The influence of iron doping on recombination characteristics of grain boundaries in polycrystalline CVD-ZnSe

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Abstract. Recombination activity of grain boundaries in Fe²⁺:ZnSe was studied. The specific lines in the spectra (425-725 nm) were identified. The distributions of exciton and defective-impurity centers were observed in the bulk and grain boundaries of the sample. A hypothesis explaining the observed characteristics of luminescence from grain boundaries is proposed.

1. Introduction
ZnSe crystals doped with iron are used as a gain medium for mid-IR solid-state lasers. Recent years have brought significant improvements in the performance characteristics of Fe²⁺:ZnSe lasers with optical pumping by Er:YAG and HF lasers [1–3]. Nevertheless, development of a small-scale highly efficient system is still a challenge. Active ions in doped semiconductor matrices can be excited by hot electrons accelerated by an electric field (electron-impact excitation and ionization) [4]. This requires detailed research into the defective-impurity structure of Fe²⁺:ZnSe crystals. Since the initial material is polycrystalline CVD-ZnSe, investigation of luminescence characteristics of grain boundaries is of importance. As shown in [5, 6], two-photon confocal microscopy allows observing the bulk and, in particular, grain boundaries in the crystal [7]. It was also demonstrated that recombination activity is dependent on the distance from the doping surface.

2. Experiment
A sample of CVD-ZnSe (a 10×3.2×2 mm parallelepiped) doped with Fe was studied in the present paper. A 1-μm iron layer was deposited on the surface. The doping process was conducted in Ar atmosphere at T = 1000 °C during 240 h. The distribution of Fe²⁺ concentration was obtained using a HIPERON 200 IR-microscope and a Tensor-27 IR-Fourier spectrometer (Bruker) from the cross-section orthogonal to the doping surface. A detailed description of this technique is reported in [8]. The luminescence experiment was carried out by two-photon confocal microscopy (Carl Zeise LSM NLO 710). Since the energy gap in ZnSe is 2.7 eV, optical pumping of an 800-nm laser leads to two-photon absorption. The setup and experimental method were described in [5, 6].
Figure 1. Planar maps of luminescence in ZnSe:Fe taken at a depth of 60 μm from the doping surface at 473 (a), 531 (b), 609 (c), and 715 (d) nm wavelengths at room temperature and (e) distribution of iron concentration.

Figure 2. Distributions of ZnSe:Fe luminescence intensity on the figure 1 planar maps and (e) distribution of iron concentration.

In the present paper we show the results obtained from the cross-section perpendicular to the doping surface. Therefore, we directly observed the influence of iron concentration on the crystal luminescence in the range from 425 to 725 nm.

3. Results
Planar luminescence maps taken at a depth of 60 μm from the doping surface at 473 (a), 531 (b), 609 (c), and 715 (d) nm wavelengths are presented in figure 1 (a-d). The distribution of iron concentration is given in figure 1 (e). Distributions of luminescence intensity on the above described planar maps are shown in figure 2. It is possible to identify three specific areas. Area 1 (0-220 μm from the doping surface) is characterized by a high concentration of Fe$^{2+}$. Area 3 (from 640 μm to the opposite edge of the sample) is distinguished by a low concentration of iron (below the detection limit), whereas Area 2 is located between Areas 1 and 3. The spectra from Areas 1, 2, and 3 are shown in figure 3. The fine structure of the grain boundary (GB) observed at wavelengths of 473 and 560 nm is presented on the high-spatial-resolution planar map. The following specific lines are found in the corresponding spectra (figure 4):

the blue line with a maximum in the range of 463-473 nm is associated with luminescence from a bound exciton of the zinc vacancy acceptor [9];
the green, yellow and red lines (broad ones with maxima at 560, 600 and 715 nm, respectively) are associated with luminescence from defective-impurity centers.
Figure 3. The spectra of ZnSe:Fe from Areas 1, 2, and 3 (figure 2) at room temperature.

The spatial distribution of luminescence lines demonstrates complex behavior. Blue, green, and yellow lines are suppressed in Area 1. Decreasing iron concentration (Area 2) leads to an increase in the luminescence intensity of these lines. Next, the blue and yellow luminescence lines are constant except the GB region in Area 3. The peak of the yellow line is found in Area 2 and appears as a light 150-μm strip (figure 1(c)) parallel to the doping surface. The iron concentration corresponding to the yellow line peak is 0.2×10¹⁹ at/cm³. The red line demonstrates a similar spatial distribution. The luminescence intensity has a maximum in Area 1 and also appears as a light 200-μm strip (figure 1(d)) parallel to the doping surface. The iron concentration corresponding to the red line maximum is 0.3×10¹⁹ at/cm³. The yellow and red lines partly overlap spatially.

