pm 15\,^\circ$C, microwave radiation power — 2.9 kW at gas pressure of 180 ± 5 mbar. Rate of p-layer growth was $\sim 1\,\mu$m/h. Boron concentration in the grown p^+-layer was determined by the method of secondary ion mass spectroscopy (SIMS) and was additionally controlled using Raman scattering spectra (RS).

After CVD-growth a square plate was cut from the produced three-layer single-crystal structure by method of laser cutting with dimensions of around $3.0 \times 3.0 \times 0.15$ mm.

Side surfaces of the manufactured plate were polished to enhance optical emission yield, enable monitoring of the EL 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 4 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

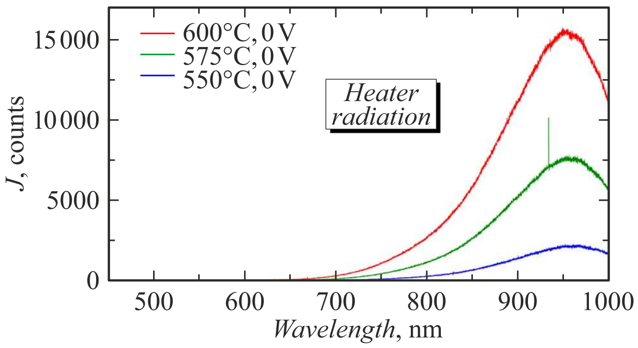

Figure 2. Spectra of heater radiation at different temperatures measured under the same conditions that spectra in fig. 3, *d–f*, in absence of diode current.

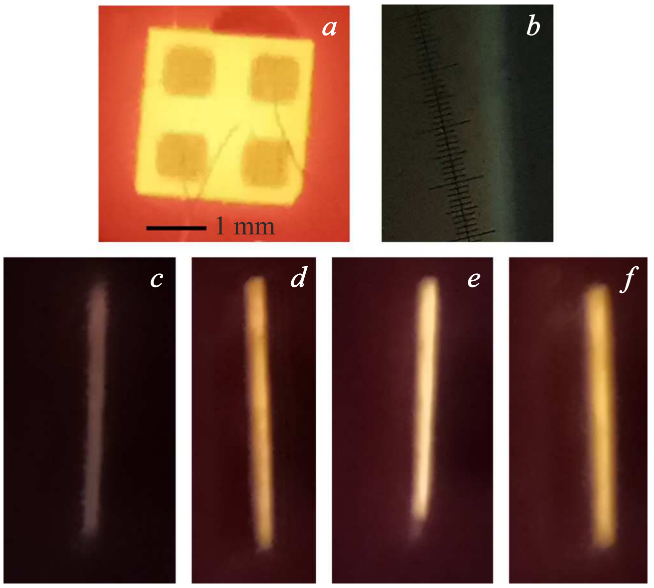

Figure 3. EL of diamond *p–i–n*-diode: *a* — at $T = 680\,^\circ$C, $U = 10$ V, $I = 20$ mA prior to irradiation with electrons and annealing, diode „top view“; *b* — view of luminescence area in *i*-layer at the end face of the diode at $T = 450\,^\circ$C, $U = 10$ V, $I = 10\,\mu$A; scale: *1* — scale division — $1.5\,\mu$m; n^+-layer on the left (yellow color), p^+-layer on the right (blue-purple color); *c–f* — EL from the end face of the diode after irradiation with electrons and annealing: *c* — at $T = 525\,^\circ$C, $U = 35$ V, $I = 0.38$ mA; *d* — at $T = 550\,^\circ$C, $U = 33$ V, $I = 0.9$ mA; *e* — at $T = 575\,^\circ$C, $U = 34$ V, $I = 0.3$ mA; *f* — at $T = 600\,^\circ$C, $U = 24$ V, $I = 3$ mA. Spectral sensitivity and color rendition of the photo camera were adapted automatically for each frame separately.

contacts, the specimen was annealed in air at a temperature of $680\,^\circ$C in order to remove the graphitized surface layer, which was produced in the process of laser cutting, and possible surface contamination.

Heating of the diode at EL spectra study was performed in argon ambient with the use of a vacuum-tight Linkam 1000TS heating stage with an optical window. 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 edge face.

Fig. 1, *b* presents IV characteristics of the diode at $T = 300$, 500 and $600\,^\circ$C prior to irradiation with electrons and after irradiation and vacuum annealing. As a result of irradiation and annealing of the diode, the current values in the forward direction decreased $\sim 5{-}10$ times at the same values of temperature, and in the backward direction, on the contrary, increased somewhat, i.e. the diode rectification coefficient decreased approximately by an order. The reasons for such change of the diode characteristics as a result of irradiation may differ for the forward and backward currents. Diode resistance in the forward direction could increase due to decrease in the concentration of donor nitrogen atoms in the substitution position when NV-centers are formed, and to a certain degree due to the effect of the structure defects. In the backward direction, on the contrary, — the presence of defects helps to increase the leakage currents, which are not related to the availability of impurity atoms and injection of holes and electrons from *p*- and *n*-layers. S-shape of IV characteristic at $T = 600\,^\circ$C after irradiation with electrons and annealing is related to the discrete deployment by voltage $\Delta U = 0.5$ V in IV-measurements. Instability of IV characteristic at $T > 600\,^\circ$C may be due to extended defects of the structure, and features of current flowing in a thin contact layer of titanium carbide at high temperatures.

