EFFECT OF THERMAL ANNEALING IN Bi AND Zn MELTS ON LOCAL CENTERS IN ZnSe

V.A.KOROTKOV*, L.E.KOVALEV*, L.I.BRUK*, O.S.GOREA*, P.I.KETRUSH*, L.V.MALIKOVA**

* Physics Department, State University of Moldova, Mateevich st. 60, Kishinev, Moldova, MD 2009, ecran@cinf.usm.md

** Physics Department and NY State Center for Advanced Technology in Ultrafast Photonic Materials and Applications, Brooklyn College of CUNY, 2900 Bedford Avenue, Brooklyn, NY 11210, lmakova@its.brooklyn.cuny.edu

ABSTRACT

Time-resolved photoluminescence (TRPL) at T=4,2K, electron paramagnetic resonance (EPR) in the range of 4,2K-77K, and wavelength modulated transmittance (WMT) spectra for both undoped and annealed in Bi and Zn melts ZnSe single crystals have been investigated. It is found that the annealing in Bi melts leads to recovery of crystal structure. This supposition is based on the increase of fine and hype fine interaction of residual Mn^{2+} ions with the simultaneous decrease of the EPR signals line width and the decrease of the F-center line. Furthermore, the band with λ_{max}=520 nm disappears, while exciton band I_1 (λ_{max}=445 nm) and edge band Q_0 - DAP (λ_{max} =460,2 nm), involving Al_{Zn} - Li_{Zn} pairs, become more revealed. At the same time, band narrowing of the TRPL spectra was observed. The annealing in Zn melt causes the increase of the number of F-center. From WMT spectra the energy position of local centers and the dominant influence on impurities and defects of the crystal structure were investigated.

INTRODUCTION

The perspectives of ZnSe utilization in fabrication of the optoelectronic devices for green and blue region of spectrum caused intensive investigations of the inherited defects influence on its properties. The first works in this direction by using thermal annealing in zinc melt were carried out by Aven et al. [1]. Annealing in Zn is efficient found reducing the zinc vacancies V_{Zn}, which are deep acceptors, participating in the selfcompensation of charged (valence) states of impurities and inherited defects as well as the extraction of same impurities. The V_{Zn}

Mat. Res. Soc. Symp. Proc. Vol. 487 © 1998 Materials Research Society

concentration decrease inhibits impurity doping by substituting Zn in the crystalline lattice. A series of works are dedicated to the investigations of the annealed crystals luminescent characteristics. The obtained results have been interpreted. Interest exists regarding ZnSe annealing in non-containing Zn melts. As an example of such studies the works [2.3] can serve, were the main of the melt was Bi. This heavy metal with an atomic radius of 0,182 nm and ionic one for Bi^{3+} - 0,120 nm and for Bi^{3-} - 0,213 nm [4]. Therefore Bi diffusion in ZnSe is inhibited and impurity defects concentration is determined by their diffusion and solubility in Bi melt and in the ZnSe crystal at the annealing temperature. In [2,3] only luminescent studies were carried out.

For a luminescent material like ZnSe it is interesting along with optical and photoluminescent characteristics the investigation of the electron paramagnetic resonance. This allows to estimate the state of internal electrical field near paramagnetic centers, stipulated by impurity-defects composition of zinc selenide.

EXPERIMENT

High resistivity ZnSe single crystal with the background impurities, possessing of photoconductivity "spectral memory" [5,6] and crystals annealed in Zn or Bi melts were studied. Initial samples of ZnSe had the resistivity ρ in the dark of $\sim 10^{12}$ Ohm$\cdot$cm, concentration of free electrons $n \sim 10^{7}$ cm^{-3}, and carrier mobility in the dark $\mu \sim 1 cm^{2}/V \cdot s$. The annealing in Zn or Bi melts was carried out during 100 hours in silica tubes, so that the whole cystal was in the metal melt. The sample volume was 10 times less than the melt volume. After annealing in molten Zn, the dark resistivity sharply decreases up to $\sim 10^{1}$-10^{2} Ohm$\cdot$cm, and in Bi melt ρ decreases to 10^{6}-10^{7} Ohm$\cdot$cm.

On selected crystals the TRPL at 4-300K as investigated. The luminescence excitation was carried out by a nitrogen laser (λ = 337,1 nm) in pulses (τ = 10ns). A box-car integrator BCI-986 having the time windows from 10ns to 40ms was used to record the TRPL. It was shifted up to 100μs after the start pulse was applied. WMT spectra were studied at 77K. The wavelength modulation of the incident radiation was carried out by the vibration of the output mirror of the grating monochromator MDR-2. The modulation frequency was 82 Hz.

EPR studies were carried out on a Thomson unit, which allowed one to record the minimum concentration of paramagnetic centers $\sim 10^{16}$ cm^{-3}. The mesurements were carried out in the temperature rage 4-300K.

