Semiconductor Physics, Quantum Electronics & Optoelectronics, 2016. V. 19, N 4. P. 391-394.
doi: https://doi.org/10.15407/spqeo19.04.394

PACS 78.55.Et, 78.60.Lc

Influence of ytterbium impurity on luminescent properties of ZnSe⟨Al⟩ crystals

V.P. Makhniy[1], N.D. Vakhnyak[2], O.V. Kinzerska[1], I.M. Senko[1]
[1]*Yuriy Fedkovych Chernivtsi National University*
[2]*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine*

Abstract. The influence of Yb impurity on evolution of luminescent properties of zinc selenide crystals doped with Al in the growth process is discussed. It was ascertained that diffusion of Yb impurity in a closed volume from vapor phase of ZnSe⟨Al⟩ substrates causes "quenching" the yellow-green band and appearance of intensive blue luminescent band that has exciton nature.

Keywords: zinc selenide, luminescence, ytterbium, point defects, associates.

Manuscript received 07.06.16; revised version received 30.08.16; accepted for publication 16.11.16; published online 05.12.16.

1. Introduction

The unique set of physical-and-technical parameters of zinc selenide determines the prospects of its practical usage in various fields of functional electronics, which stimulated development of technology for receiving bulk crystals with good quality [1]. However, the most common melt crystals of ZnSe, both undoped and doped with different elements in the process of growth, usually contains a significant number of own and uncontrolled impurity point defects, and therefore their parameters do not always correspond to the desirable ones. In particular, this applies to receiving materials with dominant edge luminescence, which can serve as a basis of blue sources for spontaneous [2] and forced [3, 4] radiations. Unfortunately, boundary luminescence of as-grown ZnSe crystals at room temperature is inefficient, and the spectra are usually kept as unwelcome long-wave bands [5]. Therefore, additional processing is used to suppress the latter ones, which requires to perform high temperature annealing in melt or vapor of own components or other elements. In particular, currently doping the crystals undoped in melt but doped in a closed volume from vapor phase with elements of I group (Li, Na, K) [6], tin [7], magnesium [8], selenium [9] and ytterbium [10] enabled to receive the samples with a single blue luminescence band at 300 K. It is obvious that usage of ZnSe with another composition of point defects should lead to other luminescent properties, which requires separate researches.

2. Samples and research methods

The initial substrates were plates with the dimensions $4\times4\times1$ mm^3 cut from bulk ZnSe⟨Al⟩ crystals. These crystals were grown from stoichiometric melt under pressure of inert gas and doped with aluminum during the process of growth. Plates were subjected to mechanical and chemical polishing in CrO_3:HCl = 2:3 enchant, and also to careful washing in distilled water and then finishing drying. As a result of these treatments, surface of such substrates visually acquired mirror look, and observed was pronounced photoluminescence (PL) that was absent in the samples polished only mechanically. Doping with ytterbium impurity was carried out using the diffusion method from the vapor phase in a close volume. The process was held in evacuated to 10^{-4} Torr and sealed silica ampoule,

placed in opposite ends of which were substrate and charge, that is mixture of crashed Yb and Se. Selenium contributes overwhelming entry Yb atoms into cationic (zinc) sublattice of compounds, and provides back pressure, remaining the surface of the plates mirrored. The annealing temperature was 1400 K, which during the time of diffusion (~3 h) ensured doping the total volume of the substrates. PL excited by N_2-laser with the wavelength 337 nm and emission spectra were measured using a universal installation, which allowed ordinary and differential regimes of operation. The complex has diffraction monochromator MDR-23 and standard synchro-detection system with automatic recording of spectral characteristics. Changing the intensity of excitation L was within range of three orders and was carried out with calibrated neutral filters. Researches of luminescent characteristics of the samples were performed within the temperature range 290…500 K, and spectra were built in the coordinates: the number of photons per unit interval of energy N_ω – photon energy $\hbar\omega$.

