

Proceedings of the XXII International School of Semiconducting Compounds, Jaszowiec 1993

## ELECTRICAL AND OPTICAL PROPERTIES OF ZnSe:Mg CRYSTALS

J. SZATKOWSKI, F. FIRSZT, H. MĘCZYŃSKA AND S. ŁĘGOWSKI

Institute of Physics, N. Copernicus University, Grudziądzka 5/7, 87-100 Toruń, Poland

ZnMgSe mixed crystals were obtained by the high pressure Bridgman method and by thermal diffusion of Mg metal into ZnSe crystals. Measurements of luminescence and transmission spectra show that the band-gap energy of such mixed crystals is larger than that of "pure" ZnSe. ZnMgSe crystals exhibit *n*-type conductivity and electrical parameters comparable with that of ZnSe. Blue-violet luminescence in the temperature range from 40 K to room temperature was observed. This feature makes this material very promising for future applications in constructing short wavelength electroluminescent devices.

PACS numbers: 78.55.Et, 71.55.Gs, 72.20.My

During last few years a significant progress has been made in constructing blue-green LED and laser diodes based on ZnSe, ZnCdSe and ZnSSe layers and quantum well structures [1-4]. Recently mixed crystals of Mg chalcogenides with wide-gap II-VI compounds have been proposed to produce a variety of new materials for optoelectronics [5-7]. ZnMgSe mixed crystals are of special interest because they offer the possibility of obtaining blue and UV emission.

ZnMgSe crystals were grown by the high pressure Bridgman method using the Koch-Light 6N ZnSe powder containing 10 and 20 mole percent of Mg metal as a starting material. After growing process crystals were annealed in liquid zinc or zinc vapour at temperatures 1070 K and 1220 K in order to obtain low-resistivity *n*-type material. Magnesium can be also easily incorporated into ZnSe by thermal annealing of undoped ZnSe crystals in Zn+Mg vapour at  $T = 1070$  K. This process forms heavily doped ZnMgSe mixed crystal surface layer. Figure 1A presents photoluminescence (PL) spectra of "pure" ZnSe (curve *a*) and ZnMgSe crystals grown from the melt with 10% (curve *b*) and 20% (curve *c*) of Mg in starting material. The PL spectrum of undoped ZnSe consists of weak exciton line at 2.802 eV, strong edge donor-acceptor (D-A) pair emission at 2.7 eV with LO-phonon replicas and deep-level band at 1.95 eV. In ZnMgSe crystals the main shape of PL spectrum is similar to that of "pure" ZnSe but a shift of each emission band towards higher photon energies is observed indicating increase in the band-gap energy of such mixed crystals. The increase in the band-gap energy of ZnMgSe crystals with increasing Mg concentration was also confirmed by measurements of transmission spectra.

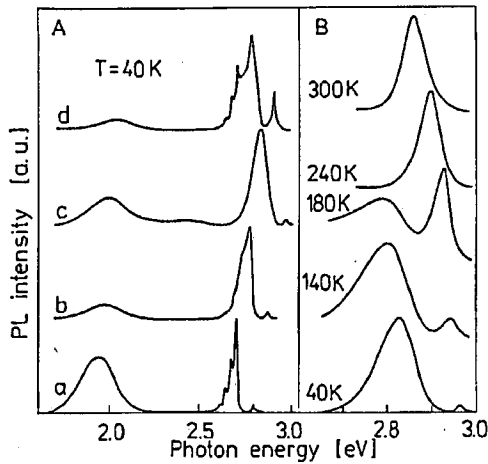


Fig. 1. Photoluminescence spectra of ZnSe and ZnMgSe crystals: (A) "pure" ZnSe — curve *a*, ZnMgSe crystals grown from the melt with 10% — curve *b* and 20% — curve *c* of Mg mole fraction in starting material, ZnMgSe crystal obtained by thermal diffusion of Mg metal into "pure" ZnSe from Zn+Mg vapour — curve *d*; (B) blue part of PL spectrum of ZnMgSe crystal grown by Bridgman method with 20% of Mg in starting material at different temperatures.

Comparing PL spectra of ZnMgSe crystals with that of "pure" ZnSe, we conclude that emission bands with maxima at 2.76 eV and 2.825 eV (Fig. 1A, curves *b* and *c*) correspond to edge emission in ZnMgSe mixed crystals with different Mg concentrations. The lines with maxima at 2.87 eV and 2.96 eV (Fig. 1A, curve *b* and *c*) are believed to be of excitonic origin. Figure 1A (curve *d*) presents the PL spectrum of ZnSe crystal into which Mg was diffused from Zn+Mg vapour. The heavily doped surface layer was partially etched before PL measurements. In PL spectrum of these crystals, except from the mentioned above exciton (2.91 eV) and edge (2.79 eV) emission from mixed crystals the edge emission from "pure" ZnSe at 2.7 eV is also observed, probably due to inhomogeneous doping of the surface layer with Mg. It should be noted here that the ratio of blue emission intensity to that of deep levels is greater for ZnMgSe than for "pure" ZnSe. Figure 1B presents blue part of PL spectra at different temperatures from 40 K to room temperature (RT) of ZnMgSe crystal grown from the melt with 20% of Mg in starting material. The edge emission is thermally quenched at temperature 200 K and only one blue band at 2.85 eV is observed at room temperature. The blue PL band at RT is observed in all ZnMgSe crystals after annealing in liquid zinc. As grown mixed crystals do not exhibit any blue luminescence at RT. At  $T = 40$  K the intensity of blue emission in these crystals is very low probably due to creation of large number of cation vacancies during high temperature growing process, which produce strong deep-level emission at about 2.0 eV and cause very high electrical resistivity of such a material. Annealing of ZnMgSe crystals in liquid Zn leads to