RESULTS

In the low temperature (4,2K) TRPL of all samples, the exciton line I_1 (4451Å) [7] (Fig.1.a,b,c) stipulated by radiative annihilation of the excitons bound to neutral accepters (V_{Zn}) are observed. The I_1 line possesses low life time after radiation and rapidly decreases with the increase of delay time of antiparalysing pulse. In TRPL spectra of the crystals annealed in Zn or Bi melt the phonon replic of I_1–LO line is observed. After annealing in Bi the phonon replica is more pronounced. In the region of the band edge radiation the Q_0 band (4600Å) is revealed, for which, supposedly, the radiative transition the donor - accepter pair (DAP) Al_{Zn} - Li_{Zn} [8] is responsible. The Q-series is characterized by higher intensity after radiation time, than exciton annihilation and it is better pronounced at the delay time higher than 60 ns, when exciton luminescence already significantly decrease. In the spectra of the initial ZnSe crystals, the wide green PL-band (λ_{max} =520nm) (Fig.1.a) is observed after long delay time. This band is related to deep acceptor levels (A-centers), situated at 0,38eV higher than ZnSe valence band top [9]. For the crystals subjected to heat treatment in Zn or Bi melt, this band in PL spectra is missing (Fig.1.b,c). After annealing in Zn in PL spectrum a band with the radiation maximum at 479 nm (Fig.1.b) and its LO-fonons replica are present in PL spectrum.

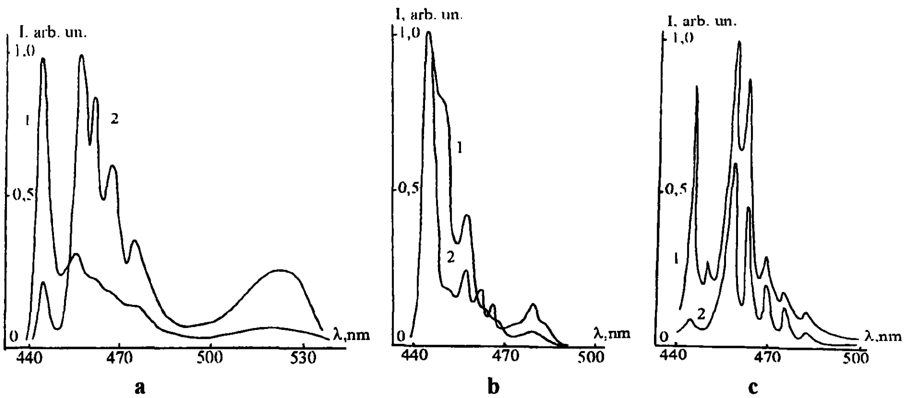

Fig.1. TRPL spectra for ZnSe crystals at 4,2 K.
a - for initial samples; b - for samples anneled in Zn melt; c - for samples anneled in Bi melt; curve 1 – time windows 5 ns; curve 2 – time windows 60 ns.

Investigation of the transmission spectra by using λ-modulation method allowed to reveal defects situated energetically in vicinity of band gap edge of ZnSe. For initial samples with different distribution of residual impurity-defects centers, a variety of the differential transmission spectra were obtained. However the maxima at 445 nm, 451 nm, 455 nm, 457 nm and 459 nm were present in the spectra of all types of the samples. This indicates, apparently, the common nature of these centers, related to ZnSe inherited and impurity background states.

Studies of EPR spectra had shown that ZnSe crystal heat treatment in Zn or Bi changes hyperfine structure (HFS), and its lines splot by the inter crystalline field. In Fig.2.a an EPR spectrum of initial ZnSe sample at 77K and magnetic field orientation along to the principal symmetry axis of crystal for Mn^{2+} centers is given. In the spectrum six lines of hyperfine interaction of paramagnetic electrons with its own Mn nucleus are clearly observed with the constant a = 67,6 Oersted and also the line with g-factor equal to 2,001. According to [10,11], Mn^{2+} ions (g = 2,007) are acting like substituting impurity of double valence Zn ions. The edge line width in Mn^{2+} EPR spectrum equals to 14,4 Oersted. EPR spectrum (77K) of the crystals annealed in Zn melts is given in Fig.2.b. The line with g = 2,001 is dominant. Moreover, the structure stipulated by Mn^{2+} ions is observed. The intensity of the line with g = 2,001 increases after crystal annealing comparable with its value in initial material. An EPR spectrum of the crystals annealed in Bi melt is given in Fig.2.c.

