H. MĘCZYŃSKA

Optoelectronic Properties of Wide Band Gap II–VI Compounds

The II–VI compounds are interesting not only from scientific point of view but also for their practical applications. These compounds are all of the direct transition type, satisfying the conditions for light — emitting materials. Unfortunately control of electrical properties of these compounds is often difficult. Besides in II–VI materials self compensation reaction take place and is very difficult to grow the p type crystals of ZnSe necessary to prepare p-n junction.

Significant progress has been made in the growth of this material by Molecular Beam Epitaxy (MBE). The elements of the group I (Li, Na) or V (N,P) are used as shallow acceptors with activation energy 110–126 meV. Recently K. Akimoto et al. [1] have found that the photoluminescence spectra of oxygen doped ZnSe at 4K are very similar to those N–doped. They established that oxygen which is an isoelectronic impurity in ZnSe acts as an acceptor. Also K. Akimoto et al. [2] have fabricated blue light emitting
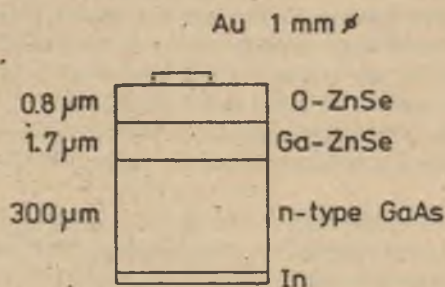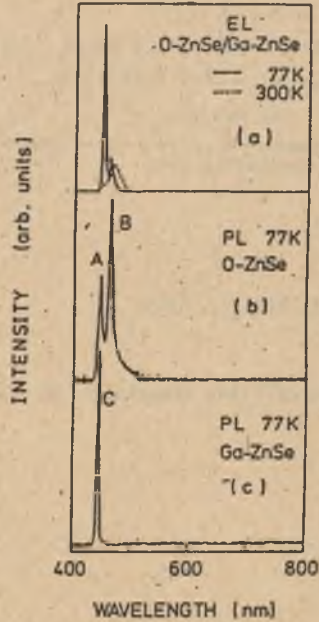

Fig. 1. Cross–section of diode

Fig. 2. (a) Electroluminescence spectra from ZnSe n – p junction diode.
Photoluminescence spectra of 0 – doped ZnSe (b) Ga – doped ZnSe

diodes. The structure of ZNSe p-n junction used is shown in fig. 1 and electro- and
photo-luminescence spectra in fig. 2.

The major efforts are directed to the growth of low resistivity p-type epilayers. The
epilayers of ZnSe grown on GaAs by MBE exhibit a free exciton peak with weak contri-
butions from donor-bound excitons [3]. Mar and Salansky[4] has demonstrated that at
high Zn to Se beam pressure ratio of 10 or higher but less than 15 is possible to grow
good quality material with photoluminescence spectrum dominated by intrinsic — exci-
ton related luminescence. Bala and Firszt [5] obtained ZnSe epilavers on GaAs substrate
by MBE under different flux rations of Zn and Se. Epilavers grown under conditions
with high Zn:Se flux ratios show strong blue emission in exciton region and weak deep
levels luminescence (Fig. 3). Observed shift of exciton lines toward higher energies in thin
films in comparison with those of single crystals was interpreted as the effect originated
from uniaxial strain imposed by the lattice mismatch between ZnSe and GaAs. Bala
[6] obtained ZnSe epilayers on GaAs by MBE under conditions with high Zn ; Se ratio
fluxes. The observed variation of the photoluminescence with thickness is interpreted in
terms of defects accumulation due to high dislocation density within a thin layer near
the ZnSe-GaAs interface.

