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Ion-beam Modification of the Local Luminescent Properties of Hexagonal Boron Nitride

© Yu.V. Petrov,[1] O.A. Gogina,[1] O.F. Vyvenko,[1] S. Kovalchuk,[2] K. Bolotin,[2] K. Watanabe,[3] T. Taniguchi[3]

[1] St. Petersburg State University,
199034 St. Petersburg, Russia
[2] Free University of Berlin,
114195 Berlin, Germany
[3] National Institute for Materials Science,
305-0047 Tsukuba, Ibaraki, Japan
e-mail: y.petrov@spbu.ru

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Hexagonal boron nitride is a promising material of modern optoelectronics. Point defects in this material can serve as single-photon sources. In this paper we investigate the modification of the luminescent properties of hexagonal boron nitride by means of local irradiation with focused gallium and helium ion beams. It is demonstrated that the intensity of band-to-band cathodoluminescence monotonically decreases with increasing ion fluence for both gallium and helium. The luminescence band of about 2 eV may become more intense after exposure to He ions with certain ion fluence. The effect of complete quenching of luminescence after gallium irradiation is used to estimate the diffusion length of excess charge carriers.

Keywords: point defects, cathodoluminescence, scanning helium ion microscope, excess charge carriers.

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Introduction

The development of single-photon light sources is one of the priorities in the development of modern technologies of quantum computer science and cryptography. Point defects in wide-bandgap semiconductors [1], in particular in diamond [2] or silicon carbide [3,4] can be used as such single-photon sources operating in the visible range. One of the most promising materials for the development of single-photon sources is hexagonal boron nitride (hBN) [5], which has a band gap of 6.08 eV [6] and a wide range of defects that make it possible to obtain photons with different energies. To date, several technologies have been developed for the formation of point defects in boron nitride, which are the centers of radiative recombination. Among others, ion beam irradiation is used, which leads to the formation of radiation-induced point defects [7], as well as carbon deposition stimulated by electron or ion beams [8]. The next step towards the creation of single-photon emitters is the manufacture of a device with a single point defect localized in it [9]. To obtain such devices and localize defects, electron lithography and photolithography methods with subsequent plasma etching can be used, as well as sputtering with a focused ion beam. Thus, the treatment of boron nitride with a focused ion beam can be used both to create luminescent point defects and to localize such centers of luminescence in the production of a separate device.

Among the systems with a focused ion beam, the most widespread are systems based on gallium liquid metal ion source, which allow locally modifying the properties of sample regions of the order of a dozen nanometers in size. However, there are no data on the effect of such irradiation on the luminescence of boron nitride in the literature, and therefore research in this direction is of some interest.

Even more interesting is the use of treatment with light ions of inert gases and, above all, helium, which can be carried out using a scanning ion helium microscope. In addition to a higher spatial resolution compared to a gallium ion microscope, helium atoms in the material do not have electrical activity and create a large number of intrinsic defects, one of the types of which, as mentioned above, may have the properties of single photon sources.

In this paper, the effect of irradiation with focused beams of gallium and helium ions on the luminescent properties of hexagonal boron nitride was studied for the first time. It has been established that exposure to gallium ions with an increase in the radiation fluence leads to a decrease of the intensity and complete disappearance of all registered luminescence bands, which can be used to estimate the diffusion length of nonequilibrium charge carriers. At the same time, at certain fluences of irradiation with helium ions, it is possible to achieve an increase in the intensity of 2 eV luminescence band, which is attributed to the luminescence center, considered as one of the variants of single photon sources in hBN.

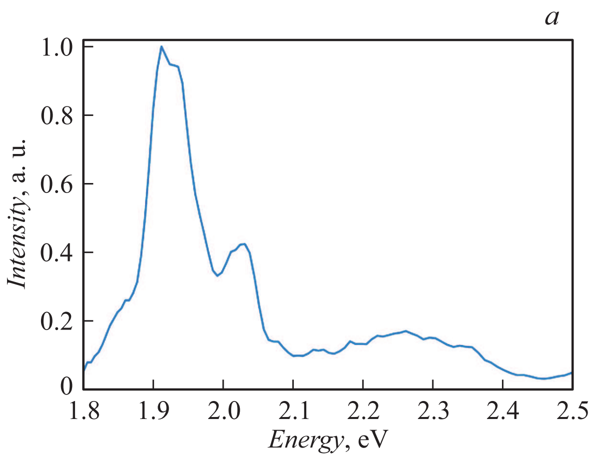

Figure 1. Normalized CL spectra of the pristine hBN sample: *a* — 1.9 eV band; *b* — 5.7 eV band.