Optical emission spectra were studied using a confocal RS-spectrometer Renishaw inVia Reflex. To collect PL spectra at room temperature, lens Leika N PLAN EPI 100×/0.85NA was used. Recording of EL spectra in the heating optical table was done with lens Olympus LMPlanFLN 50×/0.5NA having large focus distance and the diameter of the focal area $1.7\,\mu$m at $\lambda = 680$ nm.

Prior to EL spectra measurements, background emission spectra of the heater from the diode surface were recorded at each temperature value under zero diode current. The examples of the heater emission spectra acquired in this manner are shown in fig. 2. They look like a broad band starting from wavelengths ~ 650 nm with maximum on 950–970 nm depending on temperature.

Emission intensity in the studied spectral range depends greatly on temperature. With increase by 25° the intensity rises more than twice. These heater emission spectra were later substracted from the EL measured spectra with the diode current switched on. And the diode EL emission was observed in *i*-layer (fig. 3, *b*).

After the study of PL spectra of *i*-layer of the diode at room temperature and EL at various temperatures in the range from 450 to $680\,^\circ$C and current values in the forward direction to 15 mA the diode was exposed to irradiation with a flow of electrons with energy of 3 MeV on accelerator INDUSTRIAC 3E1000M with doses $1 \cdot 10^{14}\,\text{cm}^{-2}$ and $5 \cdot 10^{17}\,\text{cm}^{-2}$ and subsequent annealing at

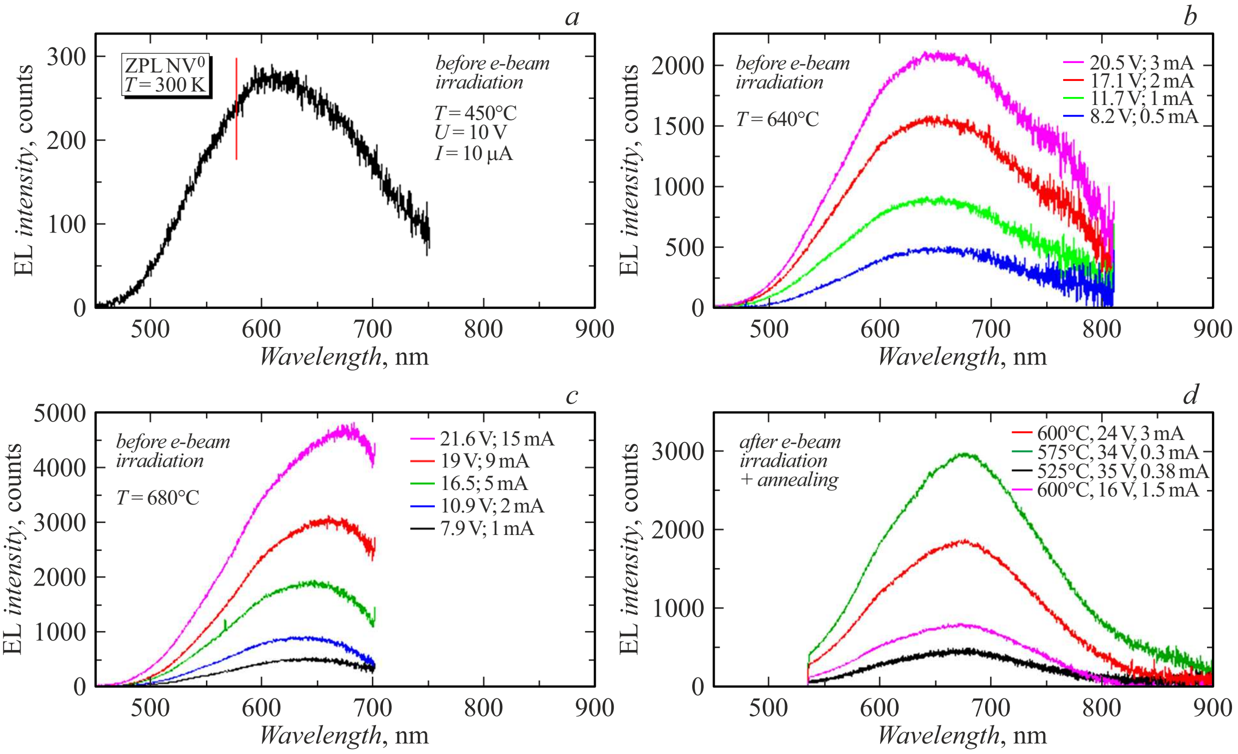

Figure 4. *a–c* — diode EL spectra prior to irradiation with electrons at different values of bias and current in forward direction and at various temperatures; *d* — diode EL spectra after the irradiation with electrons and vacuum annealing at different values of bias and current in forward direction and temperatures 525 °C–600 °C.

