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CATHODOLUMINESCENCE STUDIES OF POLYTYPE STRUCTURE IN $Zn_{1-x}Mg_xSe$*

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$Zn_{1-x}Mg_xSe$ crystals grown by Bridgman method show spatial transition from sphalerite (3C) to wurzite structure (2H) with increasing Mg content (x). Within the transition range, near $x = 0.19$, coexistence of hexagonal and cubic structure results in the formation of polytype sequences of 3C–8H–4H–2H. We have investigated the spatial distribution of the polytypes in $Zn_{1-x}Mg_xSe$ mixed crystals with a value of x close to that of the phase transition using spectrally as well as spatially resolved cathodoluminescence. Three emission bands in the cathodoluminescence spectrum have been observed, two strong lines at 2.99 eV and 2.965 eV, and a weak shoulder at 2.95 eV. The lines at 2.965 and 2.99 eV are known in the literature as an exciton recombination in the 8H and 4H polytype structure. We have found the third one at 2.95 eV to be due to luminescence in the 3C structure. These results demonstrate the usefulness of cathodoluminescence measurements for investigations of spatial distribution of inhomogeneities of mixed semiconductors.

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1. Introduction

ZnSe and related wide-gap II–VI compounds have attracted much attention due to successful fabrication of a blue-green laser device operated continuously at room temperature, with lifetime exceeding one hundred hours [1, 2]. The device lifetime is limited mainly by the generation of defects in the gain portion of the laser formed in the vicinity of preexisting stacking faults due to strain in the active zone [3, 4]. The $Zn_{1-x}Mg_xSe$ solid solution is particularly interesting since it is

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a component of ZnMgSSe, the system used as a cladding layer in construction ZnSe based diodes. It enables tuning of band energies and lattice constants by adjusting the Mg content [5–7] as well as it can be matched to some III–V alloys [8]. Thus, determination of the basic properties of $Zn_{1-x}Mg_xSe$ and particularly the understanding of the nature of defects created in such crystals is of high interest.

Transmission electron microscopy (TEM) measurements on $Zn_{1-x}Mg_xSe$ show spatial transition from sphalerite (3C) to wurtzite structure (2H) with increasing Mg content (x) [9]. Within the transition range, near $x = 0.19$, coexistence of hexagonal and cubic structure results in formation of polytype sequences of 3C–8H–4H–2H. Direct transitions 8H/4H and 4H/2H, but no direct 3C/2H transition have been observed. Luminescence measurements indicate the increase in the band-gap energy with increasing Mg concentration.

Cathodoluminescence is a very useful technique for investigations of inhomogeneities in semiconducting materials. In this paper we have used this method to characterise the correlation between structural and luminescence properties of polytype structure in $Zn_{1-x}Mg_xSe$.

2. Experimental

$Zn_{1-x}Mg_xSe$ crystals were grown from the melt by the high-pressure Bridgman method [5–7] for $x = 0.19$. The investigated ingots were formed from Koch–Light "electronic grade" ZnSe powder mixed with 15 mol% of metallic magnesium. The crystals were cut perpendicularly to the growth direction into 1.2 mm thick plates, mechanically polished and chemically etched. Several samples with a Mg content close to the sphalerite (3C)–wurtzite (2H) transition range were selected for cathodoluminescence (CL) investigations.

The CL mappings and the spectroscopic measurements of the cathodoluminescence of our samples were taken at $T = 20$ K with SEM CamScan CS 44 operated at 10 keV in energy and with a current of 800 pA. The CL system is able to detect radiation from 350 nm to 900 nm with a 0.5 nm resolution.

3. Results and discussion

Figure 1 shows the CL spectrum taken from samples in the transition range at x close to a value of 0.19. The CL spectrum consists of two peaks at 2.99 eV, 2.965 eV. The emission lines are assigned to recombination of excitons in the 4H and 8H polytype, respectively, which is in agreement with the results in [9]. Additionally, we observe a weak shoulder at about 2.95 eV, which suggests that this luminescence comes from an additional polytype.

To understand this CL spectrum, we have measured the spatially resolved CL from the same area of the sample, but taken at different photon energies, namely at 2.97 eV (Fig. 2a) and 2.99 eV (Fig. 2c). Figure 2b shows the inverted image of the CL image measured at 2.97 eV (Fig. 2a). The structure observed in the CL images consists of a set parallel dark and bright bands. The bright stripe corresponds to a structure (Fig. 2a: 8H, Fig. 2c: 4H) which shows luminescence measured at given emission energy. In the case of the coexistence of only two polytype structures of 4H and 8H, the CL images measured at different emission

