
Optical Properties of ZnSe:Mg Diffusion Layers

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Abstract

Photoluminescence, optical absorption and reflection spectra are analysed for the zinc selenide layers doped with Mg via evaporation deposition in a closed volume. The three bands detected in the spectrum of edge emission are attributed to the interband transitions, the annihilation of excitons bound at Mg centres and the recombination at the donor-acceptor pairs of $(Zn_i^{\bullet}Se_i')$.

Keywords: isovalent impurity, exciton, donor-acceptor pairs.

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Introduction

Unremitting interest of researchers in zinc selenide has been caused by certain promises for creating injection radiation sources for the visible optical range on the basis of this material [1]. Creation of materials with a luminescence predominating in a necessary spectral region represents one of serious problems in the field, especially with regards to poorly explored “dark-blue” or “blue” regions. Observation of efficient enough photoluminescence at 300 K occurred in ZnSe crystals containing isovalent impurity of Mg has been recently reported in the literature [2]. Characteristic property of such the samples is a complete absence of “orange-red” self-activated band, which is usually present in all zinc selenide crystals with the electron conductivity. It would be reasonable to relate further efficiency improvements for the blue-band emission in ZnSe:Mg crystals with systematic researches of their physical properties, first of all, the optical ones.

In compliance with the said above, the objective of this work is to investigate the effect

of Mg on the spectral characteristics of zinc selenide.

Samples and measuring methods

Wafers with the dimensions $4 \times 4 \times 1$ mm³ cut from bulk zinc selenide crystals were used as source substrates. ZnSe crystals were grown from stoichiometric melt under an excess pressure of inert gas [2,3]. The samples had low electron conductivity at room temperatures ($\sigma_n \approx 10^{-10}$ Ohm⁻¹cm⁻¹), and the photoluminescence (PL) spectrum contained two bands. Their intensities I were different, depending upon the temperature of measurements and the excitation level L , though the R -band in the PL spectra was present at any experimental conditions.

Doping with magnesium was performed using the evaporation deposition in a closed volume, under isothermal conditions (at $T_d \approx 1100$ K). This was done in the sealed silica tubes pumped out down to 10^{-4} torr, the substrate and the mixture of Mg and Zn (with the quantitative ratio Mg:Zn = 9:1) being at the opposite ends of the tube. According to the

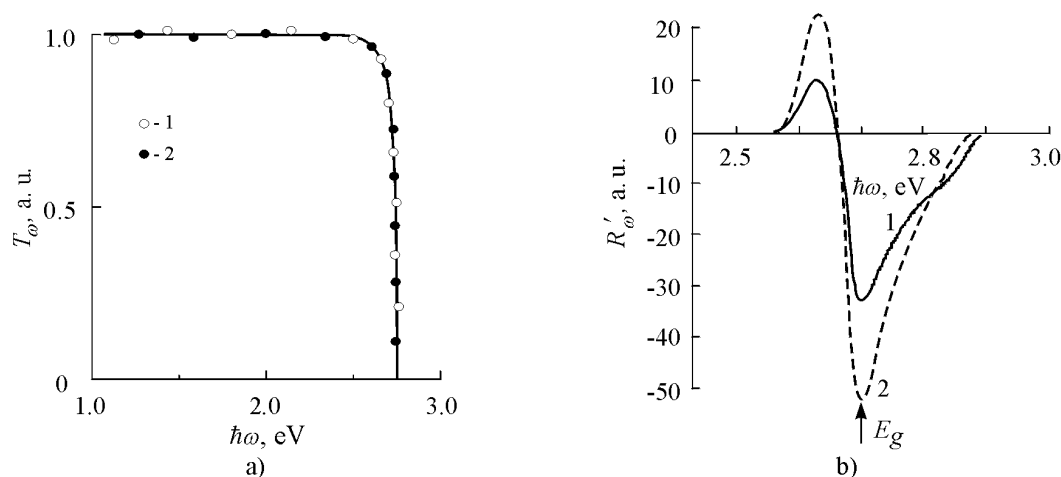


Fig. 1. Transmission (a) and reflection (b) spectra of the virgin ZnSe crystals (1) and the crystals doped with magnesium (2).

study [4], both the maximum intensities of the *B*-band and the electron conductivity of diffusion ZnSe:Mg layer have been observed exactly at such the annealing conditions.