$T = 800\,^\circ$C in vacuum for 2 h to increase the concentration of nitrogen-vacancy centers by formation of vacancies as a result of irradiation and their combination with the impurity atoms of nitrogen in process of annealing, similarly to ascribed in [39–42]. Annealing was done in vacuum furnace Red Devil WEBB 105.

2. Results and discussion

Luminescence was observed at temperatures above 400 °C when diode forward current was flowing (fig. 3).

Fig. 3, *a* shows a photograph of a glowing diode at $T = 680\,^\circ$C, $U = 22$ V, $I = 20$ mA prior to irradiation with electrons and annealing. Background glow in fig. 3, *a, c–f* is the heater radiation.

Fig. 3, *b* shows a photograph of the edge of the end surface of the diode, where one can see the luminescence of *i*-layer at $T = 450\,^\circ$C, $U = 10$ V, $I = 10\,\mu$A also prior to irradiation with electrons and annealing. The irradiation color is greenish, specific for the spectrum in fig. 4, *a* with maximum in the area of 600–610 nm. Fig. 3, *c–e* presents photographs of diode glow from the end face after the second irradiation with electrons and annealing. Images were produced at various temperatures in the range of 525 °C–600 °C and various values of diode bias and current, which correspond to the conditions for recording of the emission spectra given in fig. 4, *d*.

The diode EL spectrum prior to irradiation with electrons at $T = 450\,^\circ$C, $U = 10$ V, $I = 10\,\mu$A (fig. 4, *a*) presents a broad band with half-width ~ 150 nm with the maximum at the wavelength of 610 nm. As temperature increases to 640 °C, EL spectrum broadening is observed: the maximum is shifted to the area of 640–660 nm (fig. 4, *b*), and intensity in the maximum at $U = 8.2$ V, $I = 0.5$ mA only slightly exceeds the intensity of the maximum at $T = 450\,^\circ$C and considerably lower current of the diode (fig. 4, *a*). Also in the spectra measured at $T = 640\,^\circ$C (fig. 4, *b*), a band of relatively low intensity in the area of 740–780 nm is observed. It may presumably be the EL band of SiV$^-$-centers that are also present in *i*-layer as confirmed by PL spectra acquired at room temperature (fig. 5). It is known that temperature rise shifts the maximum of the PL spectrum in SiV$^-$-centers to the area of longer waves, in particular, at $T = 588\,^\circ$C the maximum was observed at $\lambda = 751$ nm [23].

After diode irradiation with electrons and annealing the EL spectra at all temperature values in the range of 525–600 °C, voltage of 24–35 V and current of 0.3–3 mA shifted to the area of large wavelengths with the maximum at ~ 680 nm (fig. 4, *d*). And the maximum EL intensity is observed at $T = 575\,^\circ$C.

As temperature increases to 600 °C, the EL intensity is lower even at the diode current values that are 5−10 times higher than at $T = 575\,^\circ$C. With further temperature rise the intensity of light emission became even less.

View of spectrum in fig. 4, *a* in general corresponds to EL spectra of (NV^0)-centers in $p{-}i{-}n$-diodes with n-layer doped with phosphorus [1,2,9,10] at room temperature. The key difference consists in the fact that individual narrow low-intensity peaks of ZPL of luminescence $\lambda = 575$ nm and its phonon replicas that form a broad band when overlapping with maximum at $\lambda = 610$ nm were observed against the general background of a broad band at room temperature[1,2,9,10].

In our case due to high temperature the luminescence lines are broadened and merge into a joint broad band. At $T = 640\,^\circ$C (fig. 4, *b*) the maximum of spectra at all values of diode bias and current shifts by $\lambda = 650$ nm, and at $T = 680\,^\circ$C the maxima of the spectra collected at $U = 16.5$ V, $I = 5$ mA and below these values also corresponds to $\lambda = 650$ nm (fig. 4, *c*), while at high values of bias and current the maximum is on $\lambda = 660{-}680$ nm.

After irradiation of the diode with a beam of electrons and annealing the shift of the maximum of EL spectrum to wavelength of 680 nm (fig. 3, *d*) at $T = 600\,^\circ$C means decrease of energy by 0.2 eV relative to 610 nm at $T = 23\,^\circ$C, which matches the reduction of energy in the maximum of PL phonon wing of (NV^-)-centers under the same conditions [20]. No experimental data on the temperature shift of the maximum of EL phonon wing in (NV^0)-centers in the earlier studies. Therefore, one can only state that the observed shift of the EL band maximum with the growth of temperature slightly differs from the value of shift of the PL phonon wing maximum in (NV^-)-centers under similar conditions [20], and the shift of the band center in fig. 4, *a* by $\sim 20{-}25$ nm relative to the spectrum from [9] matches the shift value at 20−25 nm of the maximum of CL spectrum phonon wing in (NV^-)-centers at $T = 500\,^\circ$C [21].

