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Electroluminescence of germanium-vacancy color centers in a diamond *p–i–n* diode

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Electroluminescence of germanium–vacancy color centers (Ge*V* centers) in a diamond *p–i–n* diode has been demonstrated for the first time. To create color centers, a layer implanted with germanium ions was created in the inner region of the diode. A narrow line at a wavelength of 602.9 nm was detected in the emission spectrum, corresponding to the emission of a germanium–vacancy color center in a negative charge state. Electroluminescence spectra of germanium–vacancy and silicon–vacancy color centers were compared.

Keywords: CVD diamond, *p–i–n* diode, color centers, electroluminescence.

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Single-photon sources are an important element of various quantum technologies [1–4]. Sources based on defects in semiconductor materials appear to be the most promising [5]. Color centers in diamond are among the objects that are being examined in this context [6]. The following color centers containing group IV elements are the best suited for single-photon sources: silicon–vacancy (Si*V*), germanium–vacancy (Ge*V*), tin–vacancy (Sn*V*), and lead–vacancy (Pb*V*) [7]. These centers have a narrow zero-phonon line at room temperature and a weak phonon band [7].

Electrical pumping of a single-photon source appears preferable to the optical one [8]. Optical emission in such a source is produced as a result of electroluminescence of a color center positioned in the *i* region of a *p–i–n* diode. It was demonstrated theoretically in [8] that the rate of emission of color centers is specified by the current density in the used *p–i–n* diodes. We have already examined the electroluminescence of an ensemble of Si*V* centers in a *p–i–n* diode of a novel design, where the *n* region was a rectangular groove filled with phosphorus-doped diamond, in [9]. This design allowed for a high current density, which made it possible to obtain a single photon emission rate of more than 10^6 photons per second. The present study is the first to investigate the electroluminescence of an ensemble of Ge*V* color centers and compare it with the electroluminescence of an ensemble of Si*V* centers. At the initial stage, the study of ensembles instead of individual centers simplifies the problem of selecting the brightest center that is most suitable for a source of single photons. The first results of our experiments on the electroluminescence of Ge*V* centers were presented at the International Symposium „Nanophysics and Nanoelectronics“ [10].

The schematic diagram of a *p–i–n* diode used to examine the electroluminescence of Ge*V* centers is shown in Fig. 1, *a*. A substrate $3 \times 3 \times 0.5$ mm in size made of type IIa synthetic diamond prepared by high-pressure high-temperature (HPHT) synthesis was used to fabricate the diode. All epitaxial layers of the diode structure were grown in a CVD reactor, which was discussed in detail in [11]. A 300-nm-thick layer doped heavily with boron to its concentration $[B] = 1.2 \cdot 10^{21}\,cm^{-3}$ was grown on the substrate to form the *p* region of the diode.

A layer of silicon-doped diamond with an approximate thickness of 300 nm was grown next. Doping from residual silicon in the reactor proceeded during growth. Earlier studies of diamond doping with silicon from silane (SiH_4) revealed that silicon compounds accumulating in the reactor provide a low doping level in subsequent experiments without any silane flow. According to secondary ion mass spectrometry (SIMS) data, the average silicon concentration was $4 \cdot 10^{17}\,cm^{-3}$ (Fig. 1, *b*). The ILU-3 ion-beam accelerator (Zavoisky Physical-Technical Institute) was used to implant Ge^+ ions with an energy of 40 keV and a dose of $5 \cdot 10^{14}$ ions/cm^2 under a pressure of $5 \cdot 10^{-5}$ Torr and a sample temperature of 480 °C to a depth of 20 nm within this layer. To activate Ge*V* centers, the sample was annealed in vacuum under a pressure of 10^{-8} Torr and a temperature of 900 °C for 3 h. Another silicon-doped layer with a thickness of 700 nm was grown afterwards. These layers formed the *i* region of the diode.