3. Results and discussion

As seen from Fig. 1 (curve *1*), the PL spectrum of base ZnSe⟨Al⟩ crystal at 300 K in the visible region is represented by one yellow-green band that is marked with the symbol G. The large halfwidth (~0.3 eV) of G-band and shift of its maximum with increasing the level of excitation to the side of higher energies indicates its donor-acceptor nature. According to [12, 13], this band is formed by two types of associates $\left(V''_{Zn}, Al^{\bullet}_{Zn}\right)$ and $\left(V''_{Zn}, V^{\bullet}_{Se}\right)$, which include negative twice-charged zinc vacancies V''_{Zn} (deep acceptors $E_a \approx 1.2$ eV) and positive single-charged centers $Al^{\bullet}_{Zn}$, as well as selenide vacancies $V^{\bullet}_{Se}$ (shallow donors with $E_d \approx 0.03$ eV). Contribution of each associate to G-band is defined by the concentration of Al in melt, conditions of annealing ZnSe⟨Al⟩ crystals in zinc, cooling mode *etc*. Moreover, the most prominent feature of initial substrate is that the edge luminescent band is not observed even at the maximum level of excitation (~10^{19} photons/s) at room temperature.

Unlike basic crystals, in substrates doped with Yb there observed is a significant increase of the efficiency η of the edge B-band (curve *2* in Fig. 1) and "quenching" G-band. It is caused by restructuring of their own impurity ensemble of point defects, which is caused by a number of reasons that we will consider in more detail. In our opinion, the main part of them is "healing" the zinc vacancies by Yb atoms, which results in a substantial decrease of associates number $\left(V''_{Zn}, Al^{\bullet}_{Zn}\right)$ and $\left(V''_{Zn}, V^{\bullet}_{Se}\right)$, responsible for formation of G-band. The basis for such assumptions is inherent high solubility of rare earth elements in semiconductor crystals, in particular, confirmed experimentally for III-V compounds [14]. On the other hand, released from these associates centers Al_{Zn} and V_{Se}, that are shallow donors, may participate in formation of edge radiation. We now turn to the analysis of B-band, halfwidth of which is significantly higher than kT, what indicates it is not elementary. First of all, note that high-energy "wing" of B-band is well described by the known expression for interband transitions where $E_g \approx 2.7$ eV [15]:

$$N_\omega \approx (\hbar\omega)^2 \sqrt{\hbar\omega - E_g}\, \exp\left(-\frac{\hbar\omega - E_g}{kT}\right). \qquad (1)$$

There is a difference between the total and band radiation, and it has a number of features that we will consider in more detail. First, we observe that contour of the obtained band is characterized by a sharp high-energy edge and prolonged low-energy "wing". Second, its maximum is close to 2.69 eV and it is shifted relatively to E_g by 0.01 eV. In this regard, dominant B_{ex}-band cannot be caused by recombination that involves local centers, because in ZnSe there are no levels of ionization energy equal to 0.01 eV [1, 12, 13]. Third, the maximum of this band $\hbar\omega'_m$ is shifted to the side of lower energies with increase of L (Fig. 2), which is usually not observed in recombination through shallow centers because of low electron-phonon interaction [15]. And finally, the intensity I of B_{ex}-band depends on the excitation level in accord with the power law of $I \sim L^{1.5}$ type. These features are typical for exciton annihilation in their inelastic scattering by free charge carriers (electrons) [16], because the investigated samples have electron conductivity. Shift of B_{ex}-band maximum toward lower values $\hbar\omega$ can be explained by increasing concentration of non-equilibrium electrons in the conduction band with increase of the excitation level, which, in turn, leads to an increase in the probability of excitons scattering.

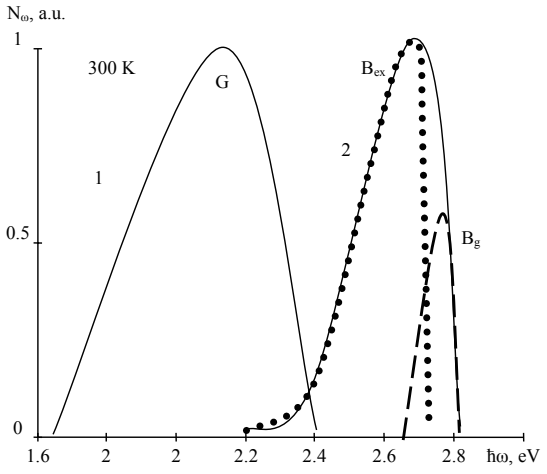

Fig. 1. Luminescence spectra of ZnSe⟨Al⟩ (*1*) and ZnSe⟨Al⟩:Yb (*2*) crystals. Solid lines – experimental data, dotted – calculation by using the formula (1), dots – difference between experimental and calculated lines.

