Electron irradiation as a method for controlling luminescence of hexagonal boron nitride

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Abstract. Hexagonal boron nitride (hBN) is characterized by two main point defect-related luminescence bands with the peaks in visible, at 650 nm (1.9 eV), and UV, 320 nm (4 eV) spectral regions, which possess the properties of single photon emitters (SPE). We demonstrate that sufficiently long irradiation of thin hBN flakes in a scanning electron microscope with electron beam with energies from 5 keV to 20 keV and the flux equal or more than 10^{15} cm^{-2}s^{-1} resulted in a drastic increase in the integral intensity of the 4 eV band previously associated with carbon-related defects. The effect of the irradiation induced luminescence enhancement increases with the decrease of the electron beam energy that corresponds well with the calculated energy losses in thin samples. An increase in the concentration of carbon-related defects introduced into the sample from surface carbon contaminated layer via recombination-enhanced migration or changes of the charge state of existing defects could be supposed to be mechanisms of the observed effect. The obtained results demonstrate the possibility of local control of UV SPE concentration in hBN.

Keywords: point defects, cathodoluminescence, scanning electron microscopy

Электронное облучение как метод управления люминесценцией в гексагональном нитриде бора

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Аннотация. Точечные дефекты в монокристаллическом гексагональном нитриде бора (h-BN), являющиеся центрами люминесценции, рассматриваются как потенциальные источники одиночных фотонов. В работе продемонстрировано, что облучение электронным пучком в сканирующем электронном микроскопе может приводить к увеличению интенсивности люминесценции в ультрафиолетовой части спектра, что

может служить перспективным методом для контролируемого локального управления люминесценцией дефектов в гексагональном нитриде бора при правильном выборе энергии и плотности потока электронов.

Ключевые слова: точечные дефекты, катодолюминесценция, сканирующая электронная микроскопия

Introduction

Modern quantum computer technologies, including quantum cryptography, require new materials for the fabrication of single photon emitters (SPE) [1−3]. It was recently reported that some point defects in hexagonal boron nitride (hBN) can serve as SPE working at room temperature with characteristic luminescence bands within a wide wavelength range from 200 nm to 700 nm [4, 5]. The most pronounced SPE luminescence bands are characterized with the main peak positions at approximately 650 nm (1.9 eV) and 320 nm (4 eV) [6] (denoted further as 1.9 eV band and 4 eV band).

Previous investigations showed that the defects responsible for the 4 eV luminescence band could be formed already during the growth of large single crystals. Though the exact nature of these defects remained unknown [1, 7], it was tentatively ascribed to a carbon-related defect such as carbon at the nitrogen atom site or a composite complex of oxygen and carbon impurities [8]. The luminescence center responsible to the 1.9 eV band was attributed to boron dangling bonds [9], vacancy-related defects or an anti-site defect where the nitrogen occupies the boron site with missing atom at the nitrogen site (N_BV_N) [10].

To create quantum communication devices utilizing the usage of SPE, it is necessary to develop experimental methods for the local tuning of the concentration of the desirable luminescence centers. In our previous paper, we demonstrated that subsequent irradiation of hBN with focused He^+ and electron beams can be used to control the intensity of the 1.9 eV luminescence band [6]. In this paper, we investigated in more details the changes in the intensity of the 4 eV luminescence band produced by the electron irradiation with various fluxes and electron beam energies.

Materials and Methods

The starting material in our experiments was hBN crystal with a declared purity of 99.99% produced by the Ossila company. The samples for the investigations were prepared by peeling from hBN single crystal the flakes of a thickness of about 200 nm then transferred onto silicon substrate.

Electron irradiations and cathodoluminescence (CL) measurements were performed using a Zeiss SUPRA 40VP scanning electron microscope (SEM) equipped with the Gatan Mono CL3+ registration system.

The experiments were carried out at room temperature with the electron irradiation in continuous scanning mode. During the irradiation, repetitive wavelength increasing-decreasing CL spectra scans were performed, and the data arrays containing the luminescence intensity, wavelength and detection time were collected with the help of specially developed software package. The electron beam energy and the irradiation flux density were varied between 5 and 20 keV and between 10^{14} and 10^{16} $cm^{-2}s^{-1}$, respectively.

