PHOTOLUMINESCENCE OF n-ZnSe SINGLE CRYSTALS DOPED WITH IODINE BY VAPOUR PHASE DIFFUSION

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Photoluminescence spectra of n-ZnSe single crystals doped with iodine are investigated in the temperature range from 83 to 300 K. It is shown that the edge PL band is formed by overlapping of the PL lines attributed to I_{Se} donor-bound ecxitons (I_2^I) and V_{Zn} acceptor-bound excitons (I_1^D). A model of radiation mechanisms, which explain the redistribution of the edge and long-wave PL bands intensities with increasing doping level of the samples, is proposed.

1. Introduction

Due to the large band gap energy (E_g ~ 2.7 eV at 300 K), zinc selenide is a perspective material for visible light-emitting diodes, especially for the diodes operating in the blue region of the spectrum. The necessity of obtaining high-intensive radiation requires good electrical and optical parameters of the crystals. These parameters depend on the type and quantity of the doping impurity, its aptitude to self-compensation and formation of complexes with native defects.

It was considered for a long time that the group III elements, such as Al, Ga, In, were good donor impurities for zinc selenide. However, it was shown later that these impurities were unsuitable for obtaining of heavily doped n-type ZnSe crystals as the probability of formation of associative acceptors, which consist of both native and doping impurity defects, rapidly increases with increasing dopant concentration [1]. The influence of Al and Cl impurities on radiative properties of ZnSe epitaxial films was analyzed in work [2]. It was shown the superiority of group VII elements over group III elements as donor dopants. The doping of n-ZnSe epitaxial films with Cl [3] and I [4] allowed the doping leve increasing up to 10^{19} cm^{-3} and $3 \cdot 10^{19}$ cm^{-3}, respectively.

The influence of ZnI_2 vapour pressure on luminescence properties of n-ZnSe single crystals is investigated in the present paper. The choice of ZnI_2 vapour as a medium of diffusion doping is caused by the fact that such a doping reduces the number of V_{Zn} native defects, which compensate donor impurity, and promotes incorporation of iodine atoms into Se sublattice vacancy sites.

2. Experimental Results and Discussion

Photoluminescence (PL) spectra of iodine-doped n-ZnSe single crystals were investigated in the temperature range from 83 to 300 K. The doping was made during a long-term (100 h) high-temperature (950 ºC) thermal treatment of n-ZnSe single crystals in ZnI_2 vapour. The doping level was varied by changing vapour pressure in quartz ampoules with the samples (the ampoules were previously evacuated to the pressure of ~10^{-4} torr). For this

