UDC 621.315.592

Yu. F. VAKSMAN[1], *Yu. A. NITSUK*[1], *Yu. N. PURTOV*[1], *S. A. IGNATENKO*[1],
Yu. V. KOROSTELIN[2], *V. I. KOZLOVSKY*[2], *A. S. NASIBOV*[2], *P. V. SHAPKIN*[2]

[1] Odessa I. I. Mechnikov National University, Odessa, Ukraine
[2] Physical Institute of P. N. Lebedev, RAS

LUMINESCENCE OF ZINC SELENIDE SINGLE CRYSTALS DOPED WITH INDIUM

The spectra of edge and long wavelength photoluminescence for single crystals ZnSe:In, obtained by free growth procedure are investigated. Spectrum of edge emission for low doped crystals ([In] = 10^{16} cm^{-3}) is characterised by lines of emission of free excitons and donor-acceptor pairs (DAP). At concentrations of indium higher 10^{17} cm^{-3}, the emission of excitons, bounded on neutral zinc vacancies, appears. Spectrum of a long wavelength luminescence evidences the presence in the crystals, charged vacancies of zinc (V_{Zn}^{-}, V_{Zn}^{-2}) included in composition of DAP.

Introduction

The zinc selenide of is a wide energy gap ($E_g = 2{,}68$ eV) semiconductor of A^2B^6 group. Due to straight zone structure it has high efficiency of an emission recombination. Now the production of blue light-emitting diodes on the basis of single ZnSe crystals is prospective [1, 2]. However, instability of the emitting characteristics of such diodes is not sufficient for their production. In this connection, the production and investigation of the crystals with perfect structure, low dislocation density and high conductivity is the very important problem. During last years the technique of free growth was designed [3], it consists in growing of crystals of A^2B^6 group from a vapour phase in conditions excluded their contact to growth camera. The obtained crystals had the perfect structure and low (less 10^4 cm^{-2}) dislocation density. In subsequent, the doping of ZnSe crystals with indium during their growth by means of this technique was realised [4]. The high-conductivity crystals ($\sigma = 1...5$ $Ohm^{-1} \cdot cm^{-1}$) were obtained as the result of subsequent annealing ZnSe:In in zinc melt [4, 5].

In this paper the luminescence of ZnSe:In single crystals, obtained by method of free growth reserved. The purpose of such investigations is to clear up the mechanisms of emitting recombination and nature of luminescence centres in crystals ZnSe, doped with indium.

Experimental technique

The investigated zinc selenide crystals were obtained by method of free growth in two crystallographic direction (111) and (100). The growth ampoule was installed in the furnace with vertical temperature gradient. The seed, container with initial (ZnSe) and alloying (In_2Se_3) materials was placed in ampoule. Temperature of vapour source was 1430...1470 K. Temperature difference between source and substrate — 10...70 K. The total pressure of gas mixture was to stationary values in all processes and made about 100 κPa. More detailed description for the technique to obtain the crystals is contained in works [3, 4]. The concentration of indium in crystals was determined through the atomic-emission analysis and varied from 10^{16} up to 10^{18} cm^{-3}.

The spectra of photoluminescence were measured by spectrophotometer ISP-51 within temperature range 77...400 K. As an excitation source, the helium-cadmium laser LGN-403к, emitting on a wavelength 441,6 nm, was used. The spectra of long wavelength luminescence were represented with allowance for spectral sensitivity of the measuring equipment.

Edge luminescence ZnSe:In

The investigations of edge luminescence spectra were carried out at 77 K. In more short-wave (excitonic) range of spectrum, two lines of emission on 2,808 and 2,797 eV (fig. 1, *a*) are detected. These

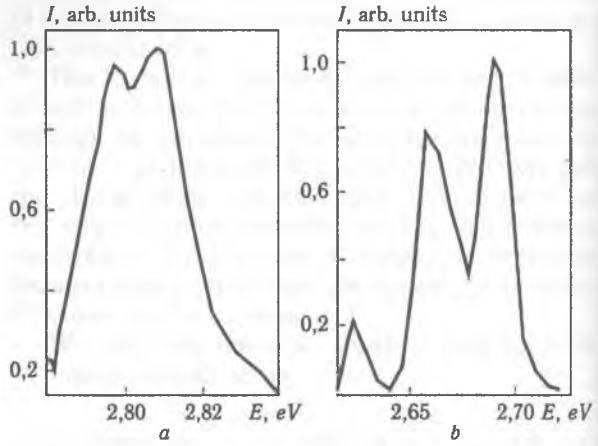

Fig. 1. Spectra of exciton (*a*) and edge luminescence (*b*)

lines are characteristic for low doped crystals ([In] = $2 \cdot 10^{16}$ cm^{-3}). In according to [6], these lines are stipulated by emission transitions of free excitons from states with $n = 2$ and 1, respectively. In spectrum of excitonic luminescence for highly doped crystals ([In] > 10^{17} cm^{-3}) the line of width 1,6 *meV* with a maximum on 2,771 *eV*, stipulated by recombination of bound exciton is detected. In this case energy of emitted photons is described by the equation

$$h\nu = E_g - E_{ex} - E_b, \qquad (1)$$

where E_{ex} — bond energy of free exciton, equal to 16 *meV* [7], E_{ex} — bond energy of localised exciton. In accordance with [7], relationship between activation energy of acceptors (donors) and bond energy of exciton — impurity complex looks like: $E_a \cong 10E_b$; $E_d \cong 5E_b$. The calculation of the equation (1) shows that radiation on 2,771 *eV* is stipulated by excitons localised on acceptors with an activation energy 190...200 *meV*. Such acceptors in zinc selenide are the neutral vacancies of zinc $V^{\times}_{Zn}$ [7].