Results and Discussion

Fig. 1, *a* represents the color map of the CL intensity in the spectral region of 3.1−4.9 eV (4 eV band) as a function of the duration of the electron beam exposure. The map was composed from the data of 90 CL spectra recorded subsequently during electron beam exposure for 10,000 seconds. It is clear from the map in Fig. 1, *a* that the 4 eV band contains several peaks and the overall intensity of CL increases with the electron irradiation time.

The acquired spectral band could be decomposed into six separate Gaussian-like components: three relatively broad (3.4, 4.1, 4.8 eV) and three more narrow (3.7, 3.9, 4.05 eV) bands. An example of the experimental CL spectrum, the components of its deconvolution and their sum are drawn over the CL map in Fig. 1, *a*. According to data presented in literature [8], three narrow bands can be attributed to one luminescence center with zero phonon line at 4.05 eV and two phonon replicas.

Fig. 1, *b* depicts CL intensity map of the investigated hBN flake at a wavelength of 320 nm acquired after 10,000 seconds of electron irradiation. Bright rectangular area of the enhanced luminescence corresponds to the region where the scans with the electron beam was performed indicating a substantial increase of the intensity at such wavelength with respect to the initial state.
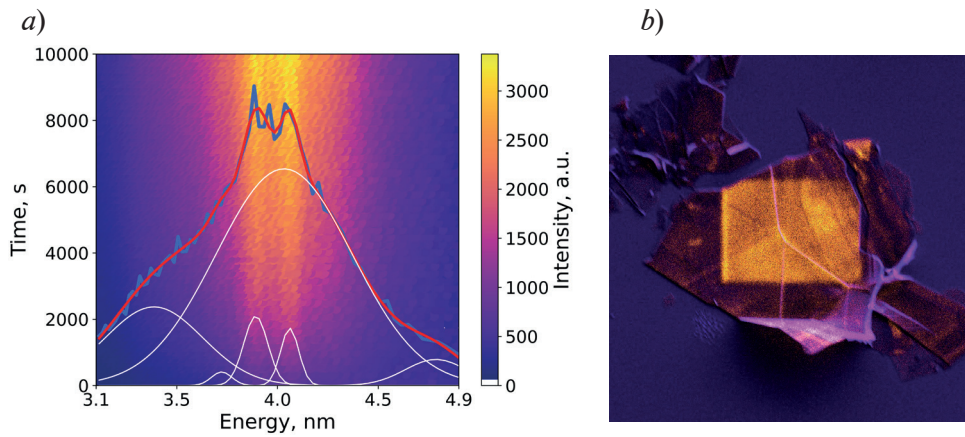

Fig. 1. Color map of temporal luminescence intensity changes of the 4 eV band with overlaid example of the experimental CL spectrum (blue line) and its decomposition into Gaussian-like components (*a*). White and red lines represent the components and their sum, respectively. CL map at a wavelength of 320 nm after the irradiation with electron irradiation dose of 10^{19} cm^{-2} (*b*). The map is semi-transparently overlaid with secondary electrons SEM image of the hBN flake to make its borders visible

It was found that the temporal evolution of luminescence intensity differs for the different spectral components. The variation of the magnitude of each of six bands obtained from spectrum decomposition with the electron irradiation duration is presented in Fig. 2, where the band peak energy is shown in the legend. The most pronounced luminescence enhancement by a factor of about 4−4.5 was observed for bands at 3.4, 4.05 and 4.1 eV, while the effect was noticeably less for their neighbors at 3.7 and 3.9 eV and small or negligible for band at 4.8 eV.

The impact of the electron irradiation on the 4 eV band luminescence intensity was found to be very sensitive to the electron beam energy. For the energy of 5 keV the intensity increases by 9 times, whereas for 20 keV it increases by approximately 3 times after the same irradiation time, that can be well recognized from Fig. 3, *a* obtained with an order of magnitude larger electron flux than one presented in Fig. 1 and Fig. 2.