Fig. 5 provides diode PL spectra at $T = 296$ K prior to irradiation and after irradiation with electrons at doses of $1 \cdot 10^{14}$ and $5 \cdot 10^{17}\,\mathrm{cm}^{-2}$ and annealing at $T = 800\,^\circ$C for 2 h. The spectra contain the band of the second order Raman of diamond and ZPL in (SiV^-)-centers with maxima at ~ 738 nm [23,52]. Silicon gets into the gas mixture at the initial stage of the homoepitaxial layer growth in the CVD-reactor due to the presence of quartz windows in it. In EL spectra measured after irradiation and annealing of the diode (fig. 4, *d*), the band of (SiV^-)-centers is not identified, probably because the EL spectrum of NV-centers shifted to the area of large wavelengths approximately by 30 nm relatively to the spectra prior to irradiation (fig. 4, *b*), and broad band of EL in SiV-centers superimposes on the area of EL spectrum fall in (NV^0)-centers.

The insert in fig. 5, *b* shows that the amplitude of the Raman scattering line of the diamond for the wavelength of the exciting radiation of the laser $\lambda = 532$ nm is the same for both spectra collected after irradiation with doses $1 \cdot 10^{14}$ and $5 \cdot 10^{17}\,e$, which makes it possible to compare the amplitudes of PL-spectra obtained as a result of irradiation with electrons using two different doses at identical conditions of annealing.

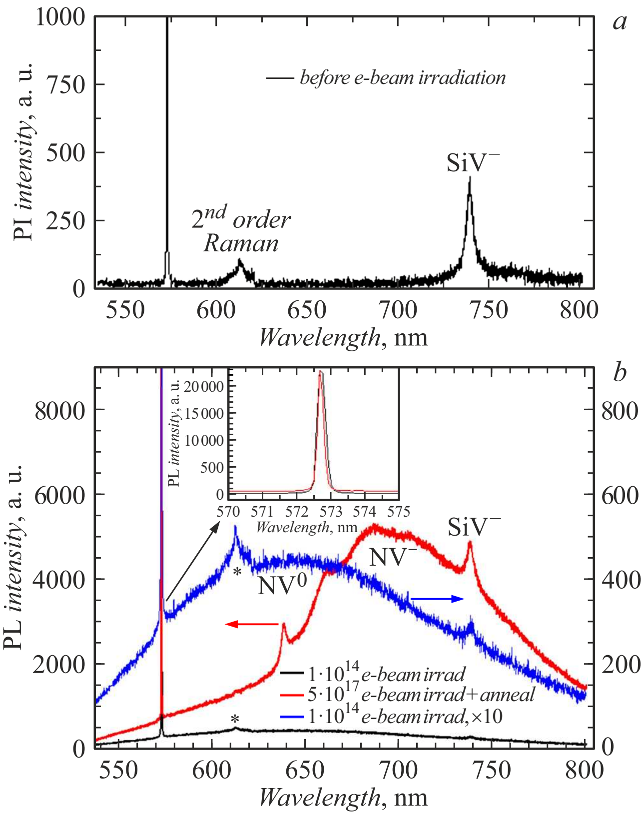

Figure 5. PL spectra of i-layer in the diode at $T = 296$ K when excited by laser $\lambda = 532$ nm prior to irradiation (*a*) and after irradiation with electrons having energy of 3 MeV with doses of $1 \cdot 10^{14}$ and $5 \cdot 10^{17}\,\mathrm{cm}^{-2}$ and annealing at $T = 800\,^\circ$C for 2 h (*b*). The insert shows in more detail the region of the spectrum 570−575 nm with the Raman line of diamond having equal amplitude for both spectra. Sign * indicates band 605−620 nm of the second order of Raman line of diamond.

One can see that the intensity of the PL spectrum after the second irradiation with high dose is approximately 10 times higher than after the first irradiation. But the PL spectrum after the first irradiation and annealing corresponds to spectrum of (NV^0)-centers, as the EL spectrum prior to irradiation (fig. 3, *a*), and PL spectrum after the second irradiation and annealing has two components — main band with maximum at 675 nm, corresponding to PL of (NV^-)-centers, and „delayed“ rise in the area of wavelengths of less than 650 nm, corresponding to a certain part of (NV^0)-centers.

