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Influence of growth non-stoichiometry on optical properties of doped and non-doped ZnSe grown by chemical vapour deposition

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Abstract

Thick poly-ZnSe layers used for optical components in infrared laser systems show strongly varying laser damage thresholds. This is due to differences in kind and concentration of carrier trapping defects in the material grown under various Se/Zn partial pressure ratios. The VI/II ratio determines a non-stoichiometric growth and determine an upper limit for the concentration of native defects. The optical properties of poly-ZnSe are studied by means of time-integrated and time-resolved photoluminescence (PL) as well as spatially resolved cathodoluminescence (CL). It is shown that samples grown in Se excess are of good quality and have the lowest defect concentrations. The changing of properties of non-stoichiometric grown samples by doping with Li and In in a post-grown diffusion process was also studied.

1. Introduction

There is some evidence that the problems of carrier type and conductivity control in wide gap II–VI compounds are strongly related to native defects generated by non-stoichiometric composition during growth or additional thermal treatment, causing the phenomena of self-compensation [1–4].

ZnSe is the most promising II–VI material for the fabrication of pn-junction devices (blue laser diode) and has been intensively studied during recent years. It is also very important for optical

components in infrared laser applications. There is, however, a very strong difference in the desired optical and electrical properties between both applications. For the infrared devices the carrier concentrations (free carriers, in shallow traps, in deep levels) must be as low as possible, asking for extremely low impurity contents and stoichiometry control. Therefore, we grow polycrystalline ZnSe sheets by a special chemical vapour deposition method (CVD), and investigate the interrelation between growth conditions, defect generation, and optical properties. The deposition temperature and the Zn/Se ratio in the gas phase are the main parameters governing the formation of stoichiometry-related defects. In this work we report on investigations on ZnSe

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platelets grown under different VI/II ratios at constant deposition temperature. We used low temperature photoluminescence (PL) and cathodoluminescence (CL) in connection with colour imaging to characterize our samples with respect to impurities and intrinsic defects.

2. Experimental procedure

ZnSe layers of comparable thickness (400–500 μm) were deposited on glassy carbon sheets in a CVD process using the reaction of the elemental vapours Zn and Se (Se_2 mainly) in argon ambient. In this work we report mainly on a “stoichiometry row” deposited at the optimum growth temperature of 675°C (optimal with respect to measured laser induced damage threshold at 10.6 μm) and a Se/Zn ratio between 0.3 and 2.4, i.e., between 70% excess of Zn and up to 140% excess of Se over the stoichiometric quantities. Growth rates were found to be 30–50 $\mu\text{m}/\text{h}$, depending on component concentration in the gas phase. The diffusion doping experiments were carried out in sealed quartz ampoules at 420°C for 48 h. Dopant source was stoichiometric ZnSe powder containing 10^{-4} g/g ZnSe of Li or In metal, respectively.

For the PL spectra the ZnSe layers are excited above the band gap by the 364 nm line of an Ar-ion laser (spectra physics), for time-resolved measurements by a dye laser synchronously pumped by an actively mode-locked Nd:YAG laser (coherent) with a frequency-tripling BBO crystal. Luminescence transients are detected by a micro-channel-plate photomultiplier tube in conjunction with the time correlated single-photon-counting technique. The transients are fitted by convolution of the apparatus response with two exponential functions, one for the luminescence rise (τ_r) and one for the luminescence decay (τ_d). CL measurements and colour imaging were made using a scanning electron microscope (JEOL-U3) at carefully controlled excitation conditions of 25 keV and 30 nA at about 77 K. The excitation depth was estimated to be 2–3 μm . Spectra were recorded with a mirror spectrometer and conventional lock-in technique. Details of

the optical arrangement were published by Menninger et al. [5]. In the case of In doping, phase-angle correlated (PAC) γ -ray spectroscopy was performed for testing the incorporation of In on Zn lattice sites.

3. Experimental results

3.1. Cathodoluminescence studies

Typical CL spectra show a series of deep-level transitions beside the known exciton lines. It is possible to distinguish between defects by studying the dependence of optical properties on the Se/Zn ratio. Fig. 1 shows the result of such an experiment for the “optimum” temperature 675°C and a VI/II ratio of 1.13. In addition to the exciton line, the donor–acceptor pair luminescence, the Y-band, the so-called Cu-green emission and the luminescence of the self-activated (SA) centre can be seen.