In all investigated crystals, the emission lines on 2,689, 2,657 and 2,623 *eV* were observed (fig. 1, *b*). The line with a maximum on 2,689 *eV* is stipulated by emission transitions within DAP. Apparently, in DAP composition the indium donors In^{+}_{Zn} enter. As acceptors the ions of uncontrolled impurities of lithium or sodium can be there. The emission lines on 2,657 and 2,623 *eV* are LO — phonon repetitions of a line on 2,689 *eV*.

Features of spectrums of a long wavelength luminescence

The spectra of long wavelength luminescence represent broad bands placed in the range 480...700 *nm*. In spectrums for luminescence of ZnSe with low concentration of indium ([In] = $2 \cdot 10^{16}$ cm^{-3}) there is a broad band with maximum on 490 *nm* (fig. 2). It is

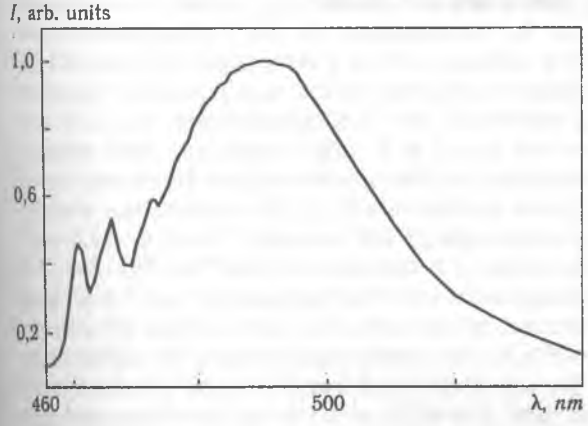

Fig. 2. Spectrum of long wavelength luminescence of low doped crystals ZnSe:In

earlier determined [8], that the isolated centres of oxygen (O_{Se}) stipulate this band of luminescence. Energy of thermal activation for luminescence centres is equal to 0,13 *eV*. It also is in agreement with data [8]. In crystals with [In] > 10^{17} cm^{-3} the luminescence of oxygen was not observed.

Spectrums of long wavelength luminescence with moderate concentration of indium ([In] $\cong 10^{17}$ cm^{-3}) contain two bands with maximums on 560 and 625 *nm*. Thus, in crystals with [In] = 10^{17} cm^{-3} the yellow-green emission predominates. With increase of indium concentration up to $3 \cdot 10^{18}$ cm^{-3} in spectrum of luminescence the specific weight of red-orange luminescence increases.

Spectrum of long wavelength luminescence ZnSe:In depends on temperature of crystals and intensity of exciting light. The rise of crystal temperature from 77 up to 170 K leads to increase of a specific weight of red-orange radiation (fig. 3). Such

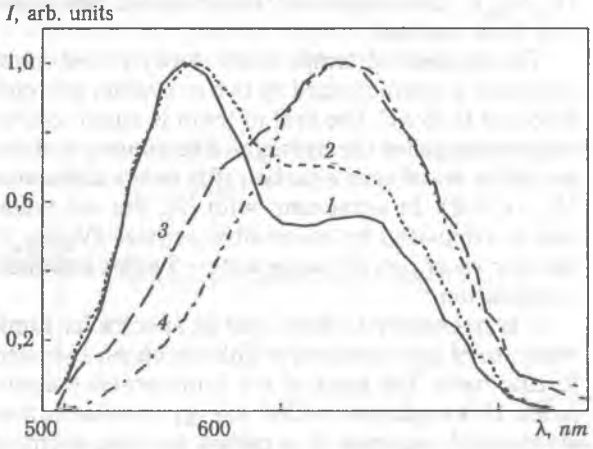

Fig. 3. Spectra of long wave length luminescence ZnSe:In, measured at:

1 — 77, *2* — 108, *3* — 133, *4* — 173 K

chacteristic influence of temperature on a spectral distribution of emission evidences about the mechanism of current transfer between luminescence centres, which is characteristic for recombination luminescence.

With decrease of exciting light intensity from 100 up to 20%, a band with a maximum on 625 *nm* becomes dominating in luminescence spectrum. At the same time the broadening of bands in long wavelength range is observed, that testifies that the indicated photoluminescence spectra, is similar to ZnSe:Al spectrums, described in [9], are not elementary.