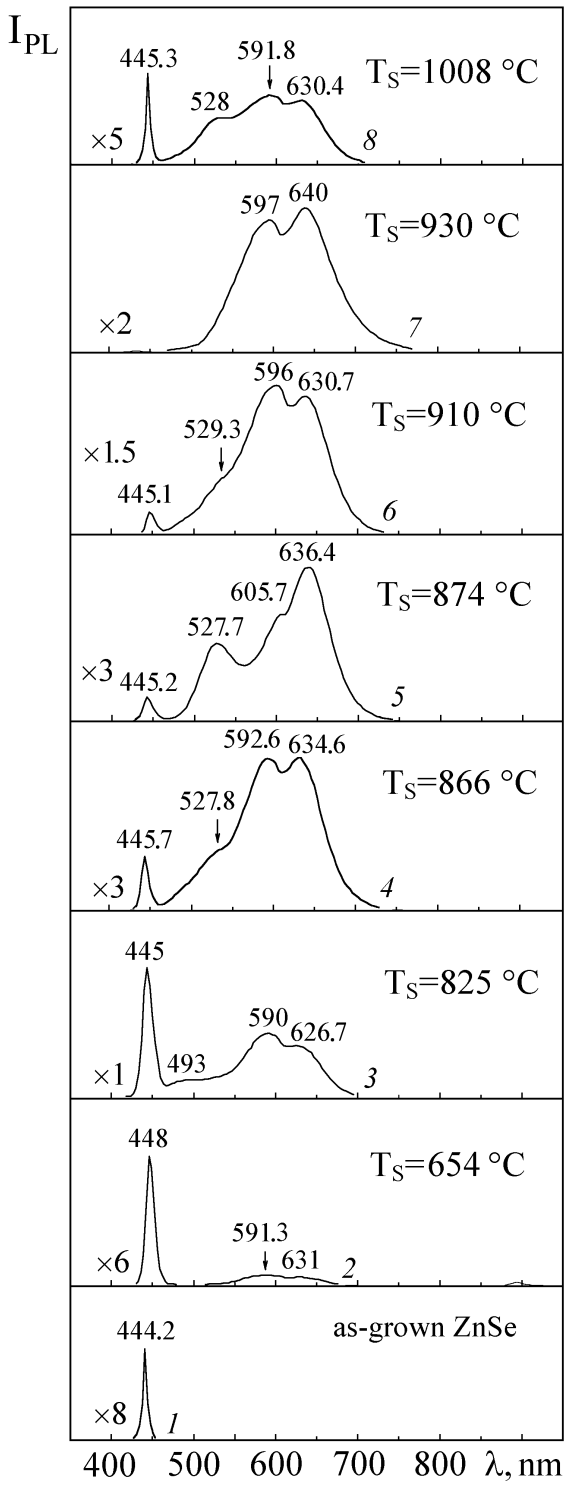

Fig. 1. PL spectra of n-ZnSe crystals annealed in ZnI_2 vapour at different temperatures of ZnI_2 vapour source.
T = 83K.

purpose, the temperature of ZnI_2 vapour source was varied from 654 to 1008 °C. After termination of the annealing, the ampoules were rapidly cooled down. Luminescence was excited by radiation of ILGI-503 nitrogen impulse laser with 337.1 nm wavelength (3.675 eV). A MDR-23 monochromator with reciprocal dispersion of 1.4 nm/mm was used.

The PL spectrum for the original n-ZnSe crystal contains one narrow (21 meV) band of excitonic radiation with a maximum at 444.2 nm (2.789 eV) (Fig. 1, curve 1). There are no other bands in the region from 500 to 800 nm. The annealing of the crystals in ZnI_2 vapour leads to a broadening of the edge PL band (3 ÷ 4 times as large) and to its shift towards long wavelengths. Overlapping wide bands of long-wave luminescence also appear after such a treatment. For instance, the PL spectrum for the n-ZnSe crystal annealed in ZnI_2 vapour at T_S = 654 °C contains wide bands with maxima at 591.3 nm (2.095 eV) and 631 nm (1.964 eV). The edge PL band is broadened ($W_{1/2}$ ~ 71 meV) and shifted towards 448 nm (2,765 eV).

The structure of PL spectra is practically unchanged with increasing temperature of ZnI_2 vapour source (Fig. 1, curves 2-8). The half-width of the edge band increases to $W_{1/2}$ = 85 meV at T_S = 866 °C, its intensity decreases (Fig. 2, a), and spectral maximum position shifts towards short wavelengths (Fig. 2, b). The further increase of the source temperature leads to a rapid decrease of the half-width and localization of the band at 445 nm (2.784 eV) (Fig. 2, a, b).

Fig. 1 shows that the decrease of the edge PL band intensity is accompanied by an increase of the long-wave PL intensity. As the source temperature T_S increases to 910 °C, the intensity ratio between the edge and long-wave (λ_{max} = (590 ÷ 596) nm) PL bands decreases. At T_S = 930 °C, the edge PL band disappears and the spectrum contains only the double-peaked band of long-wave luminescence (Fig.1, curve 7). The increase of the source temperature to 1008 °C leads again to an increase of the edge PL band intensity (Fig. 1,