By colour imaging we are able to compare different wavelength images in regard to the localization of different deep level emissions (seen in Fig. 1). It is clearly seen that the Y-band is localized at large crystallographic defects like grain boundaries, twins, or dislocation networks. The Cu-green luminescence is observed in the same crystal areas as the Y-band. The distribution is homogeneous in the neighbourhood of the defects. The SA luminescence is typically observed in point defect clouds, whereas the excitonic luminescence is only seen in those crystal regions with low crystallographic defect concentration. That means that electron–hole pairs are trapped by deep defects suppressing the excitonic luminescence.

The doping experiments add some interesting results. Comparing the Li-doped to non-doped sample pieces treated in the same run, a noticeable change is observed for near stoichiometric material where the deep levels disappear. In the Se excess layers the Y-band is strongly diminished. It is concluded that Li is bound to extended lattice defects, in this way changing the self-trapped exciton centre (Y-band). No specific feature could be found in colour imaging. It is

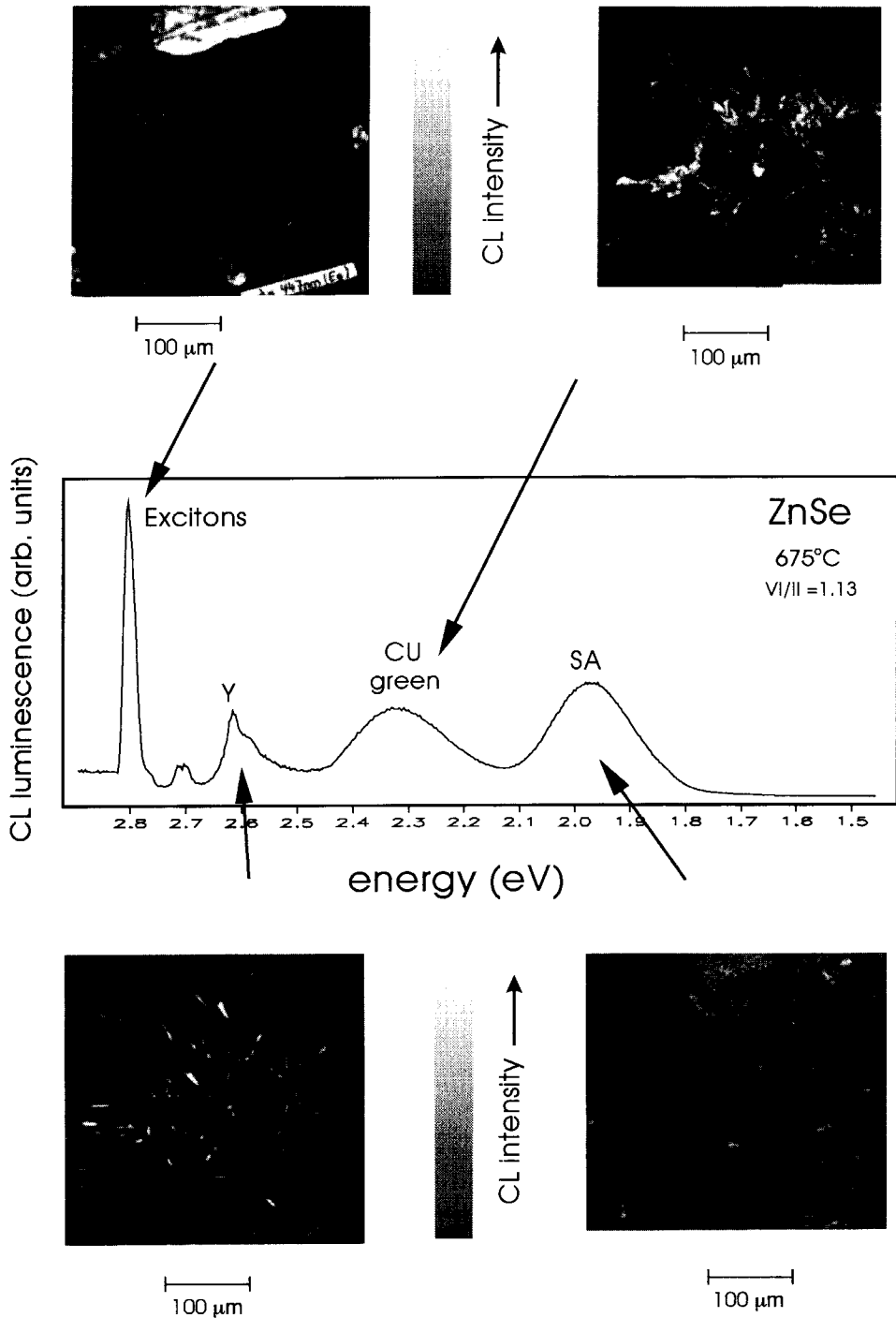


Fig. 1. 90 K cathodoluminescence spectrum of polycrystalline ZnSe grown with Se excess. Colour imaging of the exciton, the Y-band, the Cu-green and the SA luminescence, representing an area of approximately $300 \mu\text{m} \times 300 \mu\text{m}$ with a spatial resolution of about $1 \mu\text{m}$.

consistent with the results to assume Li incorporation on interstitial sites.