1. Experiment procedures

In this paper, samples representing thin hBN single crystals transferred to a Si_3N_4/Si substrate after exfoliation from a bulk crystal were studied. The thickness of the samples was determined using atomic force microscopy (AFM) and ranged from 14 to 170 nm.

The cathodoluminescence (CL) study was carried out using a Zeiss SUPRA 40VP scanning electron microscope equipped with a Gatan CL Mono CL3+ registration system. CL spectra were recorded in the wavelength range 200–700 nm when excited by electrons with an energy of 5 keV in the mode of continuous scanning by an electron beam. In order to avoid modification of the sample by the electron beam, each scan was carried out on a new section of the sample. The time of registration of one point of the spectrum varied in the range from 0.5 to 2 s, with a spectral resolution of the order of 1–2 nm.

Irradiation with a focused beam of gallium ions was carried out using a two-beam Zeiss Auriga system with an ion energy of 30 keV and fluences ranging from $5.6 \cdot 10^{12}$ to $1.1 \cdot 10^{15}\,\mathrm{cm}^{-2}$. Local irradiation with a focused beam of helium ions was carried out using a Zeiss Orion Plus helium ion microscope with an ion energy of 30 keV and fluences ranging from $5 \cdot 10^{13}$ to $1 \cdot 10^{16}\,\mathrm{cm}^{-2}$.

2. Experimental results

Fig. 1 shows the CL spectra characteristic of the initial hBN crystals, regardless of their thickness. Only two luminescence bands, with maxima energies of about 1.9 and 5.7 eV, were observed in the spectra. With an increase in the thickness of the hBN layer, an increase in the intensity of both CL bands was observed.

The dependence of the integral intensity of the observed CL bands on the fluence of irradiation with Ga ions for the sample with a thickness of 170 nm is shown in Fig. 2.

As can be seen from the figure, for both spectral bands of CL, the proportion of their residual intensity decreased with an increase in the radiation fluence. At the minimum fluence used, it was only 5 and 10% of the initial intensity for 1.9 and 5.7 eV bands, respectively.

A decrease in the brightness of the irradiated areas was also observed on the CL map. An example of such a map is shown in Fig. 3, *a*.

In the case of irradiation with helium ions (Fig. 4), a decrease in the intensity of the 5.7 eV CL band was observed, while the intensity of the 1.9 eV band varied non-monotonically and at a fluence of $2 \cdot 10^{14}\,\mathrm{cm}^{-2}$ exceeded the intensity of the same bands in the unirradiated sample by approximately 30%.

It should also be noted that the decrease in the intensity of CL with an increase in the fluence of irradiation with helium ions occurred significantly slower than in the case of irradiation with gallium ions.

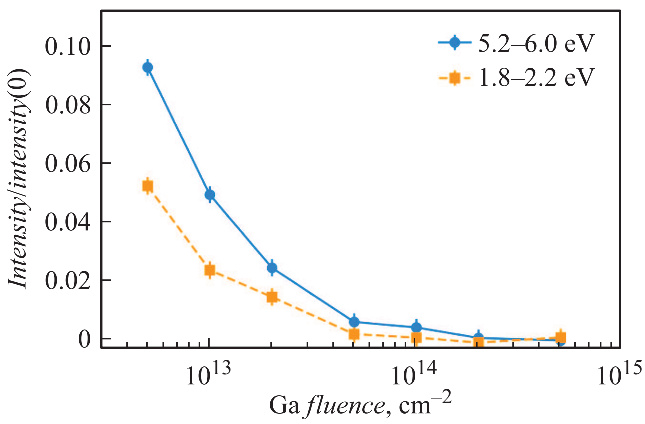

Figure 2. The dependence of the integral intensity of CL in different spectral ranges on the fluence of irradiation with gallium ions. The intensity values are normalized to the intensity of the corresponding CL bands in the unirradiated sample.

