Infrared Luminescence from Silicon Nanostructures Heavily Doped with Boron

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Abstract—Intense highly polarized radiation from silicon nanostructures heavily doped with boron to $5 \times 10^{21} \text{cm}^{-3}$ is studied as a function of temperature, forward current, and an additional lateral electric field. The features of the radiation intensity and degree of polarization suggest that an important role in the formation of the luminescence spectra is played by the ordered system of $B^+–B^–$ dipoles, formed as a result of the reconstruction of shallow boron acceptors as centers with negative correlation energy. The results obtained are interpreted within a proposed model based on two-electron adiabatic potentials, according to which radiation results from donor–acceptor recombination via boron dipole center states, involving shallow phosphorus donors.

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1. INTRODUCTION

Interest in the study of optical radiation from silicon-based structures has long been active, first of all due to the optimistic prospects offered by the development of silicon optoelectronics and optical data transmission systems [1]. The point is that, according to Moore’s law, the number of transistors per processor chip doubles approximately every year and a half. In this case, copper connections providing a connection between the chip components and individual cards are already unable to provide the required data exchange rate. The use of optical data transmission systems would make it possible to solve this problem and would open up paths for further development. Therefore, active studies are currently directed at developing an efficient silicon radiation source. Several approaches are being developed, within which systems based on porous silicon, silicon nanocrystals, plastically deformed silicon, and erbium-doped silicon are being studied [2–7]. In the last decade, a large number of papers devoted to the detection of relatively intense near-edge luminescence from single-crystal boron-implanted silicon were published [8–11]. This rather unexpected result was primarily explained by the spatial localization of carriers by dislocation loops that appeared during implantation. However, the detection of a similar effect in the case of the diffusion introduction of boron [12] and consideration of the effect of impurities trapped by dislocations cast doubt on the validity of such an explanation [13]. Based on these reasons, the answer should be searched for in another field; first of all, attention is drawn to the fact that, independently of the doping method, the boron concentration in structures with a high emission intensity was high and reached the solubility limit [14–16]. Furthermore, it was shown in [16] that the intensity increases with the doping level, reaching a maximum at the boron concentration $N(B) \approx 4 \times 10^{20} \text{cm}^{-3}$. A further increase in the concentration results in luminescence quenching which, according to [16], is associated with boron cluster formation, an inevitable process within various doping technologies. However, this limitation can be overcome in connection with the development of gas-transport doping methods [17].

The objective of this research is to study electroluminescence (EL) and photoluminescence (PL) from silicon nanostructures, which are ultra-narrow (8 nm) boron diffusion profiles with a concentration of $5 \times 10^{21} \text{cm}^{-3}$, containing a $p$-type silicon quantum well (QW) 2 nm wide, confined by $\delta$ barriers heavily doped with boron. Such structures are fabricated on an $n$-Si (100) surface after its preliminary oxidation and short-term boron diffusion controlled by fluxes of self-interstitials and vacancies. EL and PL from these nanostructures was studied in wide temperature and excitation power ranges, and under an additional lateral electric field. It was found that the radiation is of high intensity, including that at room temperature (~0.03 mW at a forward current of 50 mA) and has a high degree of linear polarization (as high as 30%). These studies have suggested that an important role in the formation of the luminescence spectra of silicon nanostructures heavily doped with boron is played by the ordered system of $B^+–B^–$ dipoles, formed as a result of the reconstruction of shallow boron acceptors as centers with negative correlation energy. Previously,
interstitials and vacancies have a preferential crystallographic direction along (111) and (100) axes, respectively [18]. In this case, intrinsic defects form pyramidal-shaped microdefects. The distribution of microdefects that formed during the initial oxidation stage probably represents the modification of a fractal such as the Sierpinski set with incorporated longitudinal ultra-narrow silicon QWs. After preliminary oxidation, photolithography, and etching, the mode of enhanced dopant diffusion from the gas phase can be implemented within the silicon planar technology by stimulating the exchange interaction of impurity atoms with self-interstitials or vacancies using additional oxygen feeding [18]. Of particular interest is the implementation of the sharp inhibition mode for impurity diffusion in the case of the complete annihilation of intrinsic defects [18]. It is in the mode of kick-out and vacancy mechanism parity that ultra-shallow boron diffusion profiles are formed, which are the basis of the silicon nanostructures under study. Depending on the conditions of preliminary oxidation and subsequent nonequilibrium impurity diffusion, the self-ordering of microdefects and dopants can stimulate the formation of both transverse and longitudinal silicon QWs heavily doped with boron, confined by δ barriers, in such profiles [17–19].