The table provides the results of measurements of EL integral brightness P_{tot} in spectra given in fig. 3, *a, b, d*, and estimation of full brightness of EL in J_{tot} $p{-}i{-}n$-diode prior to its irradiation with electrons and after it, and at various values of current density j. Estimates accounted for integral brightness of irradiation in the range of waves 450−850 nm, The number of spectrum before irradiation with electrons (№1–3) and after irradiation and annealing (№4); diode temperature T; current density j; integral brightness of EL P_{tot}, estimated using spectra in fig. 3, *a, b, d*; full brightness of EL in diode J_{tot} with account of solid angle of collection, area of the focal spot vs the entire surface area of i-layer and total coefficient of irradiation losses in the optical system and detector 0.25

№	T, °C	j, A/cm^2	P_{tot}, phot/s	J_{tot}, phot/s
1	450	$1.6 \cdot 10^{-4}$	$7 \cdot 10^3$	$9 \cdot 10^{10}$
2	640	$1.6 \cdot 10^{-2}$	$2.2 \cdot 10^4$	$2.7 \cdot 10^{11}$
3	680	$8 \cdot 10^{-2}$	$5.5 \cdot 10^4$	$6.8 \cdot 10^{11}$
4	575	$3 \cdot 10^{-3}$	$7.5 \cdot 10^4$	$9 \cdot 10^{11}$

the time of registration of spectra 80 s, angular aperture of the lens, ratio of focal spot area to the entire surface area of the i-layer, the total coefficient of losses in the optical system of around ~ 0.25.

As one can see from the table, despite the fact that the temperature of the maximum radiation and density of current of the diode after irradiation and annealing were lower than prior to irradiation, the integral brightness of EL after irradiation and annealing increased approximately 1.5 times compared to the maximum value prior to irradiation.

The results of this study demonstrate that the light-emitting diamond p–i–n-diodes on NV-centers with n^+-layer doped with nitrogen, are operable at temperatures 450 °C–680 °C. Their emission spectra correspond to the EL spectra of neutral (NV^0)-centers. To conduct the studies of the possibility of superluminescence of NV-centers in i-layer with pumping by electrical current, it is necessary to increase the concentration of NV-centers and increase of current density. This may be achieved by reduction of n^+-layer thickness to decrease the diode resistance in open state, and by optimization of i-layer thickness. Reduction of the substrate thickness to the value of less than 1 μm with the help of *lift-off*-technology used by us to make thin diamond Schottky barrier diodes of p-type [53].

Conclusion

For the first time the EL spectra were studied in a diamond p–i–n-diode with n^+-layer doped with nitrogen in the temperature range 450 °C–680 °C at various values of bias and current of the diode in the open state, and also the impact of irradiation with the electrons having energy of 3 MeV by dose $5 \cdot 10^{17}\,\text{cm}^{-2}$ and subsequent annealing to increase the concentration of nitrogen-vacancy centers of luminescence in the i-layer on the EL spectra of the diode. PL spectra of i-layer in the diode also demonstrated ZPL of luminescence of the negatively charged (SiV$^-$)-centers formed in the CVD-layer of the diamond, as a result of etching the quartz window of the reactor with plasma at the initial stage of the diamond growth process. After irradiation with electrons and annealing, the concentrations of NV- and SiV-centers increased substantially.

The main source of EL are presumably neutral (NV^0)-centers. As temperature, voltage and current of the diode increase in the open state, the EL band broadens with a shift of the maximum to the area of longer waves from ~ 610 to ~ 650 nm. As temperature increases to 680 °C and maximum current density is achieved as 0.08 A/cm^2, the maximum of the EL spectrum shifts further to 680 nm. After irradiation of the diode with electrons and annealing, the maximum of the EL spectra is also observed at the wavelength of 680 nm. A relatively weak band of EL in (SiV$^-$)-centers in the area of the wavelengths 740–760 nm, observed in the spectra measured at $T = 640\,^\circ$C prior to irradiation of the diode with electrons, is not observed in the EL spectra after irradiation with electrons and annealing, measured at temperatures up to 600 °C, probably because the irradiation spectrum of NV-centers shifted to the area of large wavelengths approximately by 30 nm relative to the spectra prior to irradiation (fig. 4, *b*), and broad band of EL of SiV-centers is superimposed on the area of the EL spectrum fall in (NV^0)-centers.

Maximum integral intensity of EL in J_{tot} diode prior to irradiation was $\sim 6.8 \cdot 10^{11}$ photon/s at $T = 680\,^\circ$C, $U = 21.6$ V, $j = 0.08$ A/cm^2. After irradiation and annealing the value J_{tot} of EL reached the value of $\sim 9 \cdot 10^{11}$ photon/s at $T = 575\,^\circ$C, $U = 34$ V, $j = 0.003$ A/cm^2.

To study the possibility of superluminescence of NV-centers in i-layer with pumping by electric current and development of a diamond injection laser on nitrogen-vacancy color centers it is necessary to increase the concentration of NV-centers, to reduce the thickness of n^+-layer for reduction of diode resistance in the open state and accordingly to increase the current density, and also to optimize the thickness of i-layer. It is possible to reduce the substrate thickness to the value of less than 1 μm with the help of *lift-off*-technology [53]. The diode self-heating effect when the current flows may be used to increase its temperature by optimization of design and initial external heating to the temperatures of around 500 °C [54].

