The Influence of Chromium Thermal-Diffusion-Based Doping on the Spatial Distribution of Luminescence Intensity in ZnSe

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We have studied the influence of chromium doping of ZnSe crystals at 1250 °C on the spatial distribution of luminescence in the spectral range of 0.44 to 0.73 μm. It is expected that several types of defective-impurity centers are formed due to the doping process. Centers of at least one type demonstrate complex distribution and lead to formation of area with high intensity luminescence looking like a bright strip parallel to doping surface.

1. Introduction

The ZnSe crystals doped with Fe^{2+} and Cr^{2+} are used as an active medium for solid state laser developed for mid-IR spectral range (3–5 μm). Recently, the lasing characteristics of ZnSe:Fe^{2+} and ZnSe:Cr^{2+} have been improved [1–5]. The medium parameters (optical transmission, absorption, and luminescence) depend on many factors including the dopant and its concentration, as well as on the nature of intrinsic and impurity defects. The lattice imperfections are due to crystal growth conditions, in particular, the influence of high temperature diffusion of dopant ions. The defect control at each preparation stage is significant for optimization of technological routes of laser element production based on ZnSe: Fe^{2+} (Cr^{2+}).

The high temperature diffusion leads to concentration inhomogeneity in laser crystals. Thus, studying of spatial distributions of different characteristics is of great importance. The two-photon excitation (TPE) microscopy is an efficient method for following spatial distribution luminescence. The method allows recording luminescence spectra inside the crystal volume, thus making possible search for correlation between luminescence variations and the dopant concentration profile [6, 7]. Previously, we reported investigation of ZnSe:Fe [8–10] based on that method. The first results of ZnSe:Cr was demonstrated in [8]. Results of the detailed studies of the chromium doped crystals are discussed in the present paper.

2. Samples and experiment

The sample investigated were polycrystalline ZnSe plates doped with chromium by high temperature diffusion. Polycrystalline plates were produced using chemical vapor deposition (CVD) technique. A chromium layer with the thickness of about 1 μm was then deposited by electron-beam sputtering. The samples were annealed for 28 h at $T = 1250$ °C and high isostatic pressure (HIP) $P = 100$ MPa. The spatial distribution of luminescence was followed by two-photon excitation (TPE) microscopy using Carl Zeiss 710 NLO confocal microscope equipped with a femtosecond pulsed Ti:sapphire laser operating in the 710–1050 nm spectral range [6, 7]. We used the wavelength of 800 nm in the experiments. The output power was varied in order to achieve contrast images. The setup operated in the 425–725 nm spectral range and provided up to 3 nm spectral resolution. In our experiments, we used 10 nm spectral resolution. The optical setup registered luminescence from the excited volume, which was of about several cubic μm. The microscope features made possible shifting the excited volume to the depth down to 2 mm from the crystal surface. Software used allows obtaining spectral characteristics of each point on the map with the 1 μm spatial resolution. The spatially resolved concentration of optically active chromium was determined by absorption measurements at 1.7 μm wavelength. The experiment was carried out on a HYPERION 2000 IR microscope equipped with a Tensor-27 IR-Fourier spectrometer (Bruker). The method is described in detail in [11].

The initial undoped samples, previously demonstrated to be high purity polycrystalline CVD-ZnSe [8], were treated in two ways, either doped with chromium with HIP or annealed with HIP without the dopant.

3. Results and discussion

Figure 1a shows the spectra at different points, marked at planar map (Fig. 1c) which was obtained at the wavelength of 473 nm at the depth of 100 μm from the surface of CVD-ZnSe:Cr crystal. The results are typical of that material. The region with low chromium concentration (Fig. 1c, black open circle) is characterized