Using the CASINO program [11], we performed calculations of the depth dependence of the total energy losses (*dE/dx*) in hBN for the electron energies of 5, 10 and 20 keV, which is presented in Fig. 3, *b*. From the energy loss profile data (Fig. 3, *b*) and the thickness of the samples (of about 200 nm), we calculated the total deposited energy (Δ*E*) and total number of electron-hole (*e*−*h*) pairs generated within the flake:

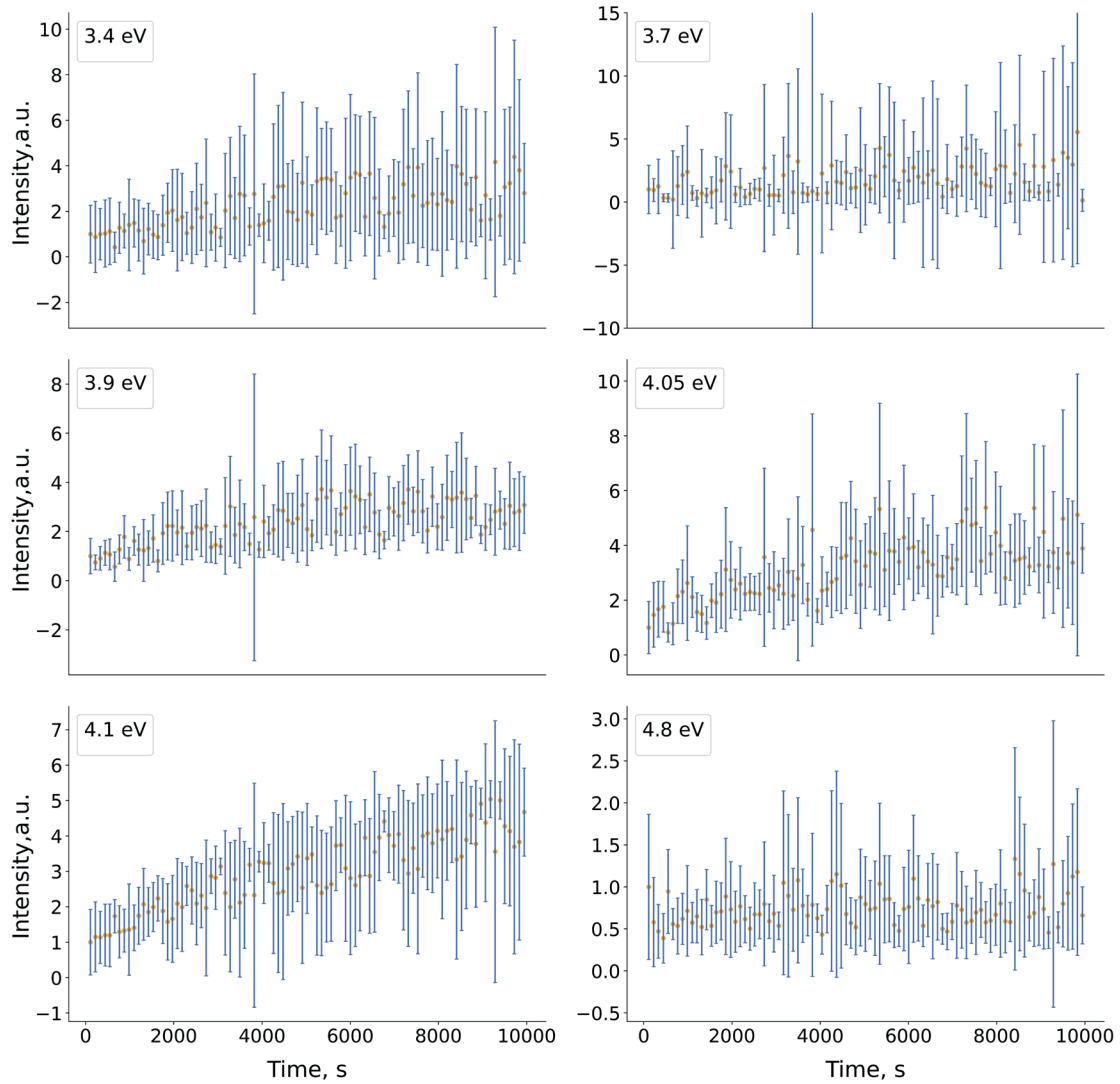$$N_{\text{pairs}} = \Delta E / \left(3 \cdot E_g \right), \tag{1}$$

Fig. 2. Temporal variation of the normalized to the initial intensity magnitude of the six spectral components of the 4eV hBN luminescent band under the irradiation with an electron beam with an energy of 5 keV and the electron flux density of about 10^{15} cm^{-2} s^{-1}.

where E_g is the band gap of the hBN of 6.08 eV [12]. The calculation results of ΔE and N_{pairs} are presented in Table.