Semiconductor Physics, Quantum Electronics & Optoelectronics, 2016. V. 19, N 4. P. 391-394.
doi: https://doi.org/10.15407/spqeo19.04.394

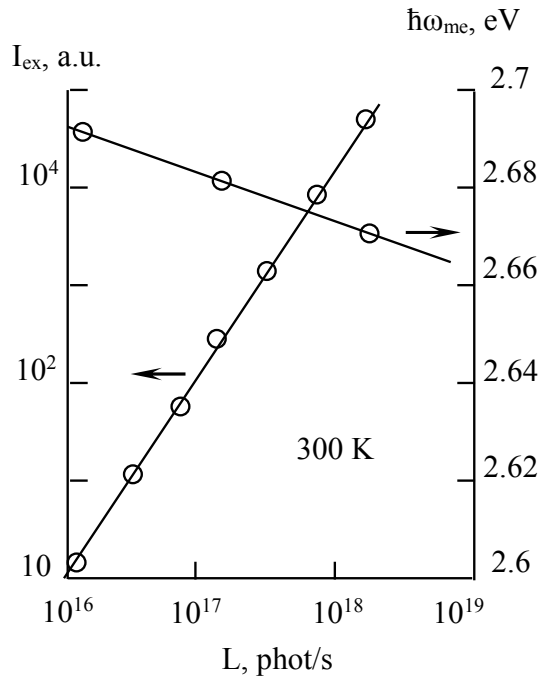

Fig. 2. Intensity and maximum position of radiation of B_{ex}-band dependence on the excitation level.

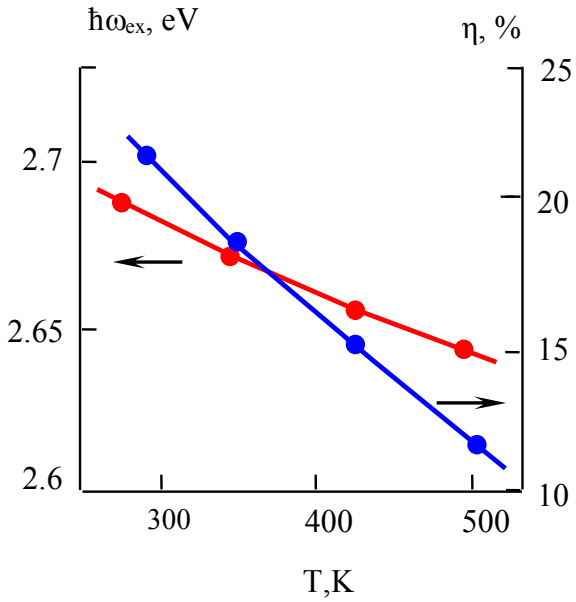

Fig. 3. Temperature dependences of maximum position and B_{ex}-band efficiency.

Let's note that such exciton luminescence band was also observed by the authors of [17] in crystals annealed in Zn melt with Yb impurity. However, regardless to high annealing time (~100 h) and wide range (0…8%) of changes in the Yb concentration in such samples, the low-energy band remains even at low temperatures (6 K). Discussed dissimilarities of luminescence spectra are caused not only by different composition of ensembles of point defects in base crystals but also by technological conditions of Yb doping process.

In addition, let us also pay attention to several features of research objects important from a practical standpoint. The first of these is the significant efficiency increase of the edge band, which can reach ~20% at 300 K. The second feature is quite weak temperature dependence of the η magnitude, which in the range of 290…490 K doesn't exceed $5\cdot10^{-2}\%\cdot K^{-1}$ (Fig. 3). In this regards, ZnSe⟨Al⟩ crystals can be the basis of high temperature blue sources of spontaneous and stimulated emission. In this relation, the crystals ZnSe⟨Al⟩:Yb can be the basis for bright blue sources of spontaneous and stimulated emission defined by its exciton nature. Unfortunately, the question of the nature of excitons remains open because of the need for research at cryogenic temperatures, which is beyond this work.