Acknowledgments

Experimental equipment provided by the shear use center of the Technological Institute for Superhard and Novel Carbon Materials was used in this study, www.tisnum.ru/suec/suec.html.

Funding

This study was funded by the Russian Science Foundation research project №24-22-00385.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A. Lohrmann, S. Pezzagna, I. Dobrinets, P. Spinicelli, V. Jacques, J.-F. Roch, J. Meijer, A.M. Zaitsev. Appl. Phys. Lett., **99**, 251106 (2011). DOI: 10.1063/1.3670332

[2] N. Mizuochi, T. Makino, H. Kato, D. Takeuchi, M. Ogura, H. Okushi, M. Nothaft, P. Neumann, A. Gali, F. Jelezko, J. Wrachtrup, S. Yamasaki. Nat. Phot., **6**, 299 (2012). DOI: 10.1038/NPHOTON.2012.75

[3] H. Kato, M. Wolfer, C. Schreyvogel, M. Kunzer, W. Müller-Sebert, H. Obloh, C. Nebel. Appl. Phys. Lett., **102** (15), 151101 (2013). DOI: 10.1063/1.4801871

[4] D.Yu. Fedyanin, M. Agio. New J. Phys., **18**, 073012 (2016). DOI: 10.1088/1367-2630/18/7/073012

[5] I.A. Khramtsov, M. Agio, D.Y. Fedyanin. Phys. Rev. Appl., **8**, 024031 (2017).

[6] I.A. Khramtsov, D.Yu. Fedyanin. Phys. Rev. Appl., **12**, 024013 (2019). DOI: 10.1103/PhysRevApplied.12.024013

[7] I.A. Khramtsov, D.Yu. Fedyanin. Semicond. Sci. Technol., **34**, 03LT03 (2019). DOI: 10.1088/1361-6641/ab0569

[8] I.A. Khramtsov, D.Y. Fedyanin. Materials, **12** (12), 1972 (2019). DOI: 10.3390/ma12121972

[9] M.A. Lobaev, D.B. Radishev, S.A. Bogdanov, A.L. Vikharev, A.M. Gorbachev, V.A. Isaev, S.A. Kraev, A.I. Okhapkin, E.A. Arhipova, M.N. Drozdov, V.I. Shashkin. Phys. Stat. Solidi RRL, 2000347 (2020). DOI: 10.1002/pssr.202000347

[10] M. Haruyama, H. Kato, M. Ogura, Y. Kato, D. Takeuchi, S. Yamasaki, T. Iwasaki, H. Morishita, M. Fujiwara, N. Mizuochi, T. Makino. Appl. Phys. Lett., **122**, 072101 (2023). DOI: 10.1063/5.0138050

[11] S.G. Buga, N.V. Kornilov, M.S. Kuznetsov, N.V. Luparev, D.D. Prikhodko, S.A. Tarelkin, T.E. Drozdova, V.D. Blank. Pisma v ZhTF (in Russian), **50** (5), 39 (2024). DOI: 10.61011/PJTF.2024.05.57184.19778

[12] S.G. Buga, A.S. Galkin, M.S. Kuznetsov, N.V. Kornilov, N.V. Luparev, D.D. Prikhodko, S.A. Tarelkin, V.D. Blank. Izv. vuzov. Khimiya i khim. tekhnologiya, **65** (11), 27 (2022) (in Russian). DOI: 10.6060/ivkkt.20226511.7y

[13] S.G. Buga, G.M. Kvashnin, M.S. Kuznetsov, N.V. Kornilov, N.V. Luparev, D.D. Prikhodko, S.A. Terentiev, V.D. Blank. Appl. Phys. Lett., **124**, 102107 (2024). DOI: 10.1063/5.0180183

[14] M. Katagiri, J. Isoya, S. Koizumi, H. Kanda. Appl. Phys. Lett., **85**, 6365 (2004). DOI: 10.1063/1.1840119

[15] I. Stenger, M.-A. Pinault-Thaury, T. Kociniewski, A. Lusson, E. Chikoidze, F. Jomard, Y. Dumont, J. Chevallier, J. Barjonet, J. Appl. Phys., **114**, 073711 (2013). DOI: 10.1063/1.4818946

[16] R.G. Farrer. Sol. St. Comm., **7**, 685 (1969). DOI: 10.1016/0038-1098(69)90593-6

[17] F.J. Heremans, G.D. Fuchs, C.F. Wang, R. Hanson, D.D. Awschalom. Appl. Phys. Lett., **94**, 152102 (2009). DOI: 10.1063/1.3120225

[18] T. Makino, K. Yoshino, N. Sakai, K. Uchida, S. Koizumi, H. Kato, D. Takeuchi, M. Ogura, K. Oyama, T. Matsumoto, H. Okushi, S. Yamasaki. Appl. Phys. Lett., **99**, 061110 (2011). DOI: 10.1063/1.3625943