In the case of In-doping only Se excess layers show remarkable changes, increasing with Se excess. This can be interpreted in terms of defect chemistry very simply with the need of Zn vacancies for In substitution on Zn lattice sites and the also likely formation of these under Se excess. High donor and acceptor concentrations and an increasing amount of deep levels (yellow-green, SA) are measured. Our results correspond with those of Shirakawa and Kukimoto [6]. The puzzling result comes from PAC measurements where 7% of In at maximum are found on lattice sites. That means that at a diffusion temperature of 420°C, practically no In atoms substitute Zn lattice atoms. Therefore, the mechanism of In impact on optical properties should be considered to involve other possibilities as interstitial positions of In or complex formation. Also no specific In-related defect could be found in the spectra and in colour images.

3.2. Photoluminescence studies

Further information on the defect concentration and the quality of the ZnSe crystals was obtained using time-integrated and time-resolved PL investigations at helium temperatures. Typical PL spectra of ZnSe with varied Se/Zn ratios at one fixed growth temperature are seen in Fig. 2. In the excitonic region (right-hand side of Fig. 2), the luminescence of the free exciton (FE), the donor bound exciton (I_2), the acceptor bound exciton (I_1), and of an exciton bound to a deep acceptor is observed (I_{1c}). With increasing Se/Zn mol ratio the line is boosted, demonstrating that this deeply bound exciton line is correlated with Zn vacancies. Decreasing the Se/Zn ratio, the intensity of the shallow bound exciton lines I_1 and I_2 is enhanced in comparison to I_{1c} .

The halfwidths of the bound and free exciton lines are comparable to those in single-crystalline ZnSe. This shows that the extension of the single crystalline regions is relatively large, i.e., for the exciton grain boundaries can be neglected. The appearance of the Y-band and the self-activated band at 2.0 eV (left-hand side of Fig. 3) is con-

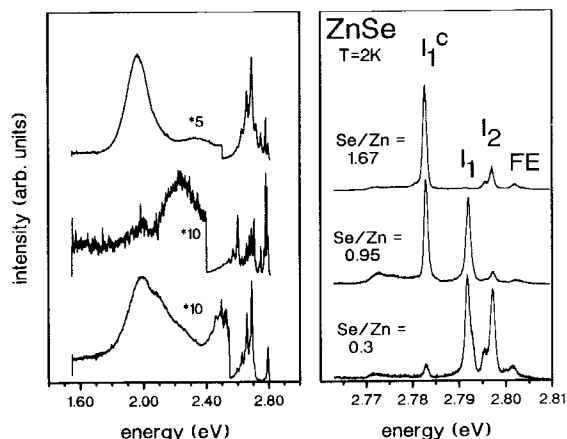


Fig. 2. Typical luminescence spectra of poly-ZnSe at 1.6 K varying the Se/Zn mol ratio.

nected with the growth condition under Se excess, indicating an association with Zn vacancies, whereas the donor–acceptor pair luminescence and the emission bands at 1.95 eV as well as at 1.85 eV are enhanced in crystals grown under Zn excess.

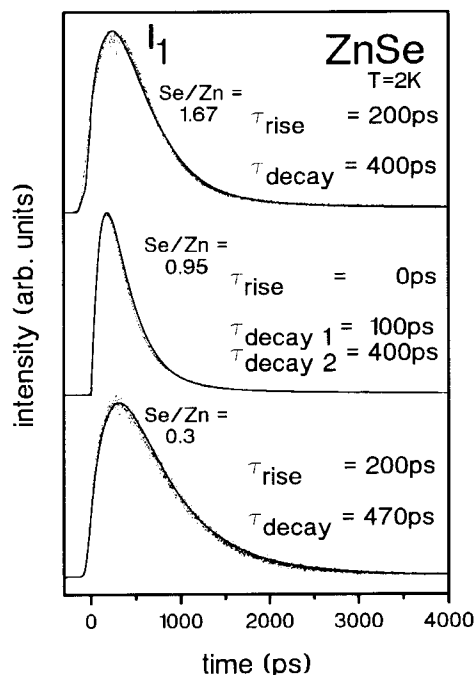


Fig. 3. Transients of the I_1 bound exciton emission varying the Se/Zn mol ratio.