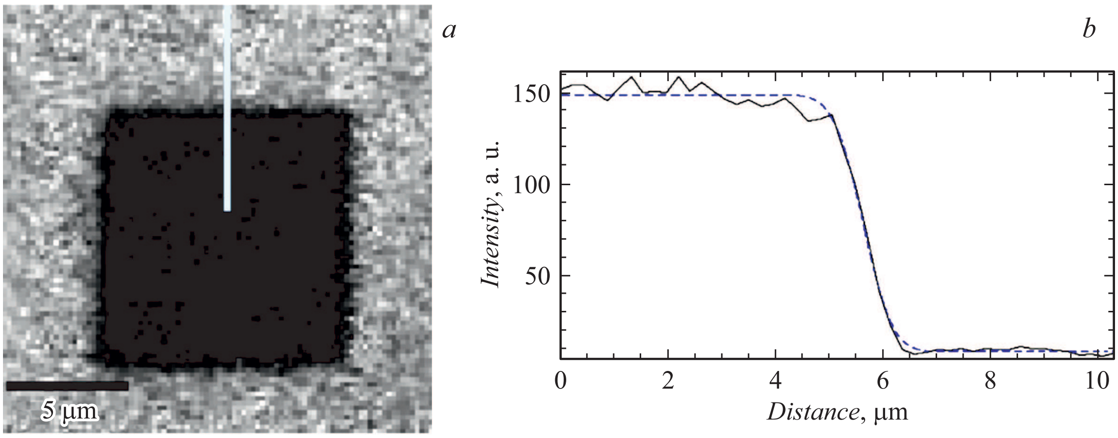

Figure 3. *a* — CL map, dark square corresponds to the area irradiated with gallium ions (radiation fluence $5 \cdot 10^{12}\,\text{cm}^{-2}$); it b — CL intensity profile, constructed along a vertical line perpendicular to the edge of the irradiated area (solid line) and the approximation of the profile with the error function (dashed line).

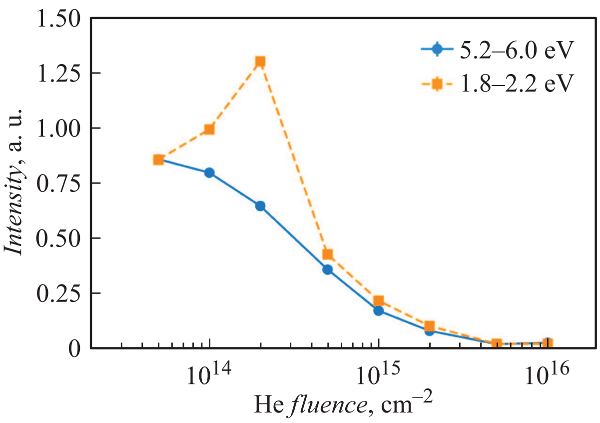

Figure 4. The dependence of the integral intensity of CL in different spectral ranges on the fluence of irradiation with helium ions. The intensity values are normalized to the intensity of the corresponding CL bands in the unirradiated sample.

3. Discussion

The CL band with a maximum of about 5.7 eV was previously observed in the hBN spectrum and can be attributed to the band-to-band transition [10]. A band with a maximum of about 1.9–2.1 eV is usually attributed to point defects, and a boron vacancy type defect V_B [11,12] is proposed as the center of luminescence. In addition, complex complexes of defects are mentioned in the literature as luminescence centers with approximately the same energy [12,13].

The decrease in CL intensity after irradiation with gallium ions (Fig. 2) is obviously due to the introduction of gallium atoms and the generation of radiation defects, at least some of which are centers of nonradiative recombination of nonequilibrium electrons and holes generated by an electron beam. According to numerical Monte Carlo simulation using the SRIM [14] package, the projected range of gallium ions is about 27 nm, and the maximum concentration of ion-induced vacancies in h-BN when irradiated with gallium ions with an energy of 30 keV is observed at a depth of about 17 nm. For a fluence of $2 \cdot 10^{13}\,\text{cm}^{-2}$, the average local concentration of gallium atoms in this region is about $10^{18}\ \text{cm}^{-3}$, and the concentrations of generated boron and nitrogen vacancies that they practically coincide, correspond to 0.06 defects per atom of the material without taking into account their recombination. Thus, in a sample with a thickness of 170 nm, as a result of irradiation with gallium ions, a near-surface damaged layer is formed, the thickness of which does not exceed 20% of the thickness of the sample, while a disproportionately greater drop in the intensity of CL by 10–20 times occurs at the minimum dose of irradiation, and its complete extinction occurs at high fluences.

To estimate the excitation function of electron-hole pairs by the depth of the sample, the process of electron scattering in boron nitride was simulated by the Monte Carlo method using the CASINO [15] software package and the dependence of the electron energy losses per unit path length was calculated. The result of this calculation for an hBN sample with a thickness of 170 nm on a substrate Si_3N_4 with a thickness of 150 nm when irradiated with an electron beam with an energy of 5 keV is shown in Fig. 5.