[19] D. Kuwabara, T. Makino, D. Takeuchi, H. Kato, M. Ogura, H. Okushi, S. Yamasaki. Jpn. J. Appl. Phys., **53**, 05FP02 (2014). DOI: 10.7567/JJAP.53.05FP02

[20] M. Attrash, O. Shtempluck, E. Buks, J. Appl. Phys., **133** (9), 094401 (2023). DOI: 10.1063/5.0128069

[21] A.G. Burachenko, V.S. Ripenko, E.I. Lipatov, K.P. Artemov, A.A. Krylov. Izv. vuzov. Fizika, **65** (11), 19 (2022) (in Russian). DOI: 10.56761/EFRE2022.N4-O-909501

[22] X.-D. Chen, C.-H. Dong, F.-W. Sun, C.-L. Zou, J.-M. Cui, Z.-F. Han, G.-C. Guo. Appl. Phys. Lett., **99**, 161903 (2011). DOI: 10.1063/1.3652910

[23] S. Lagomarsino, F. Gorelli, M. Santoro, N. Fabbri, A. Hajeb, S. Sciortino, L. Palla, C. Czelusniak, M. Massi, F. Taccetti, L. Giuntini, N. Gelli, D.Yu. Fedyanin, F.S. Cataliotti, C. Toninelli, M. Agio. AIP Adv., **5**, 127117 (2015). DOI: 10.1063/1.4938256

[24] C. Kurtsiefer, S. Mayer, P. Zarda, H. Weinfurter. Phys. Rev. Lett., **85**, 290 (2000).

[25] K. Nemoto, M. Trupke, S.J. Devitt, B. Scharfenberger, K. Buczak, J. Schmiedmayer, W.J. Munro. Sci. Rep., **6**, 26284 (2016). DOI: 10.1038/srep26284

[26] D. Genin, E. Lipatov, M. Shulepov, V. Vins, A. Yelisseyev, I. Izmailov, A. Savvin, A. Dormidonov. Stat. Sol. RRL, **18**, 2300062 (2024). DOI: 10.1002/pssr.202300062

[27] L. Lindner, F.A. Hahl, T. Luo, G.N. Antonio, X. Vidal, M. Rattunde, T. Ohshima, J. Sacher, Q. Sun, M. Capelli, B.C. Gibson, A.D. Greentree, R. Quay, J. Jeske. Sci. Adv., **10**, eadj3933 (2024). DOI: 10.1126/sciadv.adj3933

[28] S.G. Buga, G.M. Kvashnin, M.S. Kuznetsov, N.V. Kornilov, N.V. Luparev, M. Yao. FTP, Semiconductors, **57**, 360 (2023) (in Russian). DOI: 10.21883/FTP.2023.05.56206.4748

[29] Z.I. Alferov, V.B. Khalfin, R.F. Kazarinov. Sov. Phys. Solid State, **8**, 2480 (1967).

[30] R.F. Kazarinov, R.A. Suris. Sov. Phys. Semicond., **9**, 6 (1975).

[31] J. Meijer, B. Burchard, M. Domhan, C. Wittmann, T. Gaebel, I. Popa, F. Jelezko, J. Wrachtrup. Appl. Phys. Lett., **87**, 261909 (2005).

[32] J.-M. Cui, X.-D. Chen, L.-L. Fan, Z.-J. Gong, C.-W. Zou, F.-W. Sun, Z.-F. Han, G.-C. Guo. Chin. Phys. Lett., **29** (3), 036103 (2012). DOI: 10.1088/0256-307X/29/3/036103

[33] G. Davies, S.C. Lawson, A.T. Collins, A. Mainwood, S.J. Sharp. Phys. Rev. B, **46**, 13157 (1992).

[34] Y. Mita. Phys. Rev. B, **53**, 11360 (1996).

[35] J. Martin, R. Wannemacher, J. Teichert, L. Bischoff, B. Köhler. Appl. Phys. Lett., **75**, 3096 (1999).

[36] F. Waldermann, P. Olivero, J. Nunn, K. Surmacz, Z. Wang, D. Jaksch, R. Taylor, I. Walmsley, M. Draganski, P. Reichart, A. Greentree, D. Jamieson, S. Prawer. Diamond Relat. Mater., **16**, 1887 (2007).

[37] T. Wee, Y. Tzeng, C. Han, H. Chang, W. Fann, J. Hsu, K. Chen, Y. Yu. J. Phys. Chem. A, **111**, 9379 (2007).

[38] S.D. Trofimov, S.A. Tarelkin, S.V. Bolshedvorskii, V.S. Bormashov, S.Yu. Troshchiev, A.V. Golovanov, N.V. Luparev, D.D. Prikhodko, K.N. Boldyrev, S.A. Terentiev, A.V. Akimov, N.I. Kargin, N.S. Kukin, A.S. Gusev, A.A. Shemukhin, Y.V. Balakshin, S.G. Buga, V.D. Blank. Opt. Mater. Express, **10** (1), 198 (2019).