The studied silicon nanostructures were fabricated on n-Si (100) substrates 350 μm thick with the resistivity 20 Ω cm, oxidized at a temperature of 1150°C in a dry oxygen atmosphere containing CCl4 vapor. To perform short-term boron diffusion, windows were etched in the oxide layer using photolithography. Diffusion was performed from the gas phase at T_{diff} = 900°C. As shown in [19–21, 23], this temperature provides parity between different diffusion mechanisms resulting in its sharp inhibition and the formation of ultra-narrow diffusion profiles with the boron concentration 5 × 10^{21} cm^{-3}, measured using secondary ion mass spectrometry. The fabrication technology and microstructure of the samples under study is described in more detail in previous papers [24–26].

To perform the EL measurements, ten gold contacts 0.2 × 0.1 mm and 0.2 × 0.05 mm in size, whose configuration is shown in Fig. 1, were formed on the active surface of the obtained p′−n structures 4.7 × 0.1 mm² or 4.7 × 0.05 mm² in area; the structure’s rear side was coated with aluminum. The prepared samples were placed into a controlled cryostat to perform studies in the temperature range 4.2 to 300 K. EL measurements were performed under conditions of stabilized current applied in the forward direction (minus at the structure’s rear side, plus toward one of two central gold contacts on the active surface). PL was studied using a semiconductor laser with the wavelength 980 nm and power 80 mW. Radiation from the silicon nanostructures under study was analyzed using a diffraction spectrometer based on an MDR-23 monochromator and measured by an InGaAs photodiode using the conventional technique of synchronous detection. The combined transmission function for shallow acceptors.

2. FABRICATION OF SILICON NANOSTRUCTURES HEAVILY DOPED WITH BORON AND EXPERIMENTAL TECHNIQUE

Formation of the silicon nanostructures under study is based on local self-ordering processes, which occur due to the anisotropy of the diffusion of proper lattice atoms and impurity atoms introduced into the semiconductor matrix. Such self-organization of impurity atoms can arise as a result of various processes; however, it is sharply enhanced when using the nonequilibrium impurity diffusion method under conditions of controlled vacancy or self-interstitial injection [18, 19]. It is known [19–22] that the generation of excess fluxes of intrinsic defects occurs during the formation of an oxide layer on the single-crystal silicon surface. In this case, counterfluxes of self-interstitials and vacancies have a preferential crystallo-
the optical part of the experimental setup and the spectral sensitivity of the detector was determined by measuring the emission spectrum of a blackbody heated to 1500°C. The absolute spectral position of the monochromator was calibrated using narrow lines in the water vapor absorption spectrum with an accuracy of no worse than several Angströms.

3. RESULTS AND DISCUSSION

3.1. Electroluminescence Spectra of Silicon Nanostructures Heavily Doped with Boron

The electroluminescence (EL) spectra of the silicon nanostructures under study, measured at the temperatures 77 and 300 K and forward current 20 mA, are shown in Fig. 2. We can see that the emission line with a maximum at the wavelength 1126 nm and full width at half-maximum (FWHM) 18 nm and its phonon replica attributed to transverse optical (TO) phonon emission is dominant in the spectrum at $T = 77$ K. A similar spectrum is also observed in the study of PL (see the inset in Fig. 2). As the temperature was increased to 300 K, the considered emission line exhibits an increase in the FWHM to 70 nm and a spectral shift to lower energies. Furthermore, a temperature increase results in the appearance of a rather broad energy tail in the long-wavelength spectral region. As for the emission power, we can see from its dependence on the forward current $W(I)$, shown for both temperatures in Fig. 3, that it is quite high. In this case, it should be noted that these values were obtained upon EL excitation via a small-area contact, $0.2 \times 0.05$ mm$^2$.

But in the case of a forward current distributed over all gold contacts on the structure surface area $4.7 \times 0.05$ mm$^2$, the room-temperature radiation power at the current 50 mA reaches 0.03 mW. Such an approach also makes it possible to avoid structure heating which is monitored by a shift in the peak position of the luminescence spectrum.

