Vol. 87 (1995) *ACTA PHYSICA POLONICA A* No. 2

Proceedings of the XXIII International School of Semiconducting Compounds, Jaszowiec 1994

A PHOTOACOUSTIC STUDY OF $Zn_{1-x}Mg_xSe$ MIXED CRYSTALS*

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The photoacoustic spectroscopy with a piezoelectric transducer was employed to evaluate the band gaps of a series of $Zn_{1-x}Mg_xSe$ mixed crystals of different composition. The photoacoustic measurements performed at room temperature yield information about the quality of the samples. The photoacoustic spectra were measured using the continuous wave and nanosecond pulse excitation.

PACS numbers: 62.65.+k, 78.20.Hp

Wide gap II–VI semiconductors are still of great interest because they are potentially efficient in the direct generation of blue and UV light. Among binary II–VI compounds the most interesting is ZnSe because blue near band edge luminescence in low resistivity ZnSe crystals has been observed up to room temperature. The blue emission band dominating at room temperature appears to arise from a transition between donor bound electrons and free holes in the valence band as was pointed out by Shirakawa and Kukimoto [1]. It is very difficult to get efficient near band edge emission in the blue region at room temperature because competing recombination via deep levels is correspondingly more important. It is a result of doping difficulties in ZnSe because the compensation and very often the donor impurities introduced create deep centers with the crystal defects. Recently the problem of doping in II–VI compounds was examined by Chadi [2] who suggested that the MgSe–ZnSe alloy is a very interesting system because of the possibility of obtaining large band gap semiconductor that can be doped low resistance n-type. Mixed crystals II–VI binary compounds with Mg halcogenides have recently attracted much attention which results from the possibility of tuning of band gap energies and lattice constants of these materials by adjusting Mg content in the alloy.

In this paper we report the application of the photoacoustic spectroscopy for studying the nonradiative processes and band-gap shift (BGS) of mixed crystals

*This work is supported in part by the State Committee for Scientific Research (Republic of Poland) under grant No. 2 2316 91 02.

with varying composition. $Zn_{1-x}Mg_xSe$ crystals were grown at the Institute of Physics, N. Copernicus University, by the high pressure Bridgman method using the Koch Light 6N ZnSe powder containing 20 mole percent of metallic magnesium as a starting material. After annealing of the samples in liquid zinc one can obtain n-type material with low electrical resistivity and good luminescent properties. During the growth process a noticeable segregation of magnesium occurs and as a result crystals with a gradient of Mg content along the growth direction are obtained [3]. The composition of the crystals was determined with the electron microprobe JEOL-JXA-50A [4].

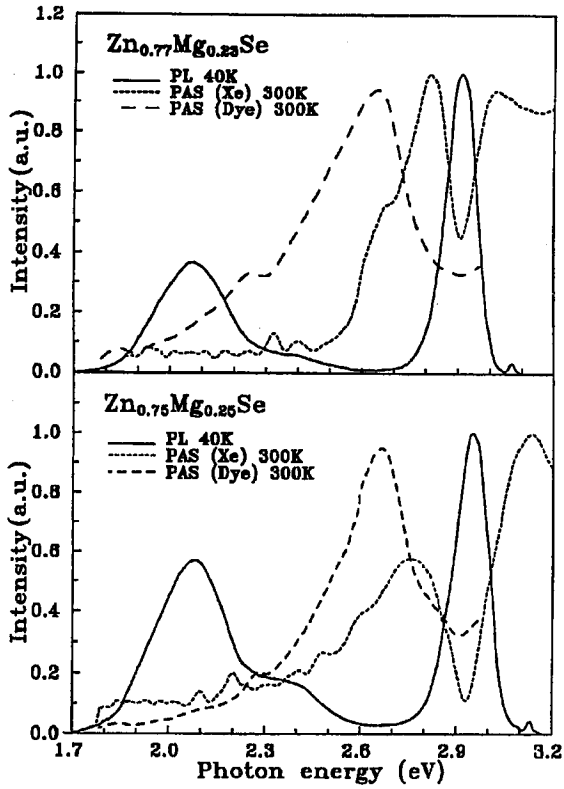

Fig. 1. Photoacoustic and photoluminescence spectra in $Zn_{1-x}Mg_xSe$.

