Vol. 84 (1993) ACTA PHYSICA POLONICA A No. 4

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

LUMINESCENCE QUANTUM EFFICIENCY OF Mn^{2+} STATES IN ZnSe:Mn AS STUDIED BY MEANS OF PHOTOACOUSTIC SPECTROSCOPY*

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The photoacoustic spectroscopy with a piezoelectric transducer was employed to determined the quantum efficiency for low Mn concentration in ZnSe monocrystals. The photoacoustic spectra were measured using the continuous wave excitation and nanosecond pulse method.

PACS numbers: 43.85.+f, 62.65.+k, 78.20.Hp

The determination of absolute luminescence quantum efficiency (QE) of ions in solids is important in both technology and basic physics. The photoacoustic spectroscopy (PAS) has been used quite successfully to obtain accurate absolute radiative quantum efficiency in solids because it does not require absolute calibration of the detector or knowledge of absolute ion concentration [1, 2]. Firstly, the PAS method was applied to highly absorbing materials even exhibiting concentration quenching of luminescence. In II–VI compounds for the first time this method was used by Ohba et al. [3] who have determined the luminescence quantum efficiency of Mn^{2+} in ZnS highly doped with Mn using the gas cell PAS method. It is well known that all wide band gap II–IV compounds with low amount of Mn show the yellow emission due to the internal transition $^4T_1(G)$–$^6A_1(S)$. In order to measure QE in ZnS with low Mn concentration Goede et al. [4] applied the transducer PZT (piezoelectric transducer) method which enables one to measure the structured PA spectra.

In this paper we describe the first determination of QE of ZnSeMn with low concentration (n_{Mn} = 0.02 mol%). The samples used in our investigations were single crystals of ZnSe doped with Mn grown by high pressure Bridgmann method. For growing the Koch–Light 6N ZnSe powder has been used.

The excitation spectra were obtained by visible lines of an Ar^+ laser (458 to 514 nm) at 300 K and 77 K. The gated photon counting system (Stanford SR 400) measured the intensity of the signal by counting the number of photons which were detected by a Hamamatsu R94302 photomultiplier in a given time gate.

*This work is supported in part by the Committee for Scientific Research under grant No. 2 2316 91 02.

The photoacoustic spectra were measured using an open PA cell with continuous wave (cw) or pulse excitation. In case of cw excitation the light source was a 600 W halogen lamp and its output was made to pass through a prism monochromator. The monochromatic light was chopped mechanically with variable frequency. Ten percent of light was split and fed to a reference detector while the rest of the light was focused on the sample. The PA signal was detected by a PZT transducer and analyzed with lock-in amplifier (Stanford SR 510) using the sine wave conversion method.

The photoacoustic spectra were also obtained using a dye laser pumped by an sealed pulsed nanosecond nitrogen laser (LN 300C Laser Photonics) with energy pulse 250 mJ. The output signal from PZT transducer was processed by a boxcar integrator.

All PA spectra were corrected for the spectral distribution of the optical system by normalizing the output signal to that of photodetector signal. The typical photoacoustic spectrum of ZnSe:Mn is shown in Fig. 1 (solid curve). As

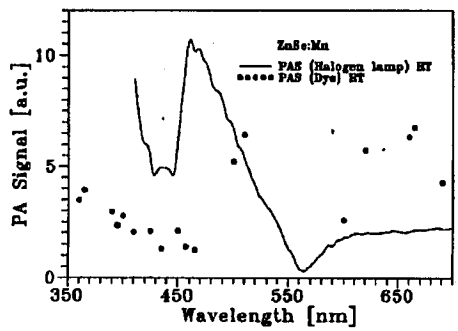

Fig. 1. Photoacoustic spectra of ZnSe:Mn.

can be seen, the transducer PZT method applied enables are to measure the PA spectrum for low Mn concentration in ZnSe.

On can find several characteristic structures in the photoacoustic spectrum. It is considered that these structures consist of light absorption due to the interband transition, shallow states near the band edge, and deep states in the band gap. The maximum at wavelength of 460 nm can be related to the light absorption by the band-to-band transition in ZnSe. The position of the observed peaks in the high absorption region corresponds to the free exciton energy as was observed for various wide gap semiconductors [4]. Clear depression of the PA signal at 575 nm shows the decrease in the nonradiative recombination processes.

As mentioned above we have extended our treatment of PAS effects to include the investigations of time dependent effects. The transient photoacoustic spectroscopy is highly sensitive and pulse response is often less difficult to analyze than the steady state one. We obtained PA "pulsed spectra" of the sample investigated within the range 350–700 nm which is also shown in Fig. 1 (full circles). It can be seen that this spectrum also exhibits a structure which differs from the "cw

spectrum". These are the first results of the transient photoacoustic measurements in II–VI semiconductors.

In order to determine the luminescence quantum efficiency we applied the procedure proposed by Rosencwaig [5] and Rockley [6]. The photoacoustic signal is directly related to the amount of light absorbed by the sample and converted into acoustic waves through nonradiative processes. When the absorption coefficient is small enough, quantum efficiency $\eta(\lambda)$ can be described by the formula

$$\eta(\lambda) = (\lambda_0/\lambda)(I_{ex}/B)/(I_{pa}/A + I_{ex}/B),$$

where λ_0 is the luminescence wavelength at the peak of the Mn^{2+} emission, I_{ex} and I_{pa} are relative intensities of the excitation and photoacoustic spectra, respectively, A and B are constants determined by the optical and thermal properties of the sample and the measurement systems. It must be noted that for the determination of $\eta(\lambda)$ only relative values are needed. Figure 2 gives the wave dependence of the quantum efficiency for ZnSe:Mn crystal.

To our knowledge this is the first PAS observation in ZnSE:Mn and more detailed investigations are carried out.

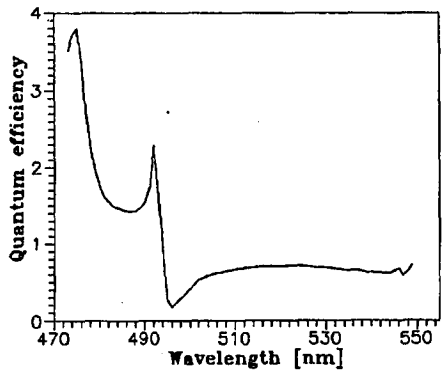

Fig. 2. Quantum efficiency for the ZnSe:Mn crystal.

References

[1] R.S. Quinby, W.M. Yen, *Opt. Lett.* **31**, 181 (1978).

[2] E. Halska, M.D. Dienstbier, P. Sladky, *Appl. Opt.* **38**, 321 (1993).

[3] Y. Ohba, M. Mizuba, H. Kukimoto, *J. Lumin.* **28**, 111 (1983).

[4] O. Goede, W. Heimbrodt, F. Sittel, *Phys. Status Solidi A* **93**, 277 (1986).

[5] A. Rosencwaig, E.A. Hildum, *Phys. Rev. B* **23**, 330 (1981).

[6] M.G. Rockley, *Chem. Phys. Lett.* **50**, 427 (1977).