To define the nature and the energy position of luminescence centre levels, responsible for yellow-green and red-orange emission, the temperature dependencies of emission intensities were investigated in the range of 560 and 625 *nm*. Activation energy of the temperature decay process was determined with inclination of linear site of dependence $I(T)$, figured in coordinates $\ln I$ from $1/T$. The temperature luminescence decay in range 560 *nm* represents a curve with two linear sites. In the range of low temperatures, the weak decay of luminescence with activation energy 0,05 *eV* was observed. In the range

from 200 up to 250 K the intensity of green emission varies insignificantly. Activation energy, determined in high-temperature range, was 0,11 *meV*. The temperature dependencies of luminescent emission with two linear decay sites are explained within the framework of model for emission recombination which is carried out on donor-acceptor pairs. In this case energy of emitted quantum is determined by the equation

$$h\nu = E_g - E_d - E_a + \frac{e^2}{\varepsilon R}, \qquad (2)$$

where E_d, E_a — activation energy of donor and acceptor; R — distance between the donor and acceptor. In accordance with [10], the green emission of ZnSe:In is stipulated by neutral associative centres $(V_{Zn}In_{Zn})^{\times}$, the single-shot vacancies of zinc enter into their content.

The process of temperature decay of red luminescence is characterised by two activation energies 0,05 and 0,35 *eV*. The first of them is equal to activation energy for the hydrogen-like donors, and the second is equal (see equation (2)) to the difference $(E_a - e^2/\varepsilon R)$. In agreement with [9], the red radiation is stipulated by associative centres $(V_{Zn}In_{Zn})^-$ the zinc vacancies in charge state -2 enter into their composition.

It is necessary to note, that in spectra for luminescence of high-conductive ZnSe:In chips, annealed in zinc melt, the band of red luminescence dominates. It is explained to that energy of substitution single-shot vacancy of a cation by zinc atom is smaller in comparison with the appropriate value for two-charge vacancy.

Outputs

1. Spectrum of edge luminescence of low doped single ZnSe crystals ($[In] \cong 2 \cdot 10^{16}\ cm^{-3}$) are characterised by lines of free exciton emission with $n = 2,1$ (2,808, 2,797 *eV*) and line of DAP emission on 2,689 *eV* with its phonon repetitions (2,657 and 2,623 *eV*).

2. In low doped ZnSe single crystals ($[In] \cong 2 \cdot 10^{16}\ cm^{-3}$) the long wavelength luminescence is observed in the range of 490 *nm*. This band of luminescence indicates presence of uncontrolled impurities of oxygen in crysrals.

3. Spectrum of edge luminescence for of ZnSe crystals with indium concentration higher than $10^{17}\ cm^{-3}$ is characterised by line for emission of excitons, bounded on neutral zinc vacancies and line of DAP emission on 2,689 *eV* with its phonon repetitions (2,657 and 2,623 *eV*).

4. Spectrum of long wavelength luminescence ZnSe:In evidences the presence of DAP, containing acceptors V_{Zn}^{-}, V_{Zn}^{-2} and donors In_{Zn}^{+} in crystals.

5. Annealing of ZnSe:In crystal in zinc leads to decreasing of Zn vacancy concentration, responsible for long wavelength luminescence. This is the reason for increase of a specific conductivity of crystals.

References

1. *Krasnov A. N., Purtov Yu. N., Vaksman Yu. F., Serdyuk V. V.* // J. Cryst. Growth. — 1992. — V. 125, № 1/2. — P. 373—374.

2. *Ваксман Ю. Ф., Краснов А. Н., Пуртов Ю. Н.* // Физ. и техн. полупроводников. — 1995. — Т. 29, № 7. — С. 1186—1189.

3. *Korostelin Yu. V., Kozlovsky V. I., Nasibov A. S., Shapkin P. V.* // J. Cryst Growth. — 1996. — V. 159. — P. 181—185.

4. *Korostelin Yu. V., Kozlovsky V. I., Nasibov A. S., Shapkin P. V.* // J. Cryst Growth. — 1999. — V. 197. — P. 449—454.

5. *Ваксман Ю. Ф., Игнатенко С. А., Пуртов Ю. Н., Шапкин П. В.* // Фотоэлектроника. — 1999. — № 8. — С. 77—79.

6. *Гавриленко В. И., Грехов А. М., Корбутяк Д. В., Литовченко В. Г.* Оптические свойства полупроводников. — К.: Наук. думка, 1987. — 608 с.

7. *Недеогло Д. Д., Симашкевич А. В.* Электрические и люминесцентные свойства селенида цинка. — Кишинев: Штиинца, 1980. — 150 с.

8. *Ваксман Ю. Ф.* // Физ. и техн. полупроводников. — 1995. — Т. 29, № 2. — С. 346—348.

9. *Serdyuk V. V., Korneva N. N., Vaksman Yu. F.* // Phys. Stat. Sol. (a). — 1985. — V. 91. — P. 173—183.

10. *Ваксман Ю. Ф., Краснов А. Н.* // Фотоэлектроника. — 1996. — № 6. — С. 8—12.