Recently Bala et al. [6] have measured the Raman scattering spectra of ZnSe-GaAs
epilayers and ZnSe crystal in the temperature range between 270 and 520 K. At room
temperature the Raman spectrum for ZnSe epilayers consists of LO phonon at 252 cm
and two LO phonon at 504 cm . With increasing temperature the change of above
LO phonon intensities for different exciting lines was observed. It was established from
Raman spectra at different temperature that the splitting between the heavy and light
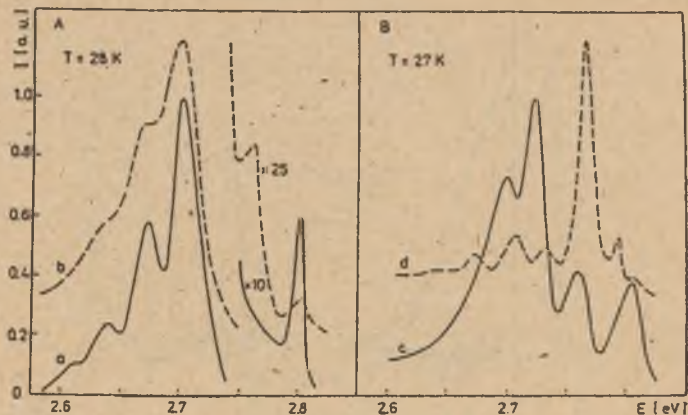
Fig. 3. Photoluminescence spectra in blue emission region of ZnSe single crystals (A) and epilayers (B); curves a and b correspond to ZnSe annealed in zinc at 1223 K and 903 K respectively; curves c and d correspond to ZnSe epilayers grown with Zn:Se = 1:1 and ZnSe = 1:2 flux ratios respectively

hole bands is nearly equal to the energy of two LO phonon. It was concluded that strain in ZnSe-GaAs epilayer are affected by the mismatch of lattice constants, the difference in thermal expansion coefficients and misfit dislocations.

Although pressure studies of semiconductors are extensive and have contributed substantially to understanding of these electronic structure relative little pressure work has been done on II–VI compounds. K. Takarabe et al. [8] have investigated pressure effects on electron thermal emission rate of n — ZnSe: In/GaAs epilayers by means of ICTS. M. Grinberg [9] proposed the model of bistable donor center for describing the metastable electron traps in cubic semiconductors. The analysis of the model suggest the possibility of investigation the metastable donor under hydrostatic pressure in II–VI compounds. The most interesting is CdTe and ZnSe, the first due to the high energy of Fermi level for heavily doped material and the second due to the wide range of changes of Γ minimum energy with pressure.

Presently the renewed interest and progress on II–VI compounds is observed. Progress in microscopic theories of defects has been achieved as well as in experiment where different techniques from atomic physics were adopted (ODMR, ESR, ENDOR) and bulk electrical measurements have been replaced by junction methods (DLTS). In addition the photoacustic and photothermal spectroscopic techniques were applied to the characterization of electronic properties and defect structures in II–VI. especially for investigation of isovalent impurities. The ability of this techniques is to yield direct information about nonradiative deexcitation [10]. But there is still much about II–IV compounds that is poor understood. For example shallow — deep instability of luminescence centers and their interaction with lattice. persistent photoconductivity, microscopis nature of defects influencing the properties of the host material.

Important problem investigated is the influence of electron — phonon interaction on the energy of localized states. M. Grinberg [11] has examined the influence of lattice deformation on shallow donors in ZnSe which is an example of weak phonon — electron interaction. He has assumed that the donor disturbs the lattice in the same way as an isovalent impurity from the same row of the periodic table. From his considerations follows that the total short range pseudopotential of donors in ZnSe are attractive for donors substituting Zn and repulsive for donors in Se position. This site effect causes an increase (decrease) of energies for donors in anion (cation) positions.
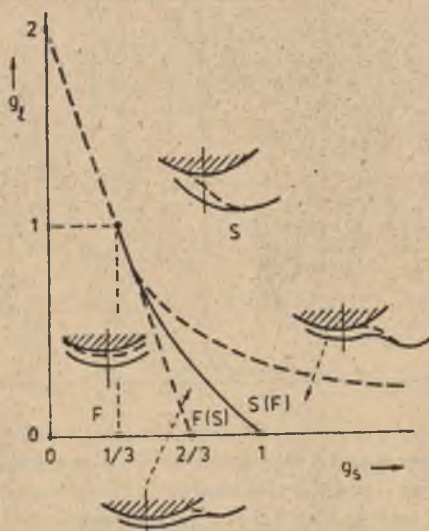
Fig. 4. Phase diagram for stable (metastable when inside a parenthesis) state of an electron subject to short range g_s interactions with lattice defect and phonon fields

A. Wójtowicz and C. Koepke [12] have investigated the temperature broadening of the green Ag_{Zn} luminescence band of $ZnSe$. The shape of luminescence band involving localized states of impurities is mainly determined by the electron — phonon interaction. Strongly nonlinear, moderately coupled resonance mode due to Ag must be assumed in order to fit the experimental data.