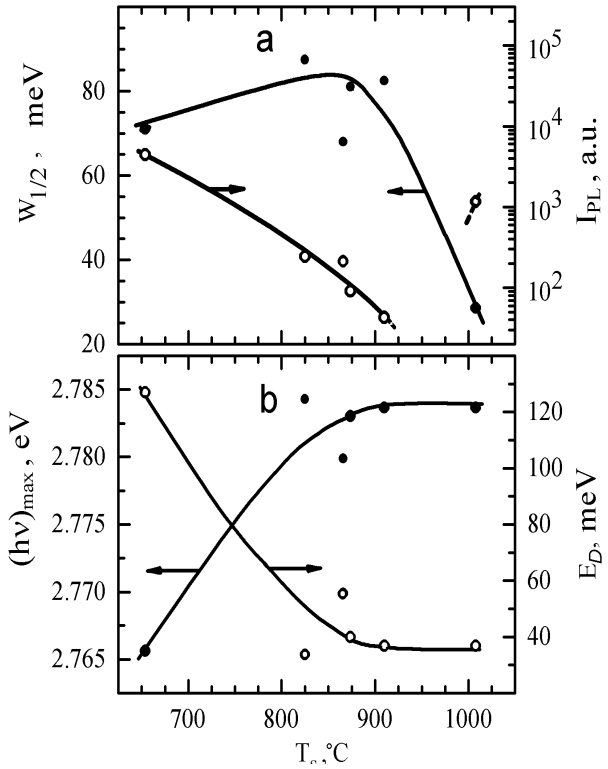

Fig. 2. Half-width and intensity (a), spectral position and donor ionization energy (b) for the excitonic PL band versus ZnI_2 vapour source temperature.

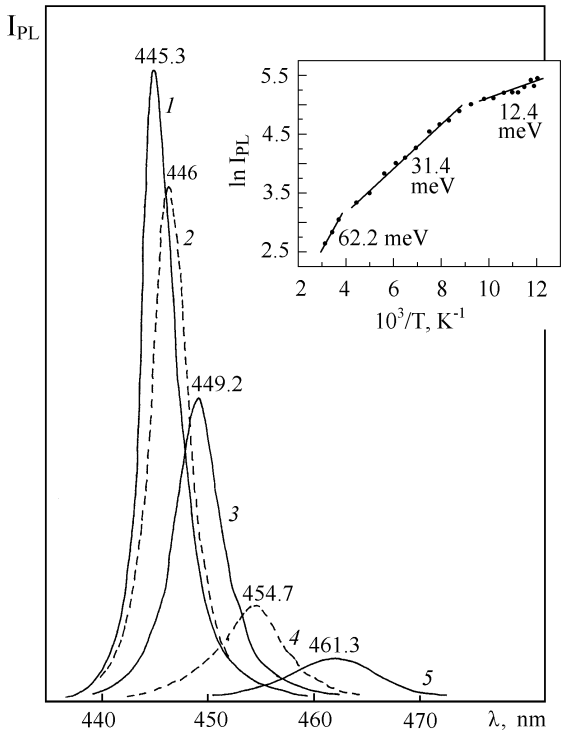

Fig. 3. Temperature evolution of the edge PL spectra for the n-ZnSe:I crystal annealed at T_S = 1008 °C.
T, K: 1–85, 2–94, 3–134, 4–200, 5–319.
Inset: Temperature quenching of the edge PL band intensity.

curve 8). It becomes narrower (Fig. 2, a) and is now dominant in the spectrum.

The temperature evolution of the edge PL spectra for the n-ZnSe:I crystal annealed at T_S = 1008 °C is given in Fig. 3. As temperature increases, the edge PL intensity decreases, the band broadens and shifts towards long wavelengths.