We can conclude from the calculated and presented dE/dx, ΔE and N_{pairs} data that the electrons of all used energies penetrate through the entire volume of hBN into the substrate transmitting to the sample the less energy the higher is their energy. Thus, the observed enhancement of the luminescence might be caused by the electron beam induced generation of emitting defects or by the change in the charge state of existing defects accompanied by the recombination of generated electron-hole pairs.

Table

Results of numerical simulation in CASINO software

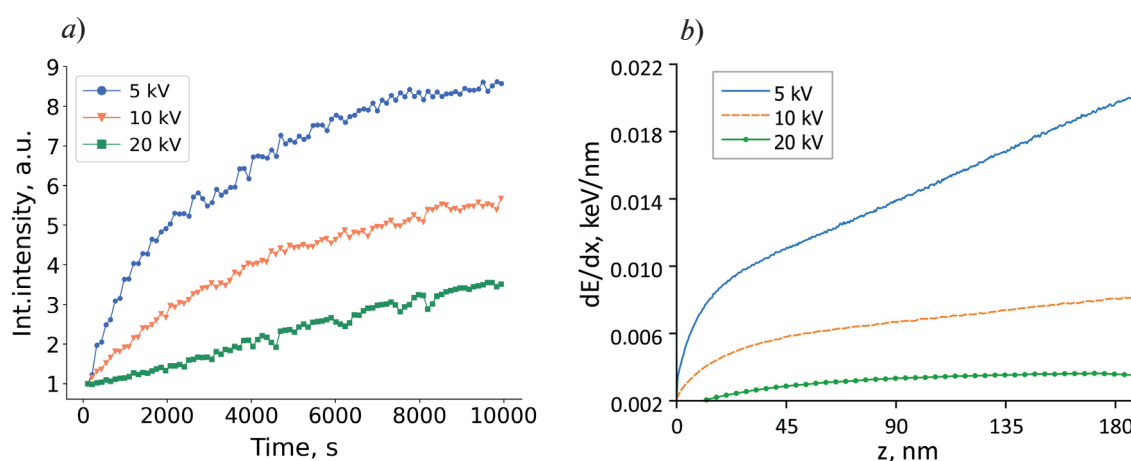| E, keV	ΔE, keV	N_{pairs}
5	2.9	158
10	1.3	71
20	0.626	34

Fig. 3. Dependences of the integral intensity of the 4 eV band on the time of electron irradiation with different electron beam energies, and electron irradiation flux of 10^{16} cm^{-2}s^{-1} (*a*). Each line is normalized by the intensity at the initial time point. Dependence of electron energy losses on depth obtained from numerical simulation using CASINO program (*b*)

Conclusion

It was established that the intensity of luminescence band in the 3.1−4.9 eV energy range in hBN increases drastically under the sufficiently long electron irradiation making it possible to use conventional SEM technique to control the density and spatial design of SPE in UV spectral region.

As pointed out in the introduction, 4 eV luminescent band is attributed to a defect somehow related to the carbon impurity. The luminescent peaks at 3.4, 3.7, 3.9, 4.05, 4.1 eV are sensitive to electron beam irradiation. That could indicate that these lines are sensitive to new carbon impurities introduced by electron irradiation.

Theoretical calculations show that the carbon dimers C_BC_N are responsible for the luminescent source with energy of 4.1 eV [13]. Similarly, earlier experimental studies have demonstrated that this line is associated with another carbon defect, a substitutional impurity at a nitrogen site C_N [1, 5, 7, 13]. In another paper this lines are associated with impurity complex C_NO_N [8].

In turn, the carbon impurity contamination under the electron beam action may be due to the deposition of hydrocarbons from the residual gases in the chamber with their subsequent decomposition on the sample surface. The formation of a carbon-rich layer on the surface can serve as a source of carbon-containing defects in the bulk. Obviously, carbon diffusion in the bulk material is negligible at room temperature, but it could be drastically accelerated in the presence of non-equilibrium free charge carriers, due to the phenomenon that is known as 'recombination-enhanced defect migration'.

Acknowledgments

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