[39] V.M. Acosta, E. Bauch, M.P. Ledbetter, C. Santori, K.-M.C. Fu, P.E. Barclay, R.G. Beausoleil, H. Linget, J.F. Roch, F. Treussart, S. Chemerisov, W. Gawlik, D. Budker. Phys. Rev. B, **80**, 115202 (2009). DOI: 10.1103/physrevb.80.115202

[40] J. Schwartz, S. Aloni, D.F. Ogletree, T. Schenkel. New J. Phys., **14** (4), 043024 (2012).

[41] S.A. Bogdanov, A.M. Gorbachev, D.B. Radischev, A.L. Vikharev, M.A. Lobaev, S.A. Gusev, D.A. Tatarsky, S.V. Bolshedvorsky, A.V. Akimov, V.V. Chernov. Pisma v ZhTF, **45** (6), 36 (2019) (in Russian).

[42] S.Yu. Troschiev, S.V. Bolshedvorsky, S.D. Trofimov, N.V. Luparev, S.A. Nosukhin, S.G. Buga. Izv. vuzov. Khimiya i khim. tekhnol., **63** (12) (in Russian), 16 (2020). DOI: 10.6060/ivkkt.20206312.12y

[43] S.V. Bolshedvorskii, S.A. Tarelkin, V.V. Soshenko, I.S. Cojocaru, O.R. Rubinas, V.N. Sorokin, V.G. Vins, A.N. Smolyaninov, S.G. Buga, A.S. Galkin, T.E. Drozdova, M.S. Kuznetsov, S.A. Nosukhin, A.V. Akimov. Phys. Status Solidi RRL, **17** (4), 2200415 (2023). DOI: 10.1002/pssr.202200415

[44] A. Savvin, A. Dormidonov, E. Smetanina, V. Mitrokhin, E. Lipatov, D. Genin, S. Potanin, A. Yelisseyev, V. Vins. Nat. Comm., **12**, 7118 (2021). DOI: 10.1038/s41467-021-27470-7

[45] E.I. Lipatov, D.E. Genin, M.A. Shulepov, E.N. Telminov, A.D. Savvin, A.P. Eliseev, V.G. Vins. Kvant. elektron. (in Russian), **52** (5), 465 (2022).

[46] N.B. Manson, J.P. Harrison. Diam. Relat. Mater., **14**, 1705 (2005). DOI: 10.1016/j.diamond.2005.06.027

[47] T. Gaebel, M. Domhan, C. Wittmann, I. Popa, F. Jelezko, J. Rabeau, J. Wrachtrup. Appl. Phys. B, **82** (2), 243 (2005). DOI: 10.1007/s00340-005-2056-2

[48] B. Grotz, M.V. Hauf, M. Dankerl, B. Naydenov, S. Pezzagna, J. Meijer, J.A. Garrido. Nature Commun., **3**, Art. num. 729 (2012). DOI: 10.1038/ncomms1729

[49] Y. Doi, T. Fukui, H. Kato, T. Makino, S. Yamasaki, T. Tashima, H. Morishita, S. Miwa, F. Jelezko, Y. Suzuki, N. Mizuochi. Phys. Rev. B, **93**, 081203(R) (2016). DOI: 10.1103/PhysRevB.93.081203

[50] Y.N. Palyanov, Y.M. Borzdov, A.F. Khokhryakov, I.N. Kupriyanov, A.G. Sokol. Cryst. Growth Des., **10**, 3169 (2010). DOI: 10.1021/cg100322p

[51] U.F.S. D’Haenens-Johansson, J.E. Butler, A.N. Katrusha. Rev. Miner. Geochem., **88**, 689 (2022). DOI: 10.2138/rmg.2022.88.13

[52] M.A. Lobaev, D.B. Radishev, A.L. Vikharev, A.M. Gorbachev, A. Bogdanov, V.A. Isaev, S.A. Kraev, A.I. Okhapkin, E.A. Arkhipova, E.V. Demidov, M.N. Drozdov. Phys. Status Solidi RRL, **17**, 2200432 (2023). DOI: 10.1002/pssr.202200432

[53] V.S. Bormashov, S.A. Terentiev, S.G. Buga, S.A. Tarelkin, A.P. Volkov, D.V. Teteruk, N.V. Kornilov, V.D. Blank. Diam. Rel. Mat., **75**, 78 (2017). DOI: 10.1016/j.diamond.2017.02.006

[54] S. Tarelkin, V. Bormashov, S. Buga, A. Volkov, D. Teteruk, N. Kornilov, M. Kuznetsov, S. Terentiev, A. Golovanov, V. Blank. Phys. Status Solidi A, **212**, 2621 (2015). DOI: 10.1002/pssa.201532213

Translated by M.Verenikina