As can be seen from the data obtained, the generation function grows in the boron nitride layer as the depth increases and reaches its maximum value only in the silicon nitride substrate. It also follows from the obtained dependence that 90% of the total number of nonequilibrium electron-hole pairs is excited deeper than the damaged near-surface layer, i.e. in the part of boron nitride that is not affected by ion irradiation.

The increase of absorption, scattering, and internal reflection in the gallium-irradiated sample layer is the simplest explanation for the decrease in luminescence intensity in the entire spectral range studied. However, no noticeable changes in the optical transparency of the sample sections irradiated with gallium ions with a fluence of up to

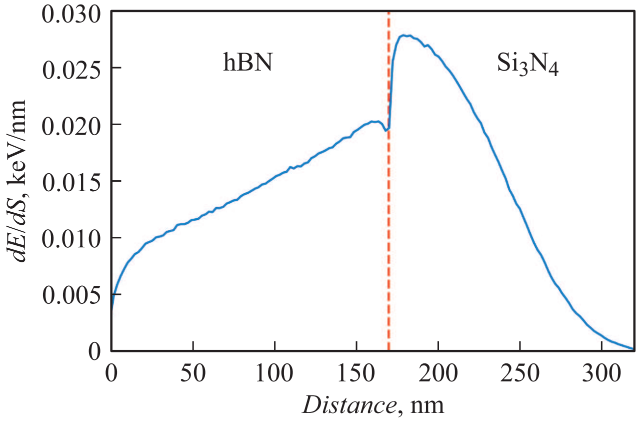

Figure 5. The dependence of the electron energy losses in the hBN sample on the Si_3N_4 substrate for electrons with energy $E = 5\,\text{keV}$ on depth, calculated by the Monte Carlo method. The dashed line corresponds to the boundary between hBN and Si_3N_4.

$5 \cdot 10^{14}\,\text{cm}^{-2}$ were detected when observed with an optical microscope, while the intensity of CL decreased by more than an order of magnitude.

For the 5.7 eV CL band, the position of which is close to the bandgap of hBN, a significant decrease in intensity is possible if the absorption coefficient is close to the inverse thickness of the damaged layer, i.e. greater than $3 \cdot 10^5\,\text{cm}^{-1}$. However, according to the data on the optical absorption spectra of [16,17], despite the spread of values published by different authors, for the energy of the main peak of CL at 5.7 eV (Fig. 1), the value of the absorption coefficient is much smaller and the observed decrease in intensity as a result of implantation with gallium ions is difficult to explain by the fact that only radiation from the near-surface layer was registered, and radiation generated at a greater depth could not be registered due to self-absorption in the sample.

The radiation of the 1.9 eV band is practically not absorbed in the material, and an increase in intensity with an increase in the thickness of the samples suggests that the luminescence centers responsible for this band are distributed throughout the volume. The decrease in the intensity of the 1.9 and 5.7 eV bands after irradiation can be explained under the assumption of a decrease in the concentration of nonequilibrium carriers in the sample volume due to their rapid diffusion into a modified near-surface region characterized by a high rate of recombination.

The properties of a system with a thin near-surface layer of enhanced recombination under conditions of equality of the number of generated carriers of both signs are similar to the well-known case of surface recombination, for which there is a simple analytical description. The average concentration of electron-hole pairs at homogeneous generation of G, a plate d thick is given by the expression [18]:

$$\Delta n = G\tau\left(1 - \frac{S(L/d)\,\mathrm{sh}(d/L)}{S\,\mathrm{ch}(d/L) + \mathrm{sh}(d/L)}\right), \qquad (1)$$

where $S = sL/D, s$ — surface recombination rate, L — diffusion length, D — diffusion coefficient, τ — lifetime of charge carriers. It can be seen from this expression that the concentration of nonequilibrium carriers decreases with an increase in the rate of surface recombination as a result of diffusion of electron-hole pairs generated over the entire thickness of the boron nitride layer into the gallium-implanted near-surface region, which explains the observed decrease in the intensity of the studied CL bands. However, the formula (1) shows that for small values of $L < d$, the carrier concentration cannot reach zero even for infinitely large S and, therefore, cannot explain the extinction of CL observed in the experiment. The last condition can be satisfied only for a thin plate when $d \ll L$, and this expression reduces to:

$$\Delta n = G\tau\left(\frac{d/L}{S + d/L}\right). \qquad (2)$$

Based on this, it can be concluded that the diffusion length of nonequilibrium charge carriers in the direction perpendicular to the boron nitride layers significantly exceeds the sample thickness of 170 nm.