To explain the obtained results we assume that simultaneous doping of iron and at least two types of defects (green and red) led to the green and red luminescence lines, respectively. The yellow defects belong to the third type of defects, which were equally spread across the bulk of the sample. The observed luminescence distribution may be due to a situation when the red defects diffuse faster than iron, and the yellow defects diffuse faster than the red ones. In addition, we suggest that non-equilibrium carriers recombined through the iron ions, either nonradiatively or with emission in the long-wave nondetective range.

Considering the applicability of the hypothesis to the observed changes of the GB recombination activity, we note that the structure of the GB was non-homogeneous. Figure 4 shows a well-recognized narrow domain with a width of about 1 μm in the middle of the GB and the atmosphere around it (the widths of about 10 μm from each side) with a high intensity of luminescence. This corresponds to the well-known ideas that a GB absorbs an impurity from the surrounding space, thus cleaning it. Next, the absorbed impurity precipitates, which terminates the luminescence. By contrast, the cleaned region demonstrates an enhanced luminescence intensity as compared to that of the grain bulk.

In Area 1, the GB absorbs more iron ions. This manifests in suppressed luminescence from the GB region in the entire detection range. A subsequent decrease of the iron concentration in the GB vicinity results in precipitation of defects in the narrow middle part of the GB. As a result, the GB attains a complex structure: a non-luminescent narrow middle part; blue, green and red luminescent atmosphere; and surrounding area (the grain bulk) with low-intensity luminescence. A further decrease
in iron content causes the complete disappearance of the non-luminescent part of the GB. In Area 1, the GB has defects responsible for blue and green lines, whereas the red line appears due to the defects located at the border of Areas 1 and 2.

In Area 2, the blue and green lines dominate among those appearing from the GB. The intensity of the yellow line from the GB is lower than that from the grain bulk. This result is in good agreement with the hypothesis proposed above. The influence of iron is less pronounced at its lower concentrations.

The GB interacted with defects. Most likely, a significant part of green and red defects diffuses via the GB to the depth of the crystal, which forms a region with a high concentration and consequently a high luminescence intensity of defects. The observation confirms that the green line is related to the regions distant from the doping surface. The low luminescence intensity near the detection threshold could be responsible for the absence of a red line coming from the deep region of the sample. The high intensity of the blue line is due to the GB-assisted purification of the defective-impurity centers that recombined either beyond the registration range or non-radiatively. The absence of a yellow line may be explained by a high concentration of green defects as well as by their absorption by the GB in the narrow middle part.

Thus, the experimental results confirm the initial hypothesis.

4. Conclusion
We have shown that the luminescence characteristics of a GB in CVD-ZnSe are dependent on iron and defective-impurity concentrations. The proposed hypothesis describing the luminescence changes is in good agreement with the obtained results. A direct experiment demonstrated purification of the GB vicinity and diffusion of defects via the GB into the bulk of the crystal. The two-photon confocal microscopy proved to be a powerful technique for investigation of GB luminescence characteristics in CVD-ZnSe crystals.

Acknowledgments
The reported study was the result of research in the framework of state assignments № 0024-2018-0010 and № 0095-2016-0015. Part of the investigation was performed at The Center of Collective Use of Scientific Equipment of GPI RAS.
References

[1] Gavrishchuk E M, Ikonnikov V B, Kazantsev S Yu, Kononov I G, Rodin S A, Savin D V, Timofeeva N A and Firsov K N 2015 Quantum Electron 45 823

[2] Mirov S, Fedorov V, Martyshkin D, Moskalev I, Mirov M and Vasilyev S 2015 Proc. of SPIE 9467 94672K.

[3] Kozlovsky V I, Korostelin Y V, Podmar’kov Y P, Skasyrsky Y K and Frolov M P 2016 J. Phys.: Conf. Ser. 740 012006

[4] Gladilin A A, Gulyamova E S, Danilov V P, Il’ichev N N, Kalinushkin V P, Odin I N, Pashinin P P, Rezvanov R R, Sidorin A V, Studenikin M I, Chapnin V A and Chukichev M V 2016 Quantum Electron 46 545

[5] Kalinuskin V P, Uvarov O V 2016 Tech. Phys. 86 119

[6] Gladilin A A, Kalinushkin V P, Uvarov O V 2018 J of Elec Materi 47 5087

[7] Gavrishchuk E M, Gladilin A A, Danilov V P, Ikonnikov V B, Il’ichev N N, Kalinushkin V P, Ryabova A V, Studenikin M I, Timofeeva N A, Uvarov O V, and Chapnin V A 2016 Inorg mater 52 1108

[8] Kotereva T V, Ikonnikov V B, Gavrishchuk E M, Potapov A M and Savin D V 2018 Tech. Phys. 88 1110

[9] Nedeoglo D D and Simashkevich A V 1984 Electrical and Luminescent Properties of Zink Selenide ed I K Andronik (Chișină: Știința) chapter 4 pp 96–134