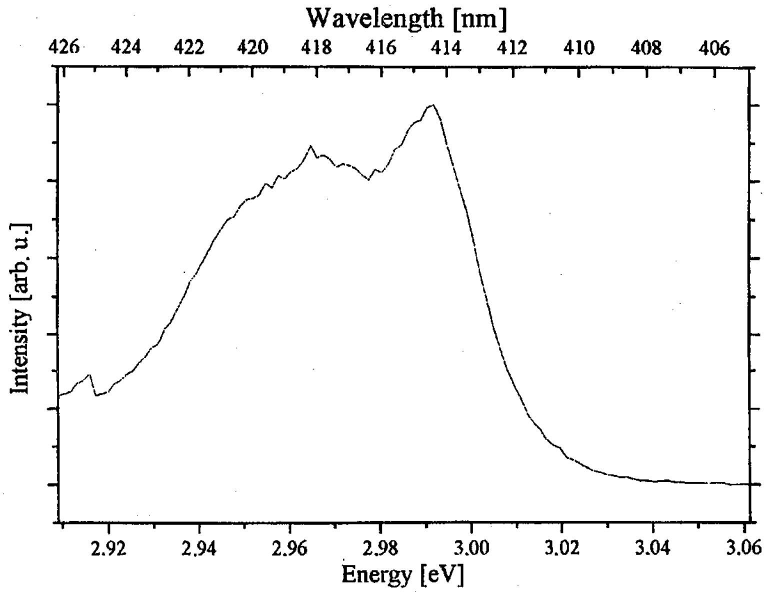

Fig. 1. CL spectrum of $Zn_{1-x}Mg_xSe$ (at $x = 0.19$) measured at $T = 20$ K.

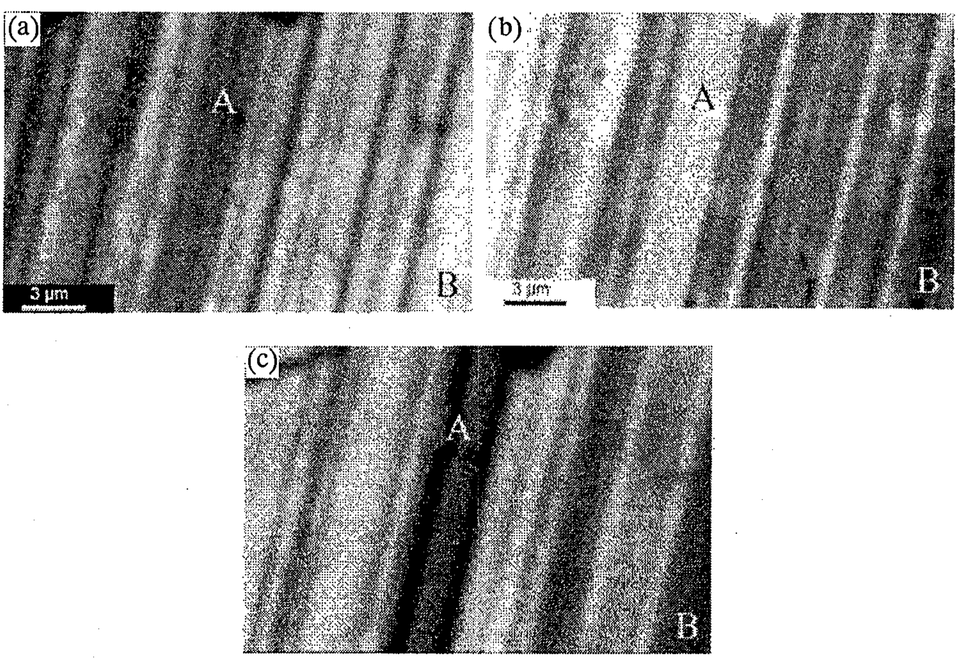

Fig. 2. CL images of the same area of sample as in Fig. 1 of $Zn_{1-x}Mg_xSe$ taken at an emission energy of 2.97 eV (a) and of 2.99 eV (c). (b) shows the inverted image of (a).

energy should be complementary. In other words, the inversion of the intensity of one of the images should lead to intensity distribution of the other image [10]. This means that the inverted image (Fig. 2b) of Fig. 2a should be comparable to the CL image measured at 2.99 eV (Fig. 2c). Apparently this is not this case (see the area marked with "A" on all images). Nevertheless, we can find some area (i.e. marked with "B"), where the inversion condition is fulfilled. Therefore the areas which fulfils the inversion condition are attributed to the 4H and 8H polytypes and the other ones as mentioned above to the additional polytype. Based on our TEM measurements [9], we can conclude that this polytype is 3C.

