Photoluminescent tomography of ZnSe bulk crystals

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Abstract. High potential of two-photon confocal microscopy for photoluminescent tomography of bulk semiconductor crystals are demonstrated in this work using ZnSe crystals as an example. The first results of investigation of ZnSe bulk crystals, both undoped and doped by 3d metals, are presented. Appearance of luminescence quenching centres in specific parts of crystals and grain recombination activity are demonstrated by the proposed method; these phenomena cannot be detected by other luminescence-based methods.

1. Introduction
Investigation of photoluminescence (PL) distribution in bulk semiconductors is of great interest for science and practical applications. Usually, the luminescence is caused by recombination of nonequilibrium carrier which is excited by radiation with quantum energy exceeding the bandgap width of the studied semiconductor. This radiation is absorbed by a thin near-surface layer with the depth of about a few micrometers in which the studied photoluminescence is generated; the obtained results are then attributed to the whole crystal bulk. That approach does not seem to be very reliable and the experimental procedure does not seem to be always correct. It has been shown previously [1–3] that results obtained using surface and bulk photoexcitations are often different. This especially relates to such problems as exploration of inhomogeneous materials produced by thermal diffusion of a dopant from the crystal surface. Investigation of bulk defects—such as grain boundaries in polycrystalline materials—and their properties which are usually different from the properties of the rest part of crystal is another challenging task.

This paper presents a method of photoluminescent tomography as a powerful tool for defect visualization and characterization in bulk semiconductor crystals.

2. Experimental technique
In the present investigation we used a Carl Zeiss LSM 710 NLO confocal microscope with a laser tunable in the wavelength range from 0.71 to 1.05 µm for two-photon excitation (the pulse duration was 150 fs, their frequency was 80 MHz). Average peak power was varied in the range from 0.1 to 1 W depending on the detection condition and was optimized to ensure the highest resolution of luminescent imaging of a sample. Photoluminescent (PL) spectra were registered in the range from 425 to 725 nm with the spectral resolutions of 10 nm. This instrument enabled the study of wide-bandgap semiconductor crystals, such as ZnSe with the bandgap $E_g = 2.71$ eV, using two-photon excitation and ob-
serving interband (460–480 nm) and impurity (480–715 nm) luminescence spectra. All measurements were carried out at room temperature.

The 3D PL imaging procedure was as follows. The exciting laser emission focused in a chosen local volume scanned an area in the focal plain. The emitted PL was detected by a photomultiplier tube. A dichotic mirror and interference filters were used to cut off the excitation light from the detector. PL spectra were obtained at each point of scanning. As a result, we scanned maps of PL spectra; each map was recorded from a volume close to a rectangular parallelepiped with a height of a few micrometers and a base of 1 × 1 mm². In such a way, we sequentially scanned studied crystals changing the depth of the mapped layer that allowed us to compose volumetric (3D) images at different PL wavelengths as well as so-called tomographic models (5D models in the X–Y–Z–λ–IPL space, where X, Y and Z are the spatial coordinates, λ is the PL wavelength and IPL is the PL intensity). Acquisition of a tomographic model with the dimensions up to 1 × 1 × 1 mm³ and the spatial resolution of 25 µm took several minutes. Planar (2D) maps IPL(X, Y) for any value of λ and any depth in a crystal (Z) could be then extracted from the tomographic models.

We used samples of single crystalline and polycrystalline ZnSe and ZnSe:Fe to present the PL tomography. Polycrystals were prepared by CVD. Single crystals were obtained by vapor-phase free growth process on the ZnSe (111) substrate. Iron or chrome doping of ZnSe crystals was performed by the thermal diffusion from the iron (chrome) film deposited on a surface by the thermal deposition process. The concentration of Fe (Cr) was up to 5×10¹⁹ cm⁻³ near the surface and exponentially decreased with Z. Since iron (chrome) concentration decreased rapidly in the depth of a crystal, we succeeded to observe significant variations of characteristics in different regions of crystals depending on the depth from the surface. In addition, the presence of grains in polycrystalline ZnSe allowed us to demonstrate capabilities of confocal microscopy for investigation of macroscopic defects in the bulk of semiconductor crystals using two-photon excitation of PL.

3. Results and discussion
We start the presentation from the results concerning the original polycrystalline ZnSe. Figure 1 shows 2D maps of an undoped ZnSe crystal at the wavelength of 473 nm and different distances from the surface. The planar distribution of the PL intensity is seen to be strongly non-uniform. The near-surface layer (Z = 0) demonstrates a low average PL intensity. The corresponding spectrum contains only one band with a maximum at about 465 nm. The average PL intensity strongly but not monotonically depends on the depth. Initially it grows with Z reaching a maximum at Z ≈ 25 μm; then it starts to decrease. The spectrum contains only one PL band at each depth. A maximum of this line moves to the long-wavelengths region with increase in Z. It “stops” at the wavelength of 475 nm at Z ≈ 50 μm. PL maps of the sample are similar for all depths; they demonstrate a granular structure. Sizes of grains

Figure 1. Photoluminescence spectra and 2D maps for the wavelength of 473 nm obtained from the depth of 0, 25 and 71 μm; points at which the spectra were recorded are shown by crosses; circles show areas over which the PL spectra are averaged.
vary in the range of tens of micrometers. PL intensity inside grains varies by more than a decade for different regions with grain boundaries always showing a low PL intensity.