The photoacoustic spectra were measured using an open cell with continuous wave (Xe lamp) or pulse (dye laser) excitation. The photoacoustic signal was detected by a PZT transducer. The typical photoacoustic spectra at 300 K of $Zn_{0.77}Mg_{0.23}Se$ and $Zn_{0.75}Mg_{0.25}Se$ for excitation by the Xe lamp and dye laser are shown in Fig. 1 together with the photoluminescence (PL) spectrum measured at 40 K. In PL spectrum emission lines at the high photon energy are of excitonic origin. Emission band at 2.8–3.0 eV were interpreted as an "edge emission" in mixed crystals. As the temperature increases, "edge emission" band is thermally

quenched and it is not observed at temperature above 200 K. The line of highest photon energy remains unquenched up to room temperature. The mechanism of the radiative recombination which is responsible for the blue violet luminescence in mixed crystals $Zn_{1-x}Mg_xSe$ at room temperature is not clear. It can be suspected that this luminescence is associated with radiative recombination of free exciton or shallow donor–valence band transition [4, 5].

The cw excitation photoacoustic signals which are related to the density of nonradiative states originating from defect or impurities have different character in the energy ranges greater and smaller than the fundamental absorption edge. The peak observed about 3.13 eV corresponds to the free exciton energy. The increase in the energetic distance between the exciton peak and peak at lower energy indicates the increasing disorder effects in the mixed crystals when the concentration of Mg increases. The same effects were observed for the different II–VI mixed crystals [6].

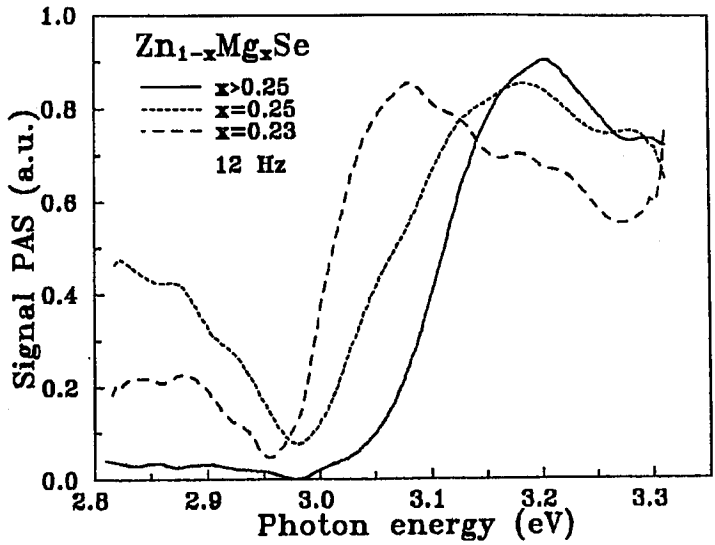

Fig. 2. The photoacoustic spectra of $Zn_{1-x}Mg_xSe$ crystals of various compositions.

We measured the band gap shift as the function of Mg concentration at 300 K. As can be seen from Fig. 2 all photoacoustic curves exhibit well expressed change of the slope at the high energy side of the minimum from which the band gap energies are determined. Within the limits of accuracy the values agree with data obtained from other measurements. The photoacoustic spectroscopy gives for the samples the following values for the energy gap: 3.03 eV, 3.13 eV, and 3.15 eV, whereas from the dependence of E_g on composition of the alloys the data obtained are: 3.07 eV, 3.13 eV, and 3.17 eV respectively. We obtained for the mixed crystals with increasing Mg concentration the increase in the band gap energies which confirms the band gap widening. It is clear that the substitution of Zn by Mg shifts the fundamental edge towards higher energies.

One of the advantages of photoacoustic spectroscopy is the possibility to obtain the optical absorption coefficient as a function of wavelength. For this purpose a suitable theoretical model has to be applied. We used the simplified model given by Poulet and Chambron [7] based upon the Rosencwaig and Gersho theory which applies to thermally thick samples. In this case the amplitude of the photoacoustic signal is equal to

$$S = A\alpha/[\omega^{3/2}(c\alpha/\omega^{1/2} + 1)^2 + 1]^{1/2}$$

with α — the optical absorption coefficient of the sample, ω — the modulation frequency, A and c — constants. The above given expression describes well the observed frequency dependence of the amplitude of photoacoustic signal for different samples investigated.

We also measured the photoacoustic spectra for mixed crystals using the pulse excitation. These spectra obtained are also shown in Fig. 1. It can be seen that in comparison to cw excitation a shift of the hole spectrum towards lower energy occurs. It can be connected with the much higher frequency response of system but for a detailed interpretation more investigations are required.

The pulse method reflects the bulk properties of crystals and is very useful for non-destructive measurements of semiconductors giving information about various defects, impurities and inhomogeneities. This problem is very important in mixed crystals obtained by Bridgman method. We investigated the inhomogeneity of the $Zn_{1-x}Mg_xSe$ sample using the photoacoustic microscope (PAM) constructed in our laboratory. The results obtained give evidence that the crystals obtained are of good quality.

Acknowledgment

The authors would like to thank M.Sci. B. Sekulska for technical support in sample preparation.

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