The values of $W(I)$ were calculated taking into account the spatial distribution of emission, based on areas under the curves of the electroluminescence spectra and experimental setup calibration using a reference source with a known power. Such a method of calculation makes it possible to determine the emission power directly in the spectral range of the considered line and to exclude the contribution of the visible and far infrared wavelength ranges that are also present in the luminescence of the silicon nanostructures under study [17, 27]. In the case of the use of, e.g., a calibrated photodiode placed in the immediate vicinity of the sample, the latter would be hardly feasible. The presence of radiation in a wide spectral range also complicates the external quantum efficiency calculation for the emission line under study, since it seems impossible to determine the forward current fraction flowing through the structure, which is involved in line formation.

We now turn to an analysis of the electroluminescence characteristics. Firstly, it should be noted that the radiation under consideration is emitted in the heavily doped region in particular, which is suggested by the shape of the dependence $W(I)$ exhibiting linearity up to high forward current values. Indeed, the total luminescence intensity is predominantly controlled by the variation rate $d(\delta n)/dt$ of the excess concentration of electron–hole pairs generated by external excitation at the rate $G_R$. The quantity $d(\delta n)/dt$ is the sum of the radiative $R_{em}$ and nonradiative $R_{nr}$ recombination rates. In this case, the main contribution to the dependence of $d(\delta n)/dt$ on $G_R$ is made by $R_{em}$, since the carrier-concentration dependent Auger process starts to become dominant at higher concentrations than those
involved in absorption in a concentration of occupied initial states that can be
The latter assumption is well substantiated, since the forward current should not play a significant role.

the nonlinear dependence of the generation rate on
reached within the considered experiment. As for \( G_R \),
the possible self-absorption effect which can lead to
the forward current should not play a significant role.
The latter assumption is well substantiated, since the
concentration of occupied initial states that can be
involves absorption in a \( p \)-type material is extremely
It is also reasonable to disregard the stimulated emission processes and to consider only spontaneous
luminescence as the main process. Then the variation
rate of the excess concentration can be written as

\[
\frac{d(\delta n)}{dt} = -\frac{R^0}{n_0 p_0} (np - n_0 p_0),
\]

where \( R^0 \) is the spontaneous radiative recombination rate in thermodynamic equilibrium, when the number of “top–down” transitions is equal to the number of “bottom–up” transitions; \( n_0 \) and \( p_0 \) are the equilibrium concentrations of electrons and holes, respectively; \( n = n_0 + \delta n \) and \( p = p_0 + \delta p \) are the total concentrations of electrons and holes, taking into account the excess ones (\( \delta n \) and \( \delta p \)) generated by external excitation [28]. To make the quantity \( d(\delta n)/dt \) linearly dependent on external excitation, the condition \( p_0 \gg \delta p \) (or \( n_0 \gg \delta n \)) should be satisfied, which is attained in the heavily doped \( p(n)\)-type region and leads to the relation (in the case of \( p_0 \gg \delta p \), taking into account that \( \delta n \approx \delta p \))

\[
\frac{d(\delta n)}{dt} = -\frac{R^0}{n_0 p_0} n_0 \delta p + p_0 \delta n + \delta n \delta p
\]

obtained under the assumption that the transition matrix element is frequency independent. Only the processes with phonon emission were taken into account, since phonon absorption at low temperatures is improbable. For the same reason, the self-absorption effect which can cause a change in the shape of the emission spectrum was disregarded.

In calculating the quasi-Fermi levels for electrons \( F_n \) and holes \( F_p \), the twelvefold degeneracy of the conduction band, as result of six equivalent valleys and two spin projections, and fourfold degeneracy of the valence band were taken into account. It should be noted that consideration of the density-of-states tails associated with a high doping level, based on [29], only leads to an insignificant change in the spectral shape. Finally, the radiative recombination rate calculated by formula (3) was corrected, taking into account the transmission function of the optical part of the experimental setup and the detector spectral sensitivity.

Thus, emission from the studied silicon nanostructures occurs namely in the \( p \)-type region heavily doped with boron. We note that no assumptions were made with respect to \( R^0 \) in deriving relation (2), i.e., the above result is independent of a particular recombination mechanism responsible for emission.