The most interesting problem is the strong electron — phonon interaction (Huang S-factor > 10) which leads to so called negative U behavior. Metastable defects states, persistent photoconductivity and recombination enhanced defect reaction. The theoretical description of the above phenomena has been given by Toyozawa [13] who assumed that the electron states are strongly localized (self trapped states S type) or delocalized one (free F type), fig. 4. The most representative defect exhibiting metastable effects characterized by very large difference between the optical and thermal ionization energies is Cl in CdTe ($E_{op} = 0.95$ eV, $E_{th} = -0.15$ eV, $E_b = 0.30$ eV) [14]. It must be noted however that in II–VI compounds electron — phonon interactions are not strong enough to cause intrinsic self-trapping but enough to cause extrinsic self-trapping. Recently M. Grinberg [15] has made a probe to extend Toyozawa's model for self-trapped electron.

Very interesting properties have II–IV compounds with donor impurities from the third and seventh group of the periodic table. These elements are in common use as coactivators in the preparation of fluorescent materials. Their function is to promote the incorporation of acceptor like activators in the desired state. The incorporation of the above mentioned donors in II–VI compounds without the simultaneous addition of foreign acceptors often leads to the formation of compensating metal vacancy acceptors and to the observation of self-activated (SA) fluorescence. For example ZnSe layers with excellent morphology compared to III–V epitaxial layers have been grown by MOCVD which exhibit a PL spectrum dominated by free exciton emission [16]. However SA emission was drastically increased by introduction of Al, which generate not only shallow donors but also SA centers. SA centers makes the luminescence color poor and electrical
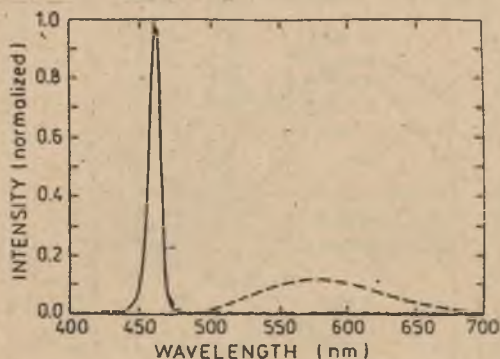
Fig. 5. Typical photoluminescence spectrum for Cl doped n – type ZnSe grown on (100) GaAs substrate

property control difficult.

Recently group VII element — donors have attracted much attention for n – type doping, because chlorine doped ZnSe exhibit doping levels as high as 10^{19} m^{-3}. ZnSE: Cl samples show strong blue luminescence for the same carrier concentration. compared to ZnSe: Al [17]. Chlorine acts mainly as a shallow donor and does not generate deep acceptor levels fig. 5. Another problem investigated in II–VI are neutral or „isoelectronic" defects characterized by a strongly localized potential for the binding of the charge carrier. The behavior of substituted impurity Te which acts as an isoelectronic center when is replacing the host anion is the subject of numerous experimental investigations.

The $ZnSe_{1-x} - ZnTe_x$ belongs to the interesting class of semiconductor alloys in which Te acts both as an isoelectronic trap and as a constituent of the system. For x = 1% alloy one can observe exciton self-trapping induced by Te atoms which is different from that observed in other II–VI mixed crystals [18] fig. 6 S. Permogorov [19] confirmed a model for exciton localization in ZnSe:Te according to which the electron moves in a large Coulomb orbit around the hole which is tightly bound by some small Te cluster.

As was mentioned before progress has been achieved by using ODMR technique which allow the identification of large number of recombination centers. For II–VI compounds ODMR can be used to: 1. identify donor — acceptor recombination bands. 2. identify centers participating in such recombination and determination the energy structure of these centers. 3. study energy transfer, 4. study exchange and hyperfine interaction [20].