A groove 100 μm in length, 4 μm in width, and 250 nm in depth was etched in the upper layer through a mask in

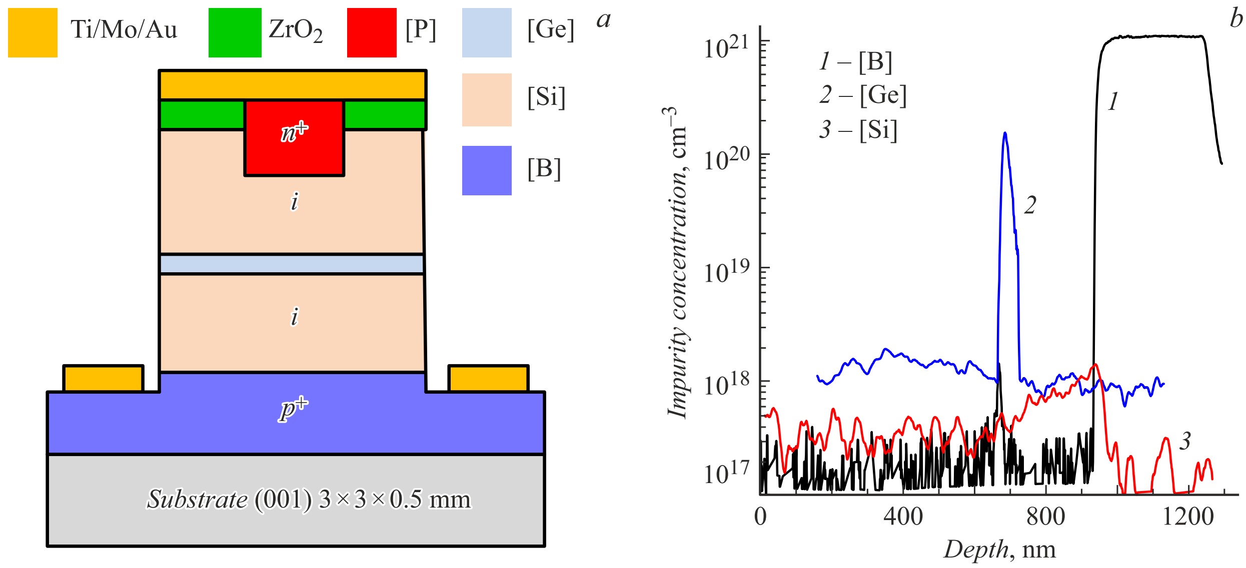

Figure 1. *a* — Diagram of a p–i–n diode (dopants are indicated in square brackets); *b* — concentration profiles of boron, germanium, and silicon impurities in the grown structure that were determined by SIMS. A color version of the figure is provided in the online version of the paper.