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by luminescence at the wavelength of 473 nm (blue band) and a broad band with the maximum at the wavelength of 500 nm and with "tail" decay up to 620 nm. The increase of chromium concentration (Fig. 1c, red triangle) leads to the less pronounced broad band. Simultaneously, the broad band is continuing up to 650–680 nm, whereas the luminescence intensity is increased in the spectral range of 590–640 nm. Further increase of the chromium concentration (Fig. 1c, green open square) leads to suppression of the blue and broad bands, as well as appearance of a band with maximum at the wavelength of 560 nm (yellow band). The blue band associated with bound exciton is observed in all samples [8–10]. The broad band is not found in the spectra of the initial undoped samples (Fig. 1c, magenta solid square). However, a similar band with a shorter declining area (to the wavelength of 560–610 nm) is observed in the CVD-ZnSe annealed with HIP without doping (Fig. 1c, blue solid circle). The intensity of the band was reported to undergo changes only in the region of structural defects [8]. The initial peak analysis allows to propose that the broad band is a product of merging of lines at the wavelengths of 500, 520, 540 nm (green band), and 560–610 nm (yellow band).

Spatial distribution of luminescence intensity of all the above mentioned bands reveals a complex behavior. Figure 2 demonstrates planar maps and spatial dependences of luminescence intensity at the wavelengths of
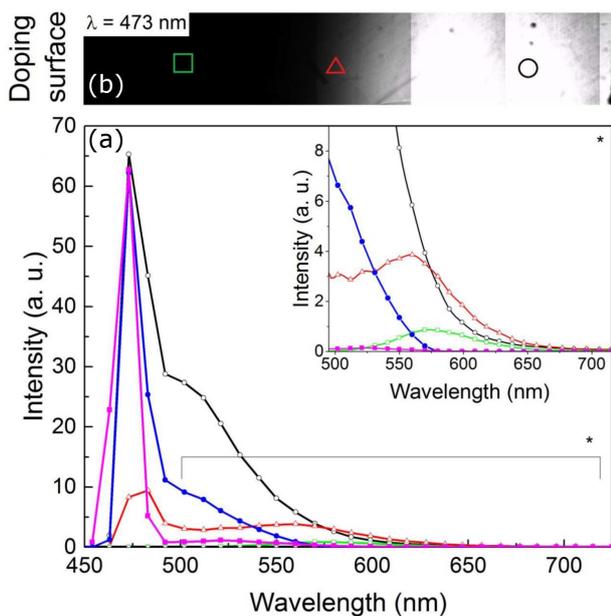
Fig. 1. (a) Two-photon excited luminescence spectra in regions with different concentrations of Cr, marked at planar map (b): low concentration (black open circle), intermediate concentration (red triangle), high concentration (green open square) of chromium, and, in addition, the spectra of undoped both initial (magenta solid square) and annealed with HIP (blue solid circle) samples. Inset: enlarged spectral region of DIC-related emission. Spectra recorded at room temperature.
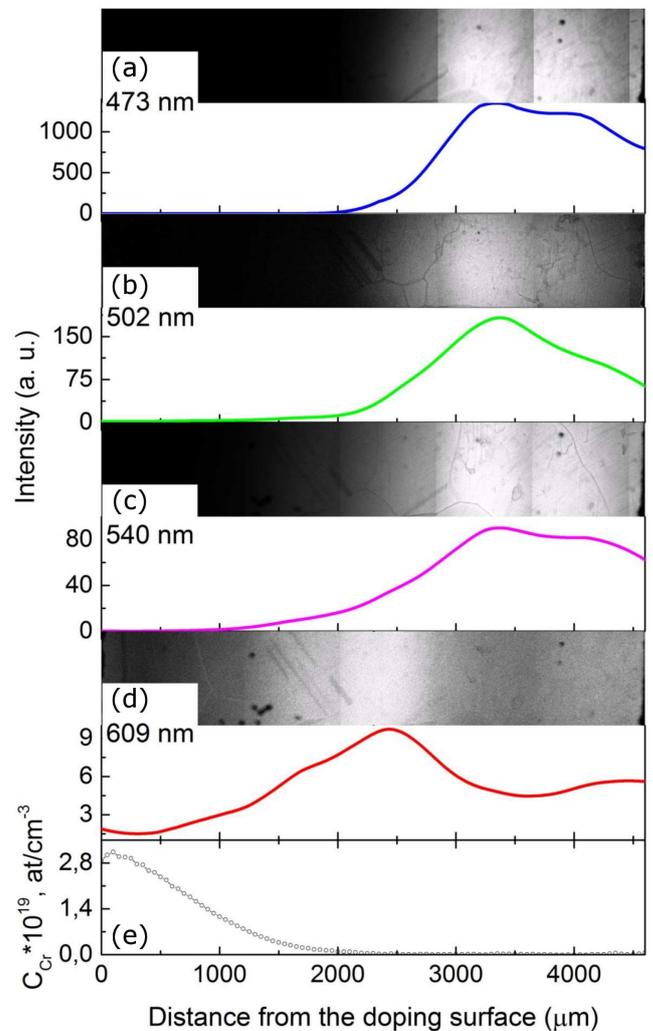
Fig. 2. Planar maps and spatial distributions of luminescence at wavelengths of 473, 502, 54 and 69 nm (a–d) in ZnSe:Cr crystal at room temperature accompanied with distribution of optically active Cr^{2+} (e).