Without going into details, it would be assumed that the emission lines shown in Fig. 2, at least at \( T = 77 \) K, correspond to an indirect transition in bulk silicon between the bottom of the conduction band and the top of the valence band, which is accompanied by TO phonon emission with the energy \( \hbar \omega_{\text{TO}} = 57.5 \) meV, necessary for quasi-momentum conservation. However, interpretation of the silicon emission spectra near the intrinsic absorption edge is a rather difficult problem. The difficulty arises, first and foremost, as a result of the low activation energies of main donors and acceptors, which is expressed in the possible overlap of various recombination channels in a relatively narrow spectral region. As a result, a slightly more detailed analysis leads to the conclusion that the above assumption is invalid. Indeed, for comparison with the experimental emission line of silicon nanostructures heavily doped with boron (solid curve), Fig. 4 shows the radiative recombination rate for an indirect transition in single-crystal silicon (dashed curve). We can see that the shapes and spectral positions of these two curves are far from identical. The values of \( R^{bb}_p \) were calculated using the expression

\[
R^{bb}_p(\hbar \omega) \propto \int \frac{1}{E_c E_v \exp \left[ \frac{E_v - E}{kT} \right] + 1} \exp \left[ \frac{E_c - E_v}{kT} \right] + 1 \times (E_c - E_g)^{1/2} (E_v - E_g)^{1/2} \omega \omega_{\text{TO}} \times dE_c dE_v,
\]

Fig. 4. Electroluminescence line of the silicon nanostructures under study (solid curve), measured at \( T = 77 \) K, and the radiative recombination rate calculated for an indirect transition in single-crystal silicon without (dashed curve) and with (dash-dotted curve) consideration for exciton effects.

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The difference between the calculated spectral position and the experimentally determined position of the emission line could be attributed to the presence of a bound state due to the formation of excitons with the binding energy \( E_x \approx 15 \text{ meV} \). However, this assumption raises strong objections associated, first of all, with an extremely low probability of exciton existence at high doping levels and high injection currents and temperatures. Furthermore, the emission spectrum shape calculated for the case at hand does not correspond to that observed (see Fig. 4, solid and dash-dotted curves). The latter was constructed based on the radiative recombination rate

\[
R_{\text{ex}}^0(\hbar \omega) \propto \sqrt{\hbar \omega - E_g - E_x - \hbar \omega_{\text{TO}}} \\
\times \exp \left[ -\frac{\hbar \omega - E_g - E_x - \hbar \omega_{\text{TO}}}{kT} \right] \tag{4}
\]

of free excitons involving TO phonons, obtained under the same assumptions as above [28, 30], and also corrected, taking into account the spectral dependence of the transmission of the optical part of the experimental setup and the detector spectral sensitivity.

Thus, it is reasonable to assume that the recombination mechanism responsible for emission in silicon nanostructures heavily doped with boron is associated particularly with the presence of impurities. In this case, recombination can occur without involving phonons as well, since the quasi-momentum conservation restriction is removed at high doping levels [31].

Information regarding phonon involvement in recombination can be obtained by analyzing, e.g., the phonon replica from the emission line under consideration. Indeed, let us assume, that recombination of the electron and hole, situated at Brillouin zone points with different wave vectors \( q_e \) and \( q_h \), occurs involving phonons. Then the quasi-momentum conservation law requires that the phonon wave vector \( q_{\text{ph}} \) be equal to the difference of the electron and hole wave vectors, \( q_{\text{ph}} = |q_e - q_h| \). But in the case of a two-phonon process, which does lead to the appearance of a phonon replica, the sum of the wave vectors for the two phonons should be equal to this difference, \( q_{\text{ph}} + q_{\text{ph}}^* = |q_e - q_h| \), hence \( q_{\text{ph}}^* \) should be zero. Therefore, the phonon replica is distanced from the main emission line by a value equal to the phonon energy at the Brillouin zone center, \( \hbar \omega_{\text{TO}}(q = 0) = 64 \text{ meV} \). But if the quasi-momentum conservation restriction is removed, any and all phonons can be involved in the phonon replica. This circumstance will result in a wider replica line in comparison with the main line width, with maxima corresponding to phonon energies near the band edges, where the density of states is at a maximum due to the approach of the phonon dispersion curves to the horizontal line. It is such a pattern that is observed in the case of the analyzed emission line (see Fig. 5). Thus, the recombination process resulting in luminescence from the studied silicon nanostructures heavily doped with boron, most likely, does not require phonon involvement and occurs via the states of shallow donors, e.g., phosphorus, and via acceptor states caused by boron. This conclusion seems quite reasonable, considering the fact that it is the donor-acceptor recombination mechanism that is probably the basic mechanism for near-band-edge luminescence in many heavily doped semiconductors [32].