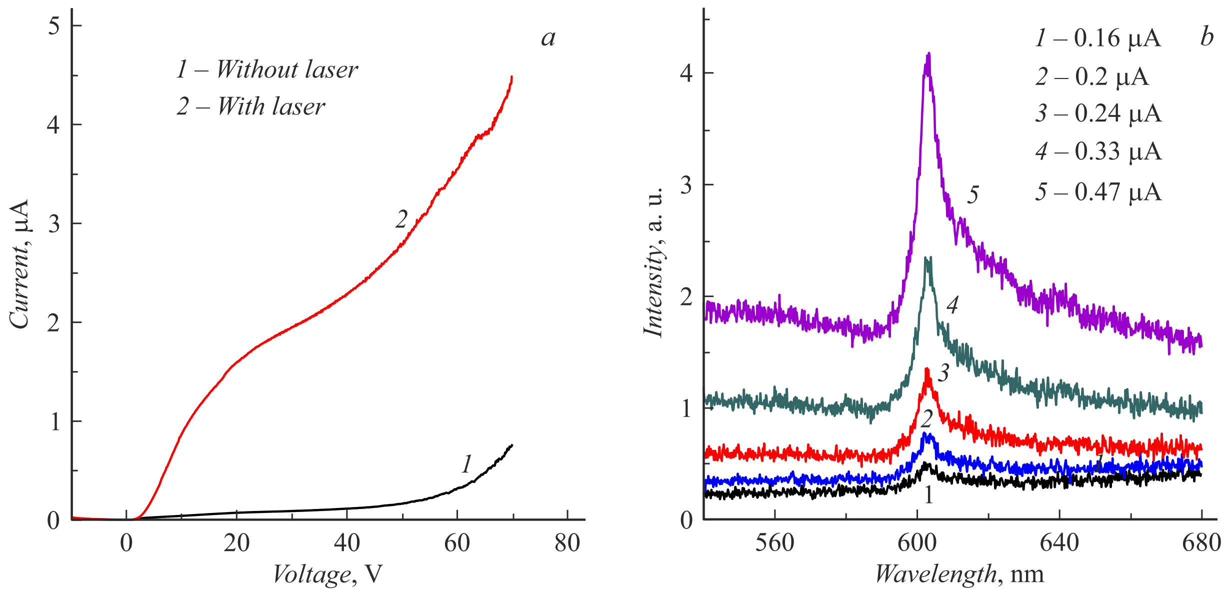

Figure 2. *a* — Current–voltage curve of the p–i–n diode measured with and without laser irradiation at a wavelength of 514 nm; *b* — profiles of zero-phonon lines of a GeV^- center at different currents through the diode.

oxygen plasma. A layer doped heavily with phosphorus was grown in the groove to form the n region of the diode. This method provides an opportunity to increase significantly the conductivity of the n region [9]. A mesostructure was then etched to expose the layer doped heavily with boron. Ti/Mo/Au metals were used to form ohmic contacts to the p and n regions of the diode. Figure 1, *b* shows the profiles of impurity concentrations in the grown structure outside the groove. It can be seen that impurity germanium is distributed in a narrow 25-nm-thick layer with a maximum concentration of $1.5 \cdot 10^{20}\,\text{cm}^{-3}$.

A RENISHAW inVia Reflex confocal Raman dispersive spectrometer was used to measure the electroluminescence and photoluminescence spectra. The emission of GeV and SiV centers was recorded from the substrate side.

Figure 2, *a* shows the current–voltage curve of the p–i–n diode. Compared to [9], the diode opening voltage increased from 5 to 60 V. At a forward voltage of approximately 80 V, a breakdown of the ZrO_2 dielectric, which was used to insulate the mesostructure outside the groove (Fig. 1, *a*), was observed. The current–voltage curve did not restore its shape after this breakdown. The mentioned increase