Fig. 4 shows the temperature dependence of free exciton band position (curve 1) calculated for n-ZnSe crystal using the formula [5]:

$$E_x(T) = 2.804 - 8.59 \cdot 10^{-4} \frac{T^2}{T + 405} \text{ (eV)},$$

where E_g = 2.804 eV is the band gap energy at T = 83 K, $\frac{dE_g}{dT} = 8.59 \cdot 10^{-4}$ eV/K is the temperature coefficient of ZnSe band gap energy changing, θ_D = 405 K is the Debye temperature for ZnSe. The temperature dependence of the edge PL band position determined experimentally for the sample annealed in ZnI_2 vapour at T_S = 1008 °C is also presented in Fig. 4 (curve 2). It is seen that the maximum of the edge PL band for the n-ZnSe:I crystal is localized at long wavelengths in comparison with the free exciton band. As temperature increases, the position of the edge PL band maximum approaches the calculated value for the free exciton band, and these two values coincide near room temperature.

Characteristic features of the edge PL band are its localization in the region of wavelengths, which correspond to excitonic luminescence, and a great value of its half-width

($W_{1/2}$ ~ 70÷85 meV). We think that such a great half-width is caused by overlapping of the PL lines attributed to I_{Se} donor-bound excitons (I_2^I) and V_{Zn} acceptor-bound excitons (I_1^D).The fact that the activation energy of the edge PL intensity temperature quenching has two values for all the I-doped samples in the temperature range from 83 to 240 K [6] (Fig. 3, inset) is the evidence of excitonic nature of this PL band. If this band had been attributed to radiative recombination of electrons localized on I_{Se} donors with holes from the valence band, the temperature quenching activation energy would have had only one value, equal to E_D (I_{Se}).

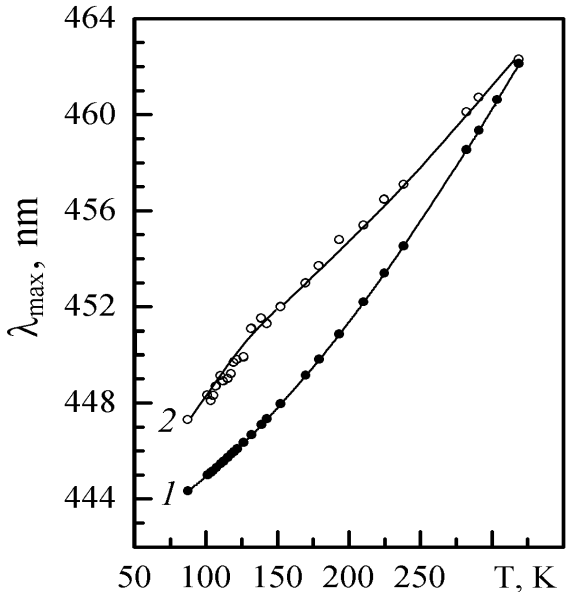

Fig. 4. The edge PL band position versus temperature for n-ZnSe:I crystal, T_S=1008 °C. 1 – calculated curve for free excitons, 2 – experimental curve.

3. Conclusion

The redistribution of the edge and long-wave PL bands intensities with increasing doping level of the samples (Fig. 1) is well described in the limits of the proposed model of radiation mechanisms for these PL bands. As the temperature of ZnI_2 vapour source increases, the iodine vapour pressure in ampoules with the samples increases too. The rising concentration of I_{Se} defects results in increasing probability of (V_{Zn}-I_{Se}) associative acceptor formation and increasing intensity of long-wave luminescence. The probability of simple I_{Se} and V_{Zn} defect formation decreases, and as they are responsible for the edge PL band, its intensity decreases down to complete disappearance in the spectrum for the crystal annealed at T_S = 930 °C (Fig. 1, curve 7). However, as it was mentioned above, a very intensive narrow band with a maximum at 445.3 nm (2.782 eV) dominates in the spectrum for the sample annealed at higher vapour source temperature T_S = 1008 °C (Fig. 1, curve 8).

We suppose that in heavily doped crystals (T_S = 1008 °C), iodine atoms effectively occupy selenium vacancies and promote the generation of native (V_{Zn}) and impurity (I_{Se}) defects. A number of I_{Se} impurity defects take part in the formation of donor-bound excitons, which are responsible for the edge PL band localized at 445.3 nm, the rest of them form (V_{Zn}-I_{Se}) associative acceptors, which are responsible for the long-wave wide PL band.

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