Luminescence from heavily doped silicon has long been studied [33–36]. The main result obtained is that emission associated with the impurity band is dominant in the luminescence spectrum even at impurity concentrations of \( \geq 10^{18} \text{ cm}^{-3} \). In this case, two main recombination channels are recognized [34]. One channel is the direct donor–acceptor recombination of impurity band holes (electrons) with carriers localized by discrete donor (acceptor) states of the background impurity (the so-called LL line). The other channel is the recombination of impurity band holes (electrons) with free carriers of one of the bands (HL line) [34]. In the latter case, a process is also possible, in which the initial and final states are at impurity levels that degenerate into a band [37]. The ratio of the HL and LL emission lines is controlled by the temperature, excitation power, and the ratio of donor and acceptor impurity concentrations; the lines themselves exhibit a number of interesting features. For example, along with the radiation accompanied by phonon emission, the spectrum contains a zero-phonon luminescence line [36, 37]. Furthermore, the HL line shape is independent of the dopant type and is identical for both silicon heavily doped with phosphorus and silicon heavily doped with boron [34]. The spectral position of both the HL and LL lines shifts to lower energies with an increasing doping level [37].
some publications [34, 38, 39], it was also indicated that, despite the low optical quantum efficiency of silicon as an indirect-gap semiconductor, heavily doped silicon exhibits a rather high emission intensity. This observation is also confirmed in the case of silicon nanostructures heavily doped with boron, studied here (see Fig. 3). However, to our knowledge, such a high boron concentration as $5 \times 10^{21} \text{ cm}^{-3}$ is reported for the first time. In what follows, we show that emission in the case at hand results from donor–acceptor recombination (DAR) between shallow donor states and states caused by boron which, at such high concentrations, form an ordered system of impurity dipole $B^+–B^–$ centers.

### 3.2. Features of Luminescence and its Relation to the Ordered System of Dipole Boron Centers

To determine the detailed structure of the ultrashallow heavily doped boron diffusion profiles, the data of a large number of techniques were used, including cyclotron resonance (CR), electron spin resonance (ESR), and scanning tunneling microscopy (STM). Electron and hole CR measurements were performed using a Brucker–Physik AG EPR spectrometer with magnetic field rotation in the planes parallel and perpendicular to the boron diffusion profile plane on the silicon (100) surface [18, 40, 41]. Quenching and shift of the CR lines, which showed $180^\circ$ symmetry for the magnetic field orientation parallel to the silicon (100) surface, made it possible to detect a longitudinal ultranarrow silicon quantum well (UNSQW) confined between heavily doped $\delta$ barriers in the ultrashallow profile. UNSQWs were also identified by EL spectra measured in the visible [27] and far infrared spectral regions and, which exhibited, respectively, interband and intraband optical transitions between size quantization levels (Fig. 6a). The energy-level diagram for two-dimensional (2D) hole quantization is shown in Fig. 6b. The detected $p$-type UNSQW contains a 2D hole gas characterized by longer free path times for heavy and light holes [40–42]. This result is rather unexpected, bearing in mind the high boron-doping level of $\delta$ barriers between which the quantum well is formed. However, according to data on the temperature dependences of the conductivity and Seebeck coefficient, and local tunneling current–voltage ($I–V$) characteristics [18, 24, 43], it was found that charge correlations, starting to become dominant at such a high boron concentration, result in the formation of a correlation gap in the density of states in the hole gas. Within the proposed model [18], a major role in the formation of this correlation gap is played by the reconstruction of shallow boron acceptors as centers with negative correlation energy [44–46], resulting in the formation of impurity dipoles with $C_{3v}$ symmetry,

$$2B^0 \rightarrow B^- + B^+.$$ (5)