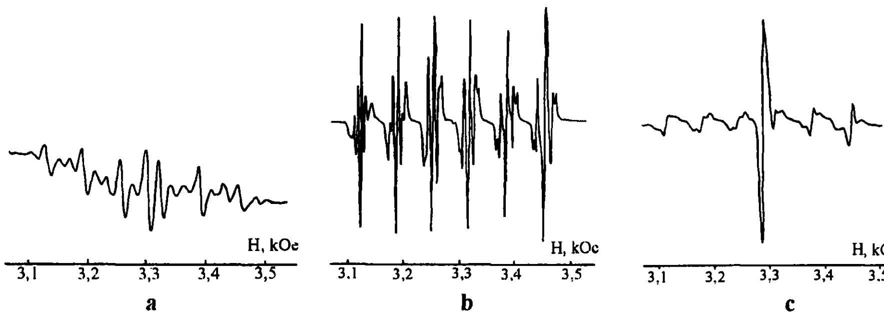

Fig. 2. EPR spectra for ZnSe crystals at 77 K.

a - for initial samples; b - for samples anneled in Zn melt; c - for samples anneled in Bi melt.

The hyperfine interaction lines in Mn^{2+} ions as well as influence of internal electrical field as a fine interaction lines are more clearly revealed the fine interaction constant a = 9,0 Oersted. The hyperfine interaction a = 5,6 Oersted extreme lines half width is less than in the initial samples. The intensity of the lines with g = 2,001 decreases comparable with the lines stipulated by Mn^{2+} and is much less than for the crystal before annealing.

CONCLUSIONS

The comparison of the results of ZnSe crystals low temperature TRPL shows that annealing in Bi melt efficiently influences the impurity defect composition. As in the case of annealing in Zn melt, the band with maximum at 520 nm (2,384 eV) stipulated, apparently, by a complex center including V_{Zn} disappears. However, the band close to 479 nm (2,588 eV), which probably is related to Zn_i, V_{Se}^{-} or V_{Zn}^{++} and their associates does not appear. After the annealing in Bi melt, the exciton edge luminescence along with simultaneous radiation band narrowing is more pronounced. In Mn^{2+} EPR spectra the hyperfine structure lines narrowing more than 2,5 times, compared to their width in the initial crystals, is observed. This allows to suppose that the regulation of ZnSe lattice regulations occurs and internal electrical field become more homogeneous. Apparently, V_{Zn} healing occurs due to the migration of interstitial Zn and of background impurities, possibly Mn, which can occupy places in the cation sub lattice. The increasing of the vacancies concentration in anion sub lattice after the annealing in Zn is indicated by the increasing of the intensity of the line with g = 2,001 in EPR spectrum, stipulated by F-center (i. e., by the electron captured by anion vacancy). Annealing in the liquid Bi leads to the opposite effect. The intensity of the line with g = 2,001 decreases, (i. e., the concentration and charge state of V_{Se} decreases). Possibly double vacancies ($V_{Zn}V_{Se}$) are forming with the reciprocal charge (valence) compensation, leading to the regulation of the internal electrical field.

Bismuth presence in Pl and EPR spectra was not revealed; although Bi, having uncompleted internal electron shell $6s^2 6p^3$, should reveal paramagnetic properties, as one unpaired 6p electron is present. Bi incorporation in the interstitial sites is improbable due to its high atomic and ionic radius. It was shown that the annealing of ZnSe crystals with background impurities annealing in Bi melt leads to the regulation of their crystalline structure.

REFERENCES

1. M. Aven, H.H. Woodbury, Appl. Phys. Lett. **1**, p.53 (1962).

2. K.D. Sushkevich, A.V. Simashkevich, A.V. Koval, Sov. Phys. Semicond., **23**, p.737 (1989).

3. A.V. Simashkevich, K.D. Sushkevich, A.C. Korol et al., Bul. Mold. Acad. of Science, Phys. and Tech., **14**, p.21 (1994).

4. V.A. Rabinovich, Z.Ya. Havin in Kratkii Chem. Sprav., Chemistry, Leningrad, 1978, p.392.

5. V. Korotkov, L. Malikova, L. Bruk et al., Abstracts MRS 1996 Fall Meeting, p.189 (1996).

6. L.I. Bruk, O.S. Gorea, V.A. Korotkov et al., Neorg. Mater. of Russia. **31**, p.1296 (1995).

7. E. Koh, D.W. Langer, J. Luminescence. **1-2**, p.514 (1970).

8. J.L. Merz, K. Nassan, J.W. Shever, Phys. Rev. B. **8**, p.1444 (1973).

9. A.A Berejnaya, P.N Zanadvorov, Yu.p. Maximov et al., Sov. Phys. Stat. Sol. **30**, p.2206 (1988).

10. B. Koch, Nachrichtentehenic, **20**, p.468 (1970).

11. A.S. Kushnir, B.G. Nosachov, S.A. Omelchenko et al., Sov. Phys. Stat. Sol. **17**, p.1471 (1975).