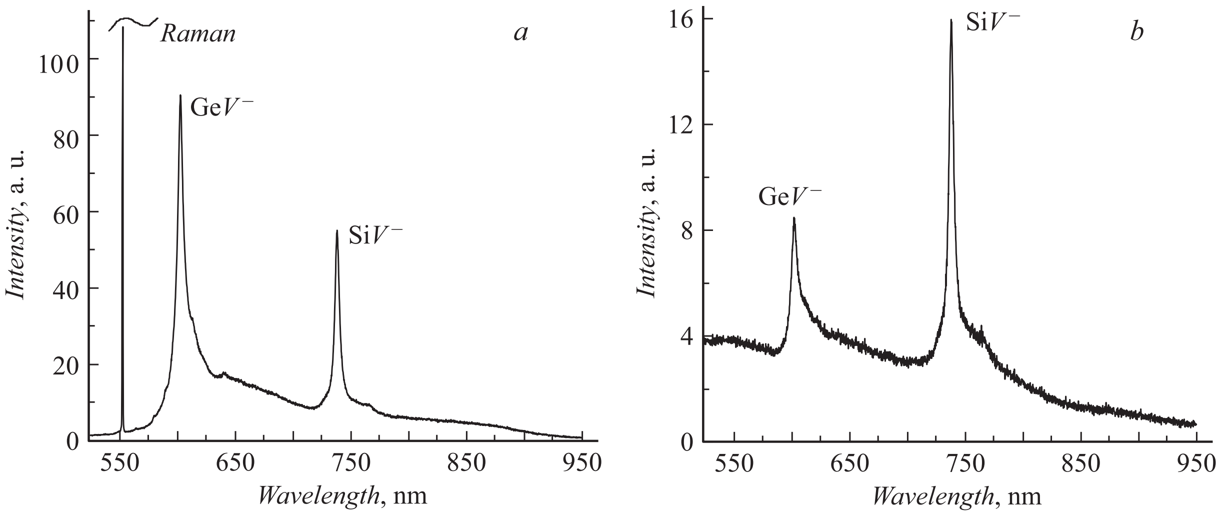

Figure 3. *a* — Photoluminescence spectrum of the *p–i–n* diode excited by a laser at a wavelength of 514 nm; *b* — photoluminescence spectrum of the *p–i–n* diode at a current of 0.47 μA.

in opening voltage is likely attributable to the presence of a fairly dense ensemble of GeV^- centers, which forms a charged region inside the *i* region of the diode that affects carrier transport. The diode current did indeed increase by an order of magnitude under irradiation with a laser with a wavelength of 514 nm (Fig. 2, *a*). Apparently, this was induced by partial photoionization of GeV^- centers.

A narrow line at a wavelength of 602.9 nm, which corresponds to the zero-phonon line of a GeV color center in its negative charge state GeV^-, was found in the electroluminescence spectrum (Fig. 2, *b*).

Figure 3, *a* shows the photoluminescence spectrum of the diode recorded in the mode of line intensity saturation by laser power. In addition to the Raman scattering line, this spectrum contained lines corresponding to the emission of GeV^- and SiV^- centers. The FWHM values of these lines were 8 and 5.7 nm for GeV^- and SiV^- centers, respectively. The concentration of SiV^- centers may be estimated based on the SIMS data on Si impurity concentration by setting the degree of conversion of Si into SiV^- to 1%. According to [6], the emission intensities of individual SiV and GeV centers in the saturation mode by laser power are approximately the same. The concentration of GeV^- centers was determined from the difference in emission intensities of SiV^- and GeV^- centers (Fig. 3, *a*) and the thickness of doped Si and Ge layers (Fig. 1, *b*). The estimated concentration of GeV^- centers was $2 \cdot 10^{17}\,\mathrm{cm}^{-3}$, while the degree of conversion of Ge into GeV^- centers was 1.3%, which agrees with the data from [12].

Figure 3, *b* shows the electroluminescence spectrum of the *p–i–n* diode at a current of 0.47 μA and a voltage of 70 V, which features narrow lines corresponding to zero-phonon lines of GeV^- and SiV^- centers. In contrast to photoluminescence, the intensity of electroluminescence line corresponding to a GeV^- center is lower than the one of a SiV^- center; i.e., the excitation of GeV^- was less efficient compared to a SiV^- center. This is likely attributable to the presence of an excessively dense ensemble of GeV^- centers, which forms a charged region inside the *i* region of the diode that affects carrier transport. As a result, the excitation of GeV^- centers in the process of electroluminescence is less efficient than the excitation of SiV^- centers [8].

Thus, the electroluminescence of GeV centers in a diamond *p–i–n* diode has been demonstrated for the first time and compared with the electroluminescence of SiV centers. It was demonstrated that a dense ensemble of GeV centers with a concentration close to $10^{17}\,\mathrm{cm}^{-3}$ may affect appreciably the carrier transport in the diode. To perform a more detailed study of the electroluminescence of GeV centers, one needs to reduce significantly the ensemble density or proceed straight to the examination of individual centers.

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Conflict of interest

The authors declare that they have no conflict of interest.

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