The large band-gape II–VI compounds (e.g. ZnO, ZnS, ZnSe) are most easily studied by ODMR. The application of the ODMR method to narrow band-gape II–VI is much harder because of fast acceptor spin relaxations processes. Using ODMR N.R.J.Poolton [21] has shown that the strong green emission band at 2.35 ± 0.02 eV (525 nm) in ZnSe:Ag is due to recombination between shallow donors and medium deep acceptors 0.31 ± 0.05 eV above the valence band. The center proposed is an acceptor like complex $(Ag_{Zn}^{2+} - Se^{2-} - Ag_i^+)$ in paramagnetic state. F. Rong, and G.D. Watkins have identified by ODMR the luminescence associated with three distinct Zn vacancy — Zn interstitial Frenkel pairs in electron irradiated ZnSe [22] and in '87 they reported for the first time the direct observation of isolated Zn — interstitial defects in ZnSe [23].
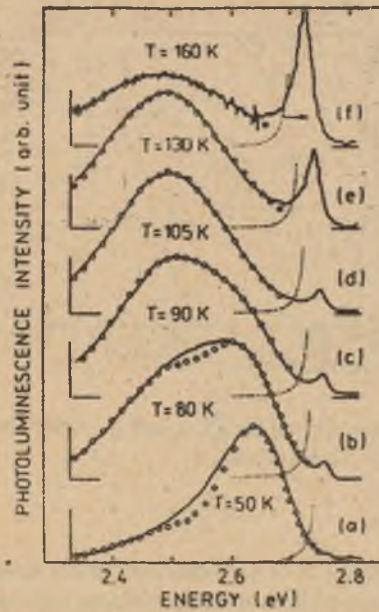
Fig. 6. Photoluminescence of a $ZnSe_{1-x}Te_x$ alloy

In the investigation of the nature of the luminescence centers especially the symmetry, the measurement of the polarization of luminescence is a very useful tool. Measurements of the polarization of luminescence give information about the nature of luminescence centers especially about their symmetries. Examining the dependence of the polarization properties of luminescence on the polarization of the excitation light is possible to decide whether or not the center has symmetry which is lower than that of the host lattice. M. Maliński [24] has investigated the polarization of luminescence of the self-activated ZnSe, ZnSe:Ag, ZnSe:Cu, ZnSe:Al and ZnSe:Ag,Al. He obtained interesting results for SA luminescence. The polarization measurements have shown that: 1. SA centers are anisotropically distributed in the crystal on the plane (111). 2. The luminescence centers is $V_{Zn}^{-2} - Al_{Zn}^+$ with C_3 symmetry. M. Maliński and H. Męczyńska [25] observed for the first time the effect due to the stacking disorder on the distribution of self activated luminescence centers in ZnSe. It can be stated that Al ions are grouped preferentially in faulted region. The centers are mainly oriented parallel to the (111) planes and give evidence that the cations distribution is caused by stacking faults itself, i.e. their electric charge. Also M. Malinski et al. [26] have investigated the nature of copper — yellow centers in ZnSe. The results obtained indicate that the center responsible for this band has the symmetry lower than T_d. It was stated from the polarization excitation spectrum and the polarization diagrams that the center responsible for the polarization characteristics has C_{3v} symmetry. The model proposed the acceptor as substitutional interestitial pair of copper ions $(Cu_{Zn}^+ - Cu_I^+)^0$ where Cu_I^+ ion occupies an interstitial site with O_h symmetry.

Another group of interesting problems connected with II–VI is to obtain a novel materials for the future optoelectronic devices. Makato Kanogoi et al. [27] obtained ZnSe — ZnTe strained — laver superlattices grown by molecular beam epitaxy. The
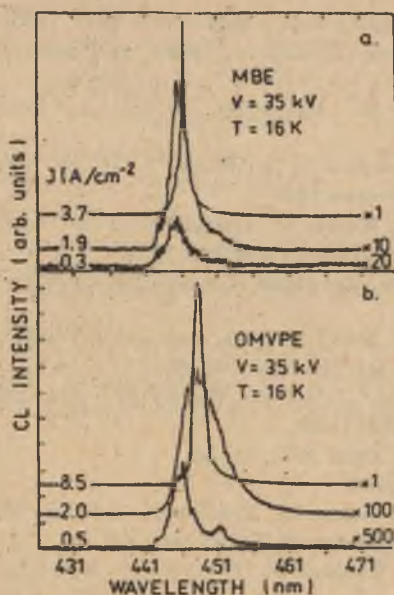
Fig. 7. Spectra of ZnSe films prepared by MBE and OMVPE method

luminescence color in the visible changed from blue — green to red. In order to obtain both n and p type conduction a modulation doping technique was used. The ZnTe:Sb samples typically had hole concentrations of $0.5 - 1.0 \times 10^{14}$ cm^{-3} and hole mobilities 120–220 cm^2/V ·s and ZnSe:Ga electron concentrations of $2–7 \times 10^{13}$ cm^{-3} and mobilities of 200–700 cm^2/V ·s. These authors also obtained for the first time the ZnSe — ZnS layer grown by metalorganic molecular beam epitaxy on GaAs substrates. J.E. Potts et al. [28] have observed lasing in ZnSe epitaxial layer on (100) GaAs under pulsed electron beam excitation at temperatures as high as 295 K fig. 7.