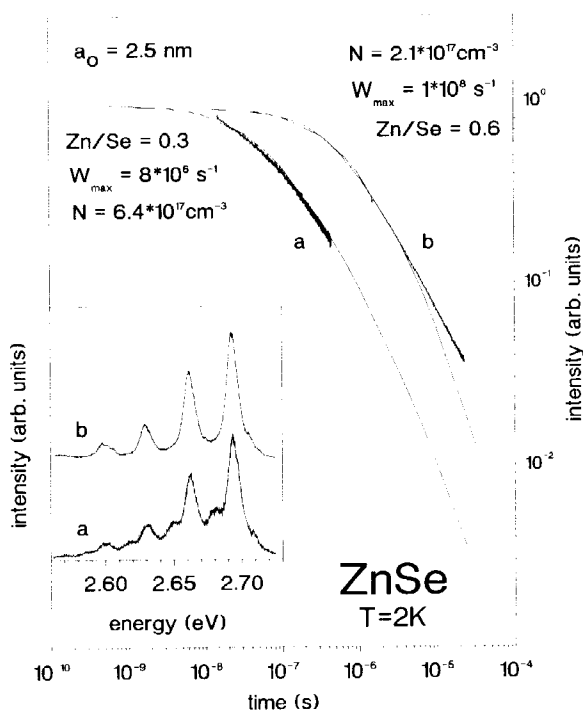


Fig. 4. Transients of the donor–acceptor pair luminescence varying the Se/Zn mol ratio. In the inset the corresponding DAP luminescence spectra are given.

Time-resolved PL measurements (Fig. 3) of samples grown with a large Se or Zn excess demonstrate that the lifetimes of the different exciton lines are relatively long and comparable with those in MBE ZnSe epilayers [8] or single crystals of good quality [9]. Obviously there is only relatively little non-radiative decay of electron–hole pairs via deep centres. We found the free exciton life times to range between 100 and 200 ps, whereas the life time of the acceptor bound exciton I_1 amounts to 400 ps in samples grown with Se excess. This demonstrates that the defect concentration in these samples is small. In crystals grown with a Se/Zn mol ratio near 1, the exciton lifetimes are drastically reduced, revealing competitive non-radiative processes introduced by a degraded crystal quality.

The inset of Fig. 4 depicts the donor–acceptor pair (DAP) luminescence band at 2 K of the same

samples grown under varying Se/Zn ratio. This ratio critically determines the concentration of deep native defects generated during growth at 675°C. Using a model proposed by Thomas et al. [10], we evaluate from DAP luminescence transients the shallow donor concentration ND of samples grown in Se excess (seen in Fig. 4), and W_{\max} , a factor proportional to the recombination probability in that model. A detailed description of the fitting procedure is given elsewhere [11]. The DAP luminescence grown with a Se/Zn mol ratio of 0.3 decays considerably faster than that of the sample with a Se/Zn mol ratio of 0.6, suggesting a much higher native defect concentration. This is obvious from the large increase of W_{\max} . However, there is no corresponding significant change in the impurity concentration, as determined from the DAP transients. So we find an increased defect generation with larger deviation from stoichiometric growth conditions.

4. Conclusion

The analysis of time-integrated and time-resolved PL as well as CL investigations yields a fast and reliable access to investigation of the influence of impurity concentrations and compensation effects on the optical properties in semiconductors. In this paper a strong influence of the stoichiometry on defect generation in poly-ZnSe is established. Assuming a constant, low impurity level, we conclude that the effects found are related to native defects in the Zn or Se sublattice. Material grown under Se excess has the lowest defect concentrations as compared to samples grown with Zn excess and with a near stoichiometric Se/Zn ratio. With respect to the doping experiments, it is noteworthy that no specific dopant-related defect emission was found, but large differences in the kind and the concentrations of defects generated in dependence on non-stoichiometric growth. Therefore, it seems possible that complexes of intrinsic defects are only modified by introducing impurities. The role of large crystallographic defects (twins, dislocations) as source or drain of optically active point defects should be studied more intensively.

5. References

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