To prove the existence of the 3C polytype, we have measured the spatially resolved CL of the same area of the sample at the emission energy of 2.95 eV (Fig. 3a). The comparison of Fig. 3a with the CL image measured at an emission energy of 2.99 eV (Fig. 3c) indicates that both images are almost complementary, except of some areas one of each is marked as B. This can be better seen from Fig. 3b representing the inverted image of Fig. 3a. By focusing the electron beam at the places indicated as "A" and "B" in our figures, we measured the CL spectra shown in Fig. 4. The CL spectrum measured at the point A consists of one emission line at about 2.95 eV, and the one measured at point B of the emission band at 2.962 eV. These lines are known in the literature [9] as exciton recombination in the 3C and 8H polytype structure.

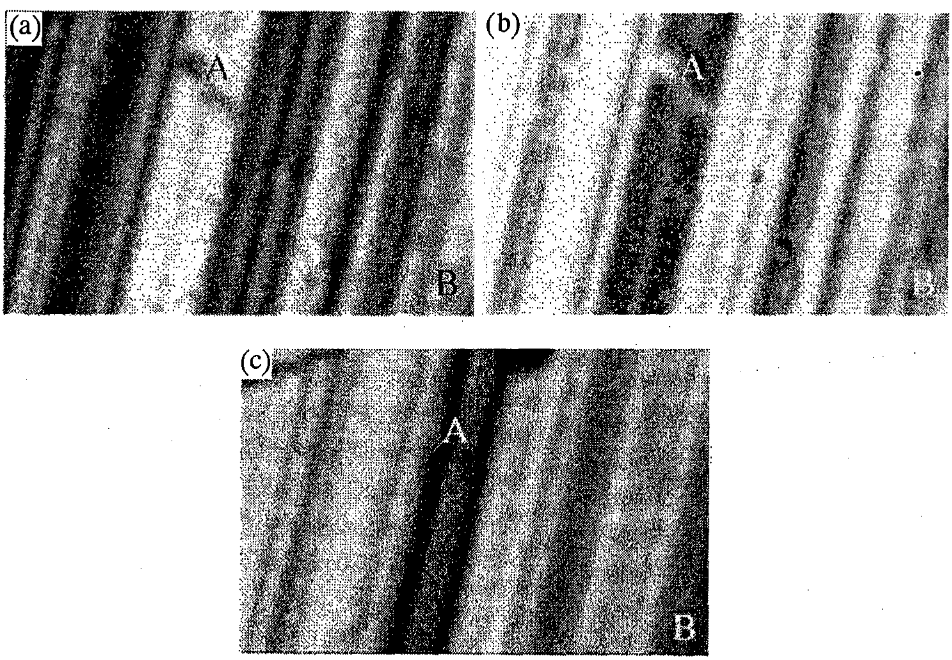

Fig. 3. CL images of the same area of sample as in Fig. 2 of $Zn_{1-x}Mg_xSe$ taken at an emission energy of 2.95 eV (a) and of 2.99 eV (c). (b) shows the inverted image of (a).

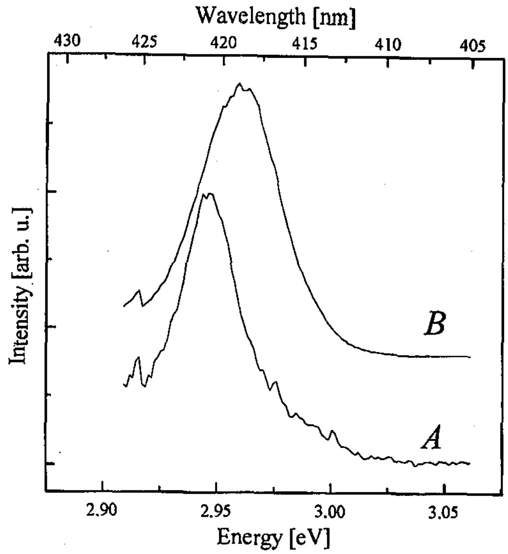

Fig. 4. CL spectra at $T = 20$ K measured at the sample area of $Zn_{1-x}Mg_xSe$ marked in Figs. 2 and 3 as "A" and "B" respectively.

4. Conclusion

In this work, we have investigated the spatial distribution of the polytypes in $Zn_{1-x}Mg_xSe$ mixed crystals with a value of x close to that of the phase transition using the spectrally as well as spatially resolved cathodoluminescence. We have observed three emission bands in the CL spectrum, two strong lines at 2.99 eV and 2.965 eV, and a weak shoulder at 2.95 eV. The lines at 2.965 eV and 2.99 are known in the literature as an exciton recombination in the 8H and 4H polytype structure [9]. We have found the third one at 2.95 eV to be due to luminescence in the 3C structure. The CL images measured at these three different emission energies are complementary.

Concluding, we have observed the coexistence of the three different polytype structures 3C, 8H and 4H in our CL measurements. This is consistent with TEM results done on the same samples [9].

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