It must be mentioned that recently a CdS chemically sprayed films were investigated. W. Dulak and H. Męczyńska [29] have found that pH value of the solution can be used as a control parameter in the above mentioned method and for the first time the elctro-absorption have been observed. The electroabsorption spectra give the evidence that we have really the exciton lines not the interference effects in films. C. Koepke [30] observed at room — temperature optical bistability caused by induced absorption in spray CdS layer.

REFERENCES

[1] Akimoto K., Miyajima T., Yoshifumi M.: Phys. Rev. B, 1989, 39, 3138.
[2] Akimoto K., Miyajima T., Yoshifumi M.: Jap. J. Appl. Phys. 1989. 28. L 531.
[3] Shahzad K.: Phys. Rev. B. 1988. 38. 8309.

[4] Park R.M., Mar H.A., Salansky N.M.: Appl. Phys. Lett. 1985, 46, 385.

[5] Bala W., Firszt F.: Procc. XVIII Int. School on Physics of Semiconducting Compounds, Jaszowiec 1989.

[6] Bala W.: Procc. of 3rd Int. Symposium of Molecular Beam Epitaxy, Velico Tarnovo,1989.

[7] Bala W., Kozielski M., Drozdowski M.: Procc. XVIII Int. School on Physics of Semiconducting Compounds Jaszowiec 1989.

[8] Takarabe K., Minomura S., Kusaka M., Matsuda K., Procc. of the Int. Conference on High Pressure Science and Technology Paderbcrn 1989.

[9] Grinberg M., Procc. of the Int. Conference on High Pressure Science and Technology, Paderborn 1989.

[10] Goede O., Heimbrodt W., Sittel F.: phys. stat. sol. (a) 1986, 93, 277.

[11]Grinberg M.: phys. stat. sol. (b) 1988, 145, 619.

[12] Wojtowicz A.J., Koepke C.: Acta Phys. Polon. 1987, A71. 385.

[13] Toyozawa Y.: Physica 1983, 116B, 7.

[14] Nelson R.J.: Appl. Phys. Lett. 1977, 31, 351.

[15] Grinberg M.: to be published

[16] Kamata A., Uemoto T., Okajima M., Hirahara K., Kawachi M., Beppu T.: 18-th Conf. on Solid State Devices and Materials, Tokyo 1986, 647.

[17] Kamata A., Uemoto T., Okajima M., Hirahara K., Kawachi M., Beppu T.: J. Cryst. Growth 1988, 86, 285.

[18] Lee D., Mysyrowicz A., Nurmikko A. V., Fitzpatrick B. J.: Phys. Rev. Lett. 1987, 58, 1475.

[19] Permogorov S., Reznitsky A., Naumov A., Stolzp H., von der Osten W.: J. Lumin. 1988, 40/41, 483.

[20] Davies J. J.: J. Cryst. Growth 1985. 72, 317.

[21] Poolton N.R.J., Davies J.J., Nicholls J.E.: Cryst. Growth 1985, 72, 336.

[22] Rong F., Watkins G.D.: Phys. Rev. Lett. 1986, 56, 2310.

[23] Rong F., Watkins G.D.: Phys. Rev. Lett. 1987, 58, 1486.

[24] Maliński M.: PhD thesis UMK Toruń 1988.

[25] Maliński M., Męczyńska H.: Procc. XVIII Int. School on Physics of Semiconducting Compounds, Jaszowiec 1989.

[26] Maliński M., Męczyńska H., Firszt F.: Abstracts of 4 th Int. Conference on II — VI Compounds, Berlin 1989.

[27]Kanagai M., Kobayashi M., Kimura R., Takahashi K.: J. Cryst. Growth 1988, 86, 290.

[28] Potts J.E., Smith T.L., Cheng H.: J. Cryst. Growth 1988, 86, 935.

[29] Dulak W., Męczyńska H.: phys. stat. sol. (a) 1986, 93. K171.

[30] Koepke C.: phys. stat. sol. (b) 1987, 141, K139: Acta Phys. Polon. A73 (1988) 395.