This model was further confirmed by a study into the angular dependences of the ESR spectra, which made it possible to directly identify the presence of trigonal dipole boron $B^+–B^–$ centers [23] oriented along the $(111)$ crystallographic axes (see Fig. 7). The correlation gap was determined based on measurements of the tunneling $I–V$ characteristics and local tunneling microscopy data (Fig. 8a). The latter method is more advantageous, since it allows direct determination of the local density of states when measuring the tunneling current under sweep voltage conditions applied to the STM tip, which is maintained in
In this case, if a negative voltage is applied to the $\delta$ barriers, then holes will tunnel, occupying free states in the sample, whereas a positive voltage will promote their depopulation. Since the conditions for 2D hole transport in the studied silicon nanostructures are close to ideal [48–51], recording of the tunneling conductance spectra provides measurements of the local density of states. The correlation gap value, determined in such a way, was found to be equal to 0.044 eV; it is defined by the ionization energies of background and correlated electrons according to the diagram shown in Fig. 8b. These energies are $E_v + 0.022$ eV and $E_v - 0.022$ eV for B(+/0) and B(0/-), respectively. The lower energy position B(0/-) is a consequence of the boron center’s negative correlation energy and is reflected in the fact that it is energetically more favorable for close boron atoms to form a dipole. This circumstance leads to the
reconstruction of a set of shallow boron acceptors into an ordered system of dipole centers according to reaction (5). It should be noted that the small-radius bipolarons that formed in this case and localized at each dipole are particles with integer spin, hence, upon reaching a certain critical density and temperature, can transit to the Bose–Einstein condensation state. This circumstance probably results in the existence of the high-temperature superconductivity previously detected in the studied silicon nanostructures upon reaching the critical temperature \( T_c \approx 145 \) K. The value of \( T_c \) was determined using a wide variety of techniques, including measurements of the temperature and field dependences of the resistivity, thermoelectric power, specific heat, and static magnetic susceptibility [17]. These techniques yielded close results.

Taking into account the very high boron dipole concentration of \( \sim 2.5 \times 10^{21} \) cm\(^{-3} \), the quantity \( T_c \) is most likely associated with the decay of the impurity dipole system itself due to the violation of reconstruction conditions, rather than with attaining critical condensation conditions. This assumption finds confirmation in measurements of the EL from the studied silicon nanostructures heavily doped with boron. Figure 9 shows the temperature dependence of the area under the curves of the EL spectra measured at the forward current 20 mA. We can see that the EL intensity increases with temperature, reaching a maximum at \( T \approx 150 \) K, whose position is in good agreement with the critical temperature for the superconducting transition. As an example, the inset of Fig. 9 shows the temperature dependence of the resistivity of the studied silicon nanostructures, measured along their surface. Small fluctuations in the total EL intensity, drawing attention close to \( T \approx 150 \) K (Fig. 9), can be attributed to critical fluctuations near the phase transition point, observed in many systems [52].

Thus, the final state in donor–acceptor recombination resulting in emission from the studied silicon nanostructures is probably a state associated with the boron dipole, i.e., \( B(+/0) \). In this case, taking into account the energy position of the luminescence line under study, it can be assumed that the initial state in this case can be that of a shallow donor, most likely phosphorus, as a main dopant in \( n \)-type silicon used for fabricating silicon nanostructures. Then, the analyzed emission results from the donor–acceptor recombination of an electron localized at phosphorus and one of the holes bound with the boron ion \( B^+ \), according to the diagram shown in Fig. 10.

The boron dipole’s involvement in recombination results in the fact that almost all features typical of the DAR, associated with the dependence of the emitted photon energy on the Coulomb interaction in the pair, do not appear. In this case, the emission line cannot change shape and exhibit the characteristic redshift as the excitation power and delay time increase. Such a situation is not new and similar examples can be found in [53–55], where donor–acceptor recombination is observed under conditions, where one or both of the components are neutral. However, in this case, the probability of recombination still rapidly decreases with pair distance. Therefore, to increase the emission intensity, it is rational/ appropriate to provide high impurity concentrations. An increase in the total emission intensity with silicon doping levels, as indicated in some studies [16, 38, 39], is probably associated with this. Certainly, removal of the quasi-momentum conservation law due to momentum relaxation near impurity centers plays a big role in this case. At the same time, it should be considered that, as
was shown in [31], the intensity of the zero-phonon luminescence line increases with the binding force of the impurity center and electron or hole involved in recombination. In this case, impurity boron dipoles have an advantage, since they provide a small localization radius of holes bound to them.

The involvement of the boron dipole system in emission from the studied silicon nanostructures is further confirmed by the fact that the detected EL exhibits a high degree of linear polarization, which reaches 30%. The high degree of linear polarization is probably caused by ordering of the boron dipole system. Here it is clear that the $C_{3v}$ symmetry of dipole centers should also manifest itself in the polarization behavior. The angular dependences of the degree of linear polarization (Figs. 11a–11c) measured at various sample orientations with respect to the observation axis confirm this assumption. We can see that the degree of polarization is maximal particularly when observed along the $\langle 110 \rangle$ axis and equivalent ones that correspond to the boron dipole center alignment direction (see Fig. 7). In this case, agreement is not only qualitative, but also quantitative. The degree of polarization in intermediate angles between directions equivalent to $\langle 110 \rangle$ decreases approximately by a factor of $\sqrt{2}$, as it should be in the case of the projection of an electric field vector oscillating along the $\langle 110 \rangle$ axis onto the $\langle 010 \rangle$ axis (Fig. 11c). The asymmetry of the angular distribution of the degree of linear polarization can be explained, e.g., by the nonideality of the dipole center sublattice, associated with the incomplete reconstruction of shallow boron acceptors. Fur-

