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OPTICAL AND ELECTRICAL PROPERTIES OF IODINE DOPED *n*-TYPE ZnSe CRYSTALS*

M. BALCERZYK, F. FIRSZT, H. MĘCZYŃSKA

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

We have studied the electrooptical properties of ZnSe single crystals doped with iodine by diffusion at high temperature. The obtained samples are highly conductive. The luminescence at 300 K (RT) is dominated by well known self activated orange emission. At 30 K the blue and orange emission is observed. The ratio of the blue emission peak intensity to the deep level one is much greater for the iodine doped samples than for the undoped intentionally ones.

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1. Introduction

The main problem in the light emitting devices based on ZnSe is to obtain the material with a controlled and high carrier concentration. Therefore, it is important to find the most suitable dopants for *n*-type ZnSe which do not cause the degradation of the photoluminescent (PL) properties. Recently, the group VII element donors are extensively investigated because of the high doping level which can be attained [1]. Among the group VII elements iodine seems to be the best one because of its weak chemical activity. There are only a few papers [2, 3] concerning thin films of ZnSe doped with iodine, but less attention has been paid to the bulk crystals [4]. We have attempted to dope with iodine ZnSe single crystals grown from the melt.

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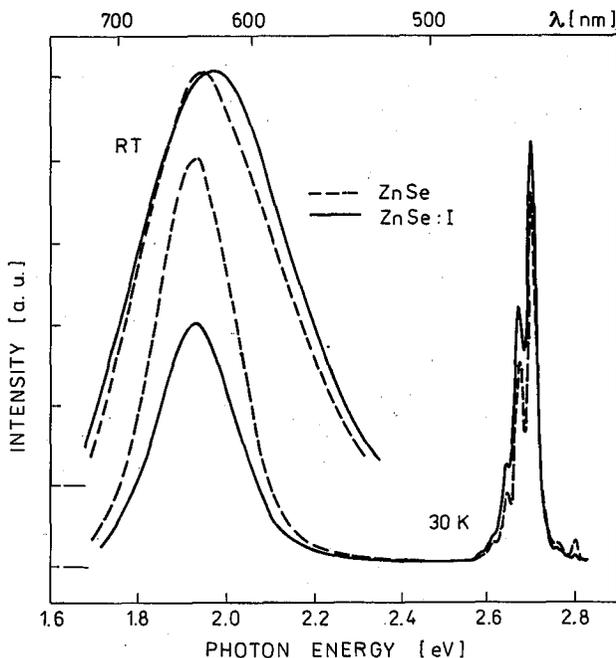


Fig. 1. Photoluminescence spectra at 30 K and room temperature of ZnSe undoped intentionally (dashed line) and ZnSe doped with iodine (solid line).

2. Experimental procedure

Samples used in this experiment were ZnSe crystals grown by high pressure Bridgman method. The crystals had the zinc blende structure involving a small amount of stacking faults. After cutting parallel to (111) crystallographic planes ZnSe plates were purified in liquid zinc at 1220 K during 47 hours and then mechanically polished and chemically etched. Two kinds of samples were prepared for measurements: first — doped with iodine by annealing ZnSe plates in evacuated quartz ampoule containing iodine and zinc vapour at 1220 K during 42 hours and second — undoped intentionally but only annealed in zinc vapour under the same conditions as the first one. After performing this process all samples were polished and etched again and indium contacts were alloyed for electrical measurements. The electrical properties were measured by van der Pauw method at the temperature range from 90 K to 300 K. The photoluminescence and photoluminescence excitation spectra were measured at 300 K and 30 K. PL was excited with ultra violet radiation (3.38 eV line from mercury lamp).

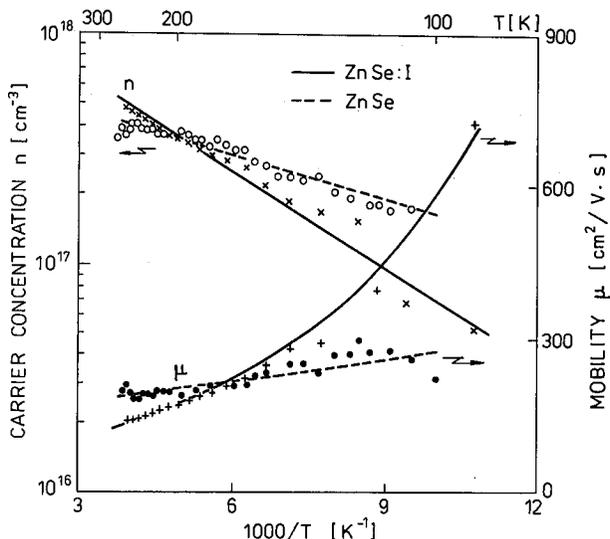


Fig. 2. Carrier concentration n and mobility μ dependence vs. inverse temperature for undoped intentionally ZnSe (dashed line) and for ZnSe doped with iodine (solid line).

3. Results and discussion

PL spectra of the investigated samples are shown in Fig. 1. At 30 K spectra of ZnSe doped with iodine and undoped intentionally consist of broad deep level emission band located approximately at 1.94 eV, blue near band-edge and exciton emission (2.6 eV–2.8 eV). At RT only the orange luminescence is observed with maxima at 1.980 eV and 1.962 eV for ZnSe doped with iodine and undoped respectively. The orange emission is associated with a self-activated center arising from a complex involving a zinc vacancy and a donor. This complex is formed at high temperature during the heat treatment. The exact nature of recombination responsible for the orange band is not perfectly understood, but it is proposed to be a donor–acceptor recombination. So far two models have been proposed: V_{Zn}^- associated with ionized donor form a (i) $(V_{Zn}^- - D^+)^0$ or (ii) $(V_{Zn}^- - D^+)^-$ complex [5]. It is observed for ZnSe doped with VII group elements that PL spectra are shifted towards higher energies in comparison with III group. In the case of Al and Cl this shift is about 40 meV [6]. In our samples the shift of about 20 meV is observed. In the case of the iodine doped ZnSe the blue emission intensity remarkably increases and the deep level emission intensity is much weaker in comparison with undoped one. The excitation spectra of the orange band at 30 K of both kinds of

crystals exhibit main maximum at 2.75 eV. For I-doped ZnSe the additional peak positioned in the vicinity of 2.45 eV is observed.

Because PL properties correlate with the electrical ones, we have measured the last ones by van der Pauw method. The results of measurements are plotted in Fig. 2. We have obtained carrier concentration: $n_{\text{ZnSe:I}} = 6 \times 10^{17} \text{ cm}^{-3}$, $n_{\text{ZnSe}} = 4 \times 10^{17} \text{ cm}^{-3}$ and mobility: $\mu_{\text{ZnSe:I}} = 140 \text{ cm}^2/(\text{Vs})$, $\mu_{\text{ZnSe}} = 170 \text{ cm}^2/(\text{Vs})$ at RT and $\mu_{\text{ZnSe:I}} = 650 \text{ cm}^2/(\text{Vs})$, $\mu_{\text{ZnSe}} = 270 \text{ cm}^2/(\text{Vs})$ at 100 K. The highest carrier concentration we have obtained for ZnSe:I was $3.5 \times 10^{18} \text{ cm}^{-3}$ at RT. This value coincides with that of ZnSe:I for the thin films.

The activation energy of 28 meV estimated for ZnSe:I is nearly equal to the value obtained for ZnSe:I layers [2]. We think that we have reported the first measurement of electrooptical properties of ZnSe:I bulk crystals grown from the melt and doped with iodine during high temperature diffusion.

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