A high surface recombination rate at mechanically polished surface is the cause of low PL intensity in the near-surface layer \((Z = 0)\). The observed PL band corresponds to the band-to-band recombination. Its shift to the long-wavelength region with growing \(Z\) is a result of high absorption of the short-wavelength part of the edge luminescence. As a consequence, only excitonic radiation is emitted from the depth of a crystal [4]. Absorption of this light is reduced but is nonzero; the intensity of the excitonic emission decreases for \(Z > 30 \mu m\). A low PL intensity at grain boundaries can likely be explained by a high concentration of centers of non-radiative recombination. This is a commonly adopted explanation for all semiconductor materials. So, most of our results obtained for the undoped ZnSe crystals correspond to the available concepts supporting and “visualizing” them.

Let us dwell on the results relating to the ZnSe crystals doped by Fe. Characteristics of these crystals appeared to be very similar but they are strongly different from the results obtained for the as-grown samples. At first, PL spectra of the ZnSe:Fe crystal (figure 2) consisted of two bands: the excitonic one (475 nm) and a “broad” band in the range from 500 to 580 nm. The intensities of these bands were close and in some cases the intensity of the broad band exceeded the intensity of band-to-band PL. A characteristic feature of the broad band was its shape variation when PL was registered from different small (a few micrometers in size) regions of crystals (figure 2); note that this peculiarity was observed in both ZnSe:Fe and ZnSe:Cr crystals.

Secondly, distribution of the bulk PL intensity strongly differed in the doped and as-grown crystals. Figure 3 shows that intense PL, both excitonic and broad-band, is observed only at \(Z > 100 \mu m\). Intensities of the PL bands are much less when closer to the surface. This result was common for this type of crystals; only the depth from which the PL intensity began to increase varied from 40 to 100 \(\mu m\) in different samples.

Interesting results were obtained for the features of the planar PL maps of ZnSe:Fe observed at different depths. Figure 4 shows 2D maps obtained at the wavelength of 473 nm (at the exitonic band) for one ZnSe:Fe sample which had an intense PL starting from \(Z = 40 \mu m\). A PL contrast of grain boundaries is well recognized. The grain sizes are increased, as it takes place in annealed crystals. Up to the depth of about 120 \(\mu m\), the contrast resembles that in the as-grown samples, i.e. the grain boundaries have lower band-to-band PL intensity than the grains. At deeper layers, the contrast decreases, disappears and then inverts at the depth of 260 \(\mu m\): from this depth the grain boundaries have higher inter-band PL intensity than the grains. However, there remains a narrow domain at the middles of the grain.
boundaries with the decreased interband PL intensity (figure 4, \(Z = 474 \mu m, \lambda = 473 \text{ nm}\)). The similar narrow domains at the middles of the grain boundaries are revealed close to the surface but in this case narrow zones of increased broad-band PL are observed inside the regions of the reduced interband emission (figure 4, \(Z = 47 \mu m, \lambda = 541 \text{ nm}\)).

Figure 3. A tomography model of a ZnSe:Fe sample: each square represents a 2D map obtained at the wavelength indicated at the abscissa axis (nm) from the depth indicated at the ordinate axis (\(\mu m\)); the photoluminescence is seen to be emitted mainly from the bulk of the crystal.

Perhaps, it is associated with formation of a lot of centers during doping, which are competing recombination channels of non-equilibrium carrier. There are at least two ways of formation of these centers. Firstly, the formation of minor precipitates of the doping impurity is possible, which could be efficient centers of the non-radiative recombination. And secondly, atoms of the dissolved doping impurity may be the competing centers of the non-radiative recombination. In this case, they may act as non-radiative recombination centers or introduce PL bands, e.g., IR bands. PL appearing at different depths may be explained, e.g., by thickness variation of a surface layer removed by mechanical polishing after the dopant diffusion which was not precisely controlled. As a result, dopant concentrations at the surface and in the volume of different samples may vary.

The inverted recombination contrast at grain boundaries confirms the fact that composition of impurities and intrinsic defects in the bulk of crystals strongly depends on the depth. Probably, the mentioned above centers are contained in impurity atmospheres around grain boundary that explains the high contrast of the grain boundaries at \(Z < 100 \mu m\). Concentration of these centers rapidly decreases with deepening in a crystal and the contrast is smoothed. The phenomena of high PL intensity at impurity atmospheres of grain boundaries in deep regions and high PL intensity of the broad band in the
middles of impurity atmospheres of grain boundaries in near-surface regions call for further investigation.

In addition to the above mentioned centers, other centers formed in the process of doping were responsible for the appearance of the broad PL band. We observed this band in different iron-doped and chromium-doped crystals; consequently, the broad band is not connected with the dopant. This band likely refers to intrinsic defects, such as the interstitial zinc–vacancy zinc Frankel pair, and interstitial oxygen [4]. Note that a number of articles reported that these defects had many modifications and gave rise to numerous close PL lines [5]. Perhaps, this explains the observed variations of the shape of the broad band in the PL spectra obtained from different points in the crystals.

![Figure 4](image)

**Figure 4.** 2D maps of polycrystalline ZnSe:Fe obtained from different depths at three of wavelengths (the corresponding depths in micrometers and wavelengths in nanometers are shown in each panel).

4. **Conclusion**

We have demonstrated that the PL tomography is a powerful tool for investigation of bulk semiconductors. This technique enables the express non-destructive 3D mapping of interband and defect or impurity related photoluminescence. Its capability could be increased by extension of detection range to near-IR and by utilization of an excitation source at longer wavelengths. If the detector spectral range is expanded to 1.5 µm, the industrially important materials, such as GaAs, InP, CdTe, could also be investigated.

Explorations of silicon and germanium are more difficult to conduct using this technique since the emissivity of Si and Ge is low. We suggest using capacitance methods or conductivity measurements at microwave frequencies for carrier detection in such researches.
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