![Image](image.png)

**Fig. 11.** Angular dependences of the degree of linear polarization (a, b, c) and the total intensity (d, e, f) of the electroluminescence lines for the studied silicon nanostructures heavily doped with boron, obtained during sample rotation in three mutually perpendicular planes. Measurements were performed at the forward current 20 mA and the temperature 77 K.
thermore, local stresses can also play an important role, as they appear in silicon nanostructures during diffusion and cause preferential alignment of boron dipoles along any equivalent axis. This circumstance probably manifests itself in the angular dependences of the total EL intensity as well (see Figs. 11d–11f). A similar angular dependence was also observed in a study into the behavior of the PL intensity and degree of linear polarization (Fig. 12).

Ordering of boron dipole centers is a result of electrostatic interaction forces. For this reason, it seems rational to consider the possibility of controlling such a system and its stability under various external exposures among which the external electric field is the simplest. Therefore, it seems very convenient for the contact configuration to be fabricated on the studied sample surface (Fig. 1), allowing EL measurements under an additional electric field parallel to the structure plane. To this end, contacts arranged around the perimeter of the boron diffusion region are used, while EL is excited via the central contact. The dependence of the total EL intensity $I_{EL}(U_{lat})$ and the degree of its linear polarization $P(U_{lat})$ on the lateral electric voltage $U_{lat}$ applied in the structure plane $U_{lat}$ is shown in Figs. 13a–13d. We can see that both the intensity and degree of linear polarization decrease with increasing voltage.

The degree of polarization can decrease for two reasons, one of which is the reorientation of impurity dipoles and their alignment along the external electric field, the other is simple disordering. To clarify which out of the two reasons is closest to the actual one, the dependence of the degree of polarization on the external electric field was measured at/for two relative orientations of the observation axis and the external field, i.e., parallel (Figs. 13a and 13b) and perpendicular (Fig. 13c and 13d) ones. We can see that the degree of polarization decreases almost identically in both cases. Hence, boron dipole reorientation does not occur, and the decrease in the degree of polarization is probably associated with their disordering and possibly with a partial decay, caused by the electric current flowing through the structure. Of interest is also the mismatch of the initial points for the positive and negative branches of the dependence $P(U_{lat})$, taking into account that the positive branch was measured first. This mismatch indicates the incomplete restoration of the boron dipole center system after relieving the external perturbation. Such a hysteresis is also present in the dependence $I_{EL}(U_{lat})$, which indicates a partial connection between the intensity decrease and boron dipole decay. However, there is another possibility, this behavior can be explained, e.g., within the context of two-electron adiabatic potentials constructed for the boron dipole center, which are considered below. It should also be noted that, as the temperature increases to room temperature, the EL polarization almost completely disappears, and its dependence on the lateral electric field becomes difficult to distinguish. In this case, the total EL intensity exhibits a smaller decrease and still remains sensitive to the lateral electric field, which reflects the preferential effect of dipole system ordering on the degree of polarization, while the intensity is probably controlled, for the most part, by the degree of shallow boron acceptor reconstruction.

### 3.3. Model of Infrared Emission in Silicon Nanostructures Heavily Doped with Boron

Since each and every component $B^+$ and $B^-$ of boron dipoles is a two-electron/hole center that is involved in recombination, it is impossible to present all emission features in a simple one-electron energy diagram. For this reason, the model should be constructed based on the (two-electron)/hole adiabatic potentials shown in Fig. 14. These potentials show the energy $E_n(Q)$ of the $B^+$ and $B^-$ centers as a function of the generalized coordinate $Q$ which reflects the change in the center’s position with respect to its equilibrium position. The direction of the axis along which $Q$ is measured is usually chosen according to the direction of an external exposure, e.g., the external electric field [45, 46]. In this case, it should be taken into account that $B^+$ and $B^-$ have a preferential shift direction along the $\langle 100 \rangle$ and $\langle 111 \rangle$ axes, respectively. In this case, the quantity $Q$ is the projection of corresponding shifts onto the external exposure axis.