The optical properties were investigated using the setup that incorporated MDR-23 grating monochromator and a standard synchronous detection circuit [5]. The main characteristic of this system was a possibility for measuring simultaneously the ordinary and differential (λ -modulated) transmissions, together with the reflection and emission spectra. The excitation level was changed within three orders of magnitude with a set of calibrated neutral light filters. All the optical spectra were adjusted with taking into account non-linearity of the components of the measuring system. The luminescence spectra were built in the following coordinates: photon quantity N_ω in a unit photon energy interval versus photon energy ($\hbar\omega$).

Results and discussion

The main characteristic feature of the samples under test is a presence of rather intensive “blue” emission, whose efficiency is equal to $\sim 20\%$ at 300 K. Notice that no one else luminescence band occurs for these samples inside the energy range of 1.0–2.8 eV at the temperatures 77–400 K. Such essential

difference in the PL spectra peculiar for the doped and as-prepared crystals raises a natural question about formation of a new, more wideband compound with magnesium on the substrate surface. It should be possible to answer it on the basis of comparative analysis of transmission T_ω and reflection R'_ω spectra for the as-prepared and annealed samples. As follows from the data represented in Fig. 1, doping of ZnSe crystals with magnesium does not influence the shape of T_ω and R'_ω curves within the limits of experiment accuracy. This indicates unambiguously that the bandgap (E_g) value remains unchanged.

It is also worthwhile that the lattice constants of the as-prepared crystals and ZnSe:Mg agree well with each other [6]. Thus, doping with Mg affects substantially the ensemble of the point defects that determines luminescence properties of the samples, yet it remains unchanged the main crystal-physical parameters of zinc selenide. Let us consider these problems in a more detail.

Let us stress at first that the *B*-band ($\Delta\hbar\omega \approx 0.05$ eV) has a large halfwidth, which is noticeably above kT_0 , and tightened “tails”. This points indirectly at its complex structure, which does not clearly manifest itself at any level of excitation (L). That is why we have analysed the emission spectra at the liquid nitrogen

temperature, enabling to reveal the three separate bands (see Fig. 2). The B_1 -band dominating at all the levels of excitation is characterized by the following properties:

- 1) the emission intensity depends on L according to the power law $I \sim L^{1.5}$;
- 2) the maximum $\hbar\omega_m$ of the band shifts to the low-energy region with increasing L (see Fig. 2, inset);
- 3) the low-energy “tail” of the B_1 -band is well approximated with a straight line in the coordinates $\ln N_\omega$ vs. $\hbar\omega$.

These properties impose the conclusion that the B_1 -band should be attributed to annihilation of excitons and their non-elastic dissipation at the free charge carriers [1]. The latter is confirmed by the data for the λ -modulated PL spectrum, where equidistant “folds” can be clearly seen, the energy distance between them being in accordance with the LO -phonon energy ($\hbar\omega_0 \approx 0.021$ eV [1,3] for the zinc selenide – see Fig. 3).