473, 502, 540, and 609 nm. The results are typical of the investigated samples. The following areas can be clearly identified: (1) the one with high chromium concentration (from the doping surface to 1.2 mm); (2) the neighboring area with the chromium concentration in the range of 5×10^{18} cm^{-3} to the detection threshold (from 1.2 to 2.5 mm from the surface); (3) the low (below the detection threshold) concentration area (from 2.5 to 4.2 mm from the surface); (4) the area at the crystal edge opposite to the doping surface with the chromium concentration of about 1–2×10^{18} cm^{-3}.

The area (1) is characterized by low intensity of the yellow band increasing with the decrease of chromium concentration attaining the maximum value at the distance of 2.3 mm from the doping surface, which is followed by the intensity decrease. As a result, a strip-like area with high intensity luminescence (AHIL) of the yellow

band with the width of hundreds of μm and parallel to the doping surface is formed in the area (2) and parallel to the doping surface is formed in the area (2). Similar AHIL were previously observed in ZnSe:Fe crystals [7]. The blue and green bands increased in the area (2) and dominated in the area (3). In the area (4) these bands slightly decreased due to marginal chromium concentration, whereas the yellow band slightly increased.

We propose that green and yellow bands are results of doping procedure and are not related directly with dopant. Apparently, at least 2 types of defective-impurity centers (DICs) related to green and yellow bands are formed during doping. Different spatial distribution of green and yellow luminescence bands are allowed to suppose that related DICs are characterized by different diffusion coefficients. The green luminescence is distributed quite homogeneously in the crystal volume. This band was not observed in initial ZnSe and was detected in annealed with HIP samples both undoped and doped with Fe. Obviously, the annealing has an effect on whole crystal volume. Taking into account all the above, we suppose that nature of related DIC formation is caused by annealing process.

The yellow luminescence band was detected only in ZnSe doped with Cr and well recognized in area with high Cr concentration whereas the luminescence is suppressed by dopant; the suppression trend being well known [12–14]. The spatial distribution of yellow band in ZnSe:Cr is similar to spatial distribution of red band in ZnSe:Fe [10]. Both band demonstrated AHIL in area with high dopant concentration. Proceeding from this observation, we suppose that the nature of formation of related DICs are caused by doping process and not dependent on specific dopant. Probably, this trend is a general phenomenon and is applicable to a set of dopants in the A2B6 type semiconductors.

4. Conclusion

The chromium thermal-diffusion-based doping process of CVD-ZnSe at $1250\,°C$ leads to the formation of at least two types of DICs associated with the green (50–540 nm) and yellow (560–610 nm) bands. DICs associated with the green band form due to annealing and are homogeneously distributed in the crystal volume. DICs associated with the yellow band are formed due to the chromium diffusion, the spatial distribution revealing a complex behavior. The AHIL are observed in the crystal regions with chromium concentration of 5×10^{18} to 1×10^{18} cm^{-3}. Formation of strip-like AHIL parallel to the doping surface previously observed in ZnSe:Fe is shown to be a general phenomenon rather than a specific property of particular crystals.

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