4. Conclusions

Thus, the results obtained in this work demonstrate the possibility of obtaining the ZnSe⟨Al⟩ crystals with efficient edge luminescence by doping Yb from vapor phase.

References

1. N.K. Morozova, V.A. Kyznetsov, V.B. Rujukov, *Zinc Selenide: Preparation and Optical Properties*. Nauka, Moscow, 1992 (in Russian).
2. A.N. Georgobiani, M.B. Kotlyarevskiy, Problems of creation injection light diodes on basis of $A^{II}B^{VI}$ widegap semiconductor compounds // *Izv. AN USSR. Ser. Fizicheskaya*, **49**(10), p. 1916-1922 (1985), in Russian.
3. O.V. Bogdankevich, Semiconductor lasers with elector beam pumping // *Kvantovaya elektronika*, **21**(12), p. 1113-1136 (1994), in Russian.
4. K.V. Beregnoi, A.S. Nasibov, P.V. Shapkin et al., Radiation of zinc selenide plates excited by pulsed electric field // *Kvantovaya elektronika*, **38**(9), p. 829-832 (2008), in Russian.
5. N.A. Kulchitskiy, A.V. Naumov, Modern optoelectronic devices based on zinc selenide // *Nanoinzheneriya*, **11**, p. 19-27 (2014), in Russian.
6. M.M. Berezovskiy, V.P. Makhniy, V.V. Melnik, Influence of Li, Cd, In and As impurities on optoelectronic properties of ZnSe // *Neorganicheskie materialy*, **33**(2), p. 181-183 (1997), in Russian.
7. V.I. Gryvul, V.P. Makhniy, M.M. Slyotov, The origin of edge luminescence in diffusion ZnSe:Sn layers // *Semiconductors*, **41**(7), p. 784-785 (2007).
8. M. M. Sletov, Edge luminescence from zinc selenide doped with isovalent magnesium impurity // Technical Physics Letters, **27**(1), p. 63-64 (2001).
9. A.N. Krasnov, Yu.F. Vaksman, Yu.N. Purtov, Hole conductivity in monocrystals with an metalloid excess // *Pis'ma v zhurnal tekhnicheskoi fiziki*, **18**(12), p. 1-5 (1992), in Russian.

10. V.P. Makhniy, O.V. Kinzerska, I.M Senko, O.M. Slyotov, The properties of edge luminescence band of zinc selenide with ytterbium impurity // *IX Intern. Conf. on Topical Problems of Semiconductor Physics*, May 16-20, 2016, Truskavets, Ukraine, p. 68.
11. *Patent 107292 Ukraine*, CI (2016.01) C30B 25/00, C30B 31/00. V.P. Makhniy, O.V. Kinzerska, I.M. Senko, Methods of doping ZnSe⟨Te⟩ crystals with rare-earth elements. Appl. date 24.12.2015; published 25.05.2016, Bul. № 10.
12. D.D. Nedeoglo, A.V. Simashkevich, *Electrical and Luminescent Properties of Zinc Selenide*. Chisinau, Shtiintsa, 1984.
13. Y.F. Vaksman, Luminescence of zinc selenide monocrystals and emitting structure on their basis // Diss. … doct. fiz.-mat. nauk, Odessa, 1993 (in Russian).
14. A.T. Gorelenok, A.V. Kamanin, N.M. Shmidt, Rare-earth elements in the technology of III–V compounds and devices based on these compounds // *Semiconductors*, **37**(8), p. 894-914 (2003).
15. V.P. Gribkovskiy, *Absorbtion and Light Emitting Theories in Semiconductors*. Minsk, Nauka i tekhnika, 1975 (in Russian).
16. E. Koh, D.W. Langer, Luminescence of ZnSe near the band edge under strong laser light excitation // *J. Lumin.* **1-2**, p. 514-527 (1970).
17. I. Radevici, K. Sushkevich, V. Sirkeli, H. Huhtinen, D. Nedeoglo, P. Paturi, Luminescent properties of the ZnSe:Yb crystals in the visible spectral range // *J. Lumin.* **143**, p. 275-279 (2013).