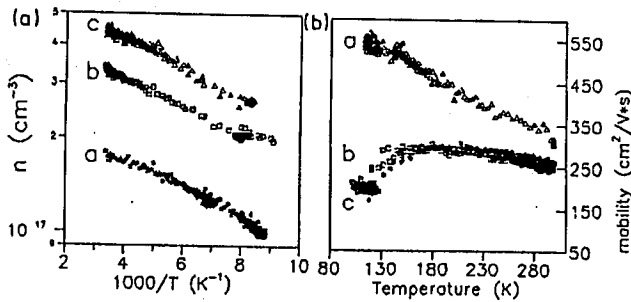


Fig. 2. Temperature dependence of electron concentration (a) and Hall mobility (b) in: *a* — ZnSe crystal, *b* and *c* — ZnMgSe crystals annealed in liquid zinc and Zn+Mg vapour at  $T = 1070$  K, respectively.

*n*-type conductivity with resistivity less than  $0.5 \Omega \text{ cm}$ . Electrical properties of such crystals were measured by the Van der Pauw method.

Figure 2 shows the electron concentration and the Hall mobility as a function of temperature for "pure" ZnSe (*a*) and for ZnMgSe crystals grown from the melt with 10% of Mg metal in starting material and then annealed in liquid zinc and Zn+Mg vapour (*b*, *c*). The electron concentration is larger in ZnMgSe crystal than in "pure" ZnSe which indicates that the concentration of isolated zinc vacancies or zinc vacancies complexes, which act as deep compensating acceptors, is lower in mixed crystals than in ZnSe. Using nondegenerate statistics, we obtained an activation energy about 10 meV for electrons in "pure" ZnSe and similar value for ZnMgSe crystals. This value is considerably smaller than the activation energy of 28 meV for isolated III-group donors in ZnSe derived from optical spectroscopy [8]. The small value observed for the activation energy in the temperature dependence of the free-carrier concentration is therefore a strong indication that *n*-type ZnMgSe crystals are in large degree compensated. From the study of the Hall data, various possible scattering mechanisms were considered within the theoretical analysis presented by Ruda [9]. The Hall mobility for undoped ZnSe crystal increases monotonically with decreasing temperature in the range 100–300 K, indicating that the major scattering mechanism is the scattering by optical phonons. The temperature dependence of mobility in ZnMgSe crystals indicates that the scattering by charged impurities plays an important role at temperatures lower than 140 K. The effect of the hydrostatic pressure on electron concentration and the Hall mobility was also measured but we did not observe any significant changes of electrical parameters with pressure up to 10 kbar.

To our knowledge ZnMgSe mixed crystals grown from the melt have not been investigated previously. Our results (low electrical resistivity and blue PL observed up to room temperature) indicate that this material can be very promising for future applications in constructing blue-violet electroluminescent devices.

## References

- [1] X.W. Fan, J. Woods, *IEEE Trans. Electron. Devices* **ED28**, 428 (1981).
- [2] M.A. Haase, J. Qiu, J.M. DePuydt, H. Cheng, *Appl. Phys. Lett.* **59**, 1272 (1991).
- [3] A.W. Livingstone, K. Turvey, J.W. Allen, *Solid State Electron.* **16**, 351 (1973).
- [4] W. Xie, D.C. Grillo, R.L. Gunshor, M. Kobayashi, H. Jeon, J. Ding, A.V. Nurmiko, G.C. Hua, N. Otsuka, *Appl. Phys. Lett.* **60**, 1999 (1992).
- [5] H.J. Łożykowski, P.O. Holtz, B. Monemar, *J. Electron. Mater.* **12**, 653 (1983).
- [6] H. Okuyama, K. Nakano, T. Miyajima, K. Akimoto, *Jpn. J. Appl Phys.* **30**, L1620 (1991).
- [7] Y. Morinaga, H. Okuyama, K. Akimoto, *Jpn. J. Appl. Phys.* **32**, 678 (1993).
- [8] W. Stutius, *J. Appl. Phys.* **53**, 284 (1982).
- [9] H.E. Ruda, *J. Appl. Phys.* **59**, 1220 (1986).