Within the model shown in Fig. 14, emission in the studied silicon nanostructures heavily doped with boron can be presented as follows. In the first stage, an electron injected from the $n$-type region is trapped by the phosphorus ion, transforming it to a neutral state. The high boron concentration results from the fact...
that a large number of dipoles appear within the localization region of this electron, providing a pronounced overlap of the electron wave functions and one of holes at B⁺. Their annihilation, which therefore occurs with high probability, results in the production of an emission photon $h\nu$, indicated by a bold arrow in Fig. 14. In this case, the momentum relaxation necessary for an indirect transition occurs via the interaction of carriers with boron and phosphorus ions. We note that the luminescence line’s shape as a result of such a process will be mainly controlled by the density of states created by the B⁺ ion in the band gap (see Fig. 8). The state B⁰ formed via annihilation transforms to B⁻, which is accompanied by trapping of the second (correlated) electron. The high trapping cross section for such a process due to the negative correlation energy of the boron center results in permanent depletion of the B⁰ state [45, 46]. This circumstance also provides high radiation intensity and, furthermore, an absence of flattening in the dependence of the EL intensity on the forward current, despite the relatively low phosphorus concentration in the initial n-type silicon (100). At the same time as the above process, the reaction $B^- \rightarrow B^0 \rightarrow B^+$ occurs at the second dipole ion in the presence of two holes injected into the p-type region. In this case, the system returns to its initial state, and the above recombination process can start from the beginning.

The model presented shows that the luminescence intensity will be controlled in many respects by the number of free final states that are boron dipoles. In this case, their number mainly depends on temperature whose increase causes higher population of B⁰ states, since carriers overcome the energy barrier separating it from B⁺ and B⁻. Technically, this means reconstruction suppression and gradual dipole decay.

Fig. 13. A decrease in (a, c) the degree of linear polarization and (b, d) the total intensity of the EL line of the studied silicon nanostructures, detected under an additional lateral electric field (a, b) parallel and (c, d) perpendicular to the observation axis. The forward current is 20 mA, $T = 77$ K.
The height of such a barrier at a particular temperature depends also on the external electric field which causes relative shifts of the $B^+$ and $B^-$ potentials shown in Fig. 14 with respect to the $B^0$ potential.

The above-described model predicts the appearance of one more emission line in the near spectral region, which is related to the $B^0 \rightarrow B^-$ transition accompanied by electron trapping. This line should appear in the spectrum at rather low temperatures, when the thermal energy is insufficient to overcome the energy barrier separating these two states, and the transition occurs due to optical photon emission. Such an emission was indeed detected in the EL spectra at $T < 25$ K (Figs. 15a, 15b). In this case, an increase in temperature results in a decrease in the EL intensity, which is accompanied by a simultaneous increase in the intensity of the main line that is dominant at high temperatures. Since $B^0$ states are involved in the formation of this line, its shape is probably controlled by the distribution of energy levels associated with neutral boron atoms and the spread of local electric fields which result in a relative shift of the adiabatic potentials $B^0$ and $B^-$ [45, 46].

4. CONCLUSIONS

Emission from silicon nanostructures heavily doped with boron to a concentration of $5 \times 10^{21}$ cm$^{-3}$ was studied. Linearly polarized luminescence detected in this study, which exhibits high intensity even at room temperature, was studied as a function of temperature, forward current, and an additional lateral electric field. The spectral characteristics and features of electroluminescence and photoluminescence, being in agreement with previous data obtained using various experimental techniques, demonstrated that heavily doped boron diffusion profiles are based on trigonal dipole $B^0$--$B^-$ centers. Such centers result from the reconstruction of shallow boron acceptors as centers with negative correlation energy, which occurs along the $\langle 111 \rangle$ crystallographic axis, detected by measuring the angular dependences of the ESR spectra and was confirmed in similar dependences of the degree of the linear polarization of luminescence. The results of the study allowed the formulation of an emission model considering all of the observed experimental facts. The model is constructed in the context of (two-electron)/hole adiabatic potentials and is based on donor--acceptor recombination occurring via states associated with an ordered system of trigonal dipole boron centers, involving phosphorus ions.

In our opinion, the results obtained are quite interesting. The case in point is not only the possibility of developing efficient radiation sources based on silicon planar technology, characterized by a relatively high intensity and a high degree of polarization which can be controlled by an additional lateral electric field. It also seems important that there is the possibility of studying a highly correlated system of dipole centers and mechanisms for high-temperature superconductivity onset in it using such flexible and powerful experimental techniques as electroluminescence and photoluminescence.
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