At the same time, within the framework of the carrier recombination model in the near-surface layer, it is not possible to explain why the intensity drop associated with luminescence defects is noticeably greater than the interband one. The exact reason for this difference is not yet known. It can only be assumed that there is an additional mechanism that is associated with the presence of interaction of radiation defects with defects responsible for the impurity band of CL, leading to passivation of the latter. As a result of irradiation with heavy gallium ions, a large number of vacancies and interstices are formed. Interstitial atoms of both nitrogen and boron are extremely mobile even at room temperature, as follows from the results of theoretical calculations for hBN [12]. They can penetrate to a considerable depth from the implantation area and recombine with vacancies, which, as mentioned above, are considered as luminescence centers 1.9 eV. As a result, the number of vacancies in the non-irradiated part of the sample will decrease. At the same time, in the near-surface layer, when implanting such heavy ions as gallium, a disordered region containing a high concentration of point defects is formed around the trajectory of the primary particle. Vacancies created in this area, which, unlike interstitial atoms, are much less mobile at room temperature [12], can be part of complexes that include several simplest defects, including implanted gallium atoms. Such complexes, apparently, are responsible for the high rate of nonradiative recombination.

In the plane of the layers, the diffusion length can be estimated from the CL signal profiles constructed perpendicular to the boundaries of the irradiated region. One of these profiles and its approximation with the error function are shown in Fig. 3, *b*. Averaging over several profiles perpendicular to the boundary of the irradiated region gives an estimate of the profile width at 680 ± 90 nm. This spread can be caused by three factors: the scattering of ions outside of the irradiated region, the spread of the CL generation function caused by electron scattering, and the diffusion of nonequilibrium charge carriers. The scattering of ions outside of the irradiated region, according to the results of numerical modeling, is about 20 nm. The CL generation function in the plane, according to the results of numerical modeling, can be described by a two-dimensional Gaussian function with a full width at half maximum equal to 18 nm. Thus, the obtained estimate of the profile blurring is mainly determined by the diffusion length of nonequilibrium charge carriers in the plane of the layers of hexagonal boron nitride, which suggests that the diffusion length of charge carriers in the plane is on the order of several hundred nanometers.

In the case of irradiation with helium ions, the observed decrease in the intensity of band-to-band radiation, as well as in the case of irradiation with gallium ions, is caused by the appearance of additional recombination channels due to the presence of radiation-induced defects. In contrast to the case of irradiation with gallium ions, the projected range for helium ions with an energy of 30 keV is about 240 nm, therefore, for the studied samples, the penetration depth exceeds the thickness of the hBN layer. A quantitative estimation of the concentration of ion-induced defects for the radiation fluences used in this work under helium irradiation gives concentration values in the same range as under gallium irradiation. Nevertheless, in the case of helium irradiation, a much slower decrease in the intensity of CL is observed with an increase in the fluence. This effect may be due to the fact that, unlike gallium ions, when irradiated with light helium ions, there are no collision cascades and separate non-interacting point defects are created along the trajectory of the primary ion. As a result, the generation of complex complexes of defects under the influence of helium ions begins to occur at significantly higher fluences than for gallium ions.

An increase in the intensity of the 1.9 eV band at low fluences of irradiation with helium ions suggests that the corresponding luminescence centers are formed, which, according to the assumption expressed in [12], may be boron vacancies. The nonmonotonic nature of this dependence indicates the existence of competing processes that intensify with an increase in the radiation fluence. Such processes can be the recombination of vacancies with interstitials at relatively small fluences of radiation and the formation of complex defective complexes described above at the highest fluences.

Conclusions

The study of the effect of irradiation with gallium and helium ions on the luminescent properties of hexagonal boron nitride shows that as a result of such irradiation, there is a decrease in the intensity of band-to-band radiation, while the nature of the change in the intensity of red luminescence associated with defects depends on both the ion type and the radiation fluence. Irradiation with gallium ions leads to the formation of nonradiative recombination centers, which can be associated with both the formation of complexes of defects that occur when irradiated with heavier ions, and the presence of implanted gallium in the material under study. The relatively small size of the gallium ion scattering region made it possible to estimate the diffusion length of nonequilibrium charge carriers in hexagonal boron nitride, which is several hundred nanometers in order of magnitude. The nonmonotonic dependence of the intensity of red luminescence on the fluence of irradiation with helium ions suggests the possibility of creating optimal conditions for the formation of appropriate luminescence centers, which makes local irradiation with helium ions a promising method for the localized production of single radiation sources in the visible range.

Acknowledgments

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Conflict of interest

The authors declare that they have no conflict of interest.

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