Notice that the maximum of the B_1 -band in

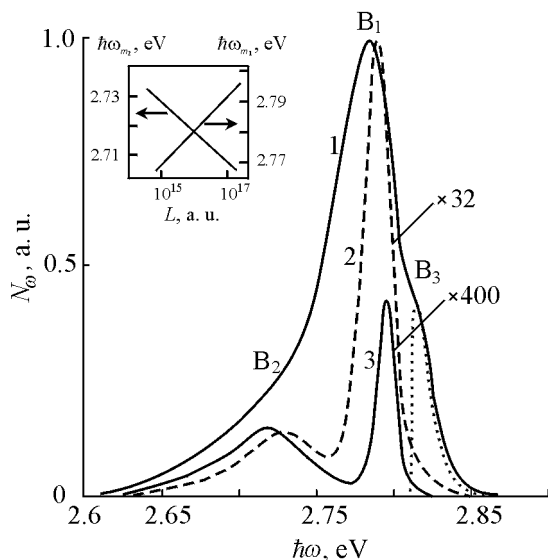


Fig. 2. PL spectra of ZnSe:Mg layer at different L : curve 1 – 10^{18} , 2 – 10^{16} and 3 – 10^{15} sq./s. The insert shows L -dependences of the maxima positions for the exciton ($\hbar\omega_{m_1}$) and donor-acceptor ($\hbar\omega_{m_2}$) bands. $T = 77$ K. The dotted curve is calculated according to the known formula (2) (see the text below) and corresponds to the interband transitions.

the ordinary PL spectrum corresponds to the point of intersection of the curve N'_ω with the energy axis (i.e., the B_1 -point in Fig. 3). The nature of the centre responsible for the formation of the exciton band will be considered below.

Another point B_2 of intersection of the curve N'_ω with the abscissa (see Fig. 3) corresponds to the maximum of the B_2 -band, which manifests itself at low L values (Fig. 2). Its behaviour differs substantially from that of the B_1 -band discussed above. First, the B_2 -band is characterized by noticeably larger halfwidth ($\Delta\hbar\omega_{1/2} \sim 0.1$ eV), which depends upon neither L nor the temperature. Second, as the excitation level increases, the band maximum shifts to the region of high energies (see Fig. 2, insert). The properties marked here are characteristic of recombination with participating donor-acceptor pairs (DAP) [7].

It is possible to identify the DAP partners after involving the information on qualitative changes in the point defects ensemble in ZnSe:Mg samples, when compare to the as-prepared samples. It is shown in the work [8] that the Schottky defects dominate in the undoped melt-grown zinc selenide crystals, in which the associate ($V_{Zn}''V_{Se}^{*}$) responsible for the formation of R -band is built from the former. Mg and Zn atoms fill the vacancies of zinc (V_{Zn})

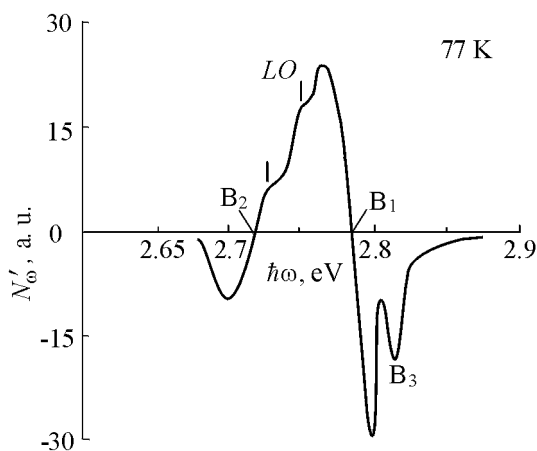


Fig. 3. λ -modulated PL spectrum of ZnSe:Mg layer at $L = 10^{18}$ sq./s.

and “destroy” the associate, as a consequence of decreasing concentration of doubly negatively charged zinc vacancies (V_{Zn}''). This causes a reduction of the R -band intensity and, under certain conditions, determined by the annealing temperature and the relation between the mixture ingredients, its complete quenching [4]. The analysis of the present results leads to the conclusion that Mg atoms “cure” zinc vacancies more efficiently, in comparison with Zn. This is confirmed by increase in the exciton B_I -band intensity with augment of Mg part in the mixture and the behaviour of I_{B_1} reaching its maximum at the ratio 0.9:0.1 of the mixture contents of Mg and Zn. Note that the efficiency of the “blue” emission band increases also when a superstoichiometric zinc is introduced into the crystal, though the B -band in this case is caused by a recombination through selenium vacancies V_{Se} [9]. In this way, it may be stated that the B_I -band in ZnSe:Mg samples is formed with participation of the magnesium impurity, at which the exciton is bound.

It is known that isovalent impurity (IVI) causes additional generation of intrinsic point lattice defects (IPD), their type being determined by the relation of effective carriers of the basic semiconductor and the compound formed with the IVI. In case of ZnSe:Mg, vacancies of zinc (V_{Zn}) and interstitial selenium atoms (Se_i) are to be formed in the crystal [10]. At the same time, generation of V_{Zn} by magnesium should be impossible, as far as the latter is known to “cure” zinc vacancies available in the initial crystals in sufficient quantity. As the quantity of V_{Zn} decreases, compensation of positive charge of the shallow donor V_{Se} centres “released” from DAP takes place owing to the other acceptors, e.g., the interstitial Se_i atoms. Consequently, besides of a decrease in the zinc vacancies number, generation of Se_i atoms also takes place during the doping of ZnSe crystals with the isovalent magnesium impurity. Let us also remind that all the Se_i centres are located in the

ionised conditions, since ZnSe:Mg possesses the electron conductivity.

Upon falling into crystal from the vapour phase, zinc, as a part of the mixture, enters into interstices and forms deep donor levels ($E_d \approx 0.6$ eV) [11]. These centres, together with the interstitial selenium atoms, form the ($Zn^+Se_i^-$) associates responsible for the B_2 -band. Really, the photon energies emitted owing to recombination at the DAP are determined by the well-known relation [7]

$$\hbar\omega = E_g - E_a - E_d + \frac{Z_1 Z_2 e^2}{2\pi\epsilon_0 \epsilon R_i} - \Delta, \quad (1)$$

where E_a and E_d are respectively the depths of the acceptor and donor levels, Z_1 and Z_2 the charges of the centres, R_i the distance between the pair partners and Δ the *Frank-Condon* shift, which is equal to ~ 0.2 eV for ZnSe. Assuming $\hbar\omega_m \approx 2.72$ eV at 77 K and taking into account that $E_d \approx 0.33$ eV, $E_a \approx 0.6$ eV, $\epsilon = 8.8$ and $E_g \approx 2.81$ [3], we obtain $R_i \approx 2.3$ Å.

Let us now remind the main factors producing inaccuracies in the calculated energy of *Coulomb* interaction. The first of them, μ_k , consists in illegality of employing the medium macroscopic parameter (ϵ) in case of so small distances between the DAP partners. The latter can additionally cause an exchange interaction, which is not accounted for in Eq. (1). Nevertheless, the calculated value R_i does not contradict the sum of tetrahedral radii $R_{Zn} + R_{Se} \approx 2.4$ Å, even if we disregard the sources of the calculation errors considered above. Hence, the B_2 -band may be determined by the recombination at DAP, consisting of interstitial atoms of zinc and selenium. At the same time, a final answer to the quantitative composition of the IPD ensemble in the samples may be obtained through applying proper calculation methods, e.g., that of quasi-chemical reactions. However, this problem lies outside the scope of this article, and should be a subject of a more in-depth study.

Finally, the most short-wavelength B_3 -band in the ordinary PL spectra is not observed separately. It manifests itself only in the shape of “fold” at the high-energy “wing” of the “blue” band occurring at the maximum excitation level (see Fig. 2). The presence of photons with $\hbar\omega_m > E_g$ allows one to suggest that this band is caused by interband recombination. The spectral curve calculated according to the known formula valid in the absence of electron-phonon interaction [12],

$$N_\omega \sim \hbar\omega^2 (\hbar\omega - E_g)^2 \exp\left[-\frac{\hbar\omega - E_g}{kT}\right], \quad (2)$$

describes fairly well the high-energy “wing” in the experimental data for the “blue” emission. The most short-wavelength maximum on the curve N'_ω agrees with the value E_g for zinc selenide at 77 K, thus confirming additionally the interband character of the B_3 -band. It is also worth remarking that the position of the B_3 -band maximum, as it has been expected, does not depend on the excitation level, being shifted with increasing temperature according to dE_g/dT , the same as for the zinc selenide. This distinguishes the B_3 -band from the first two bands mentioned before.

Conclusions

Thus, doping of zinc selenide crystals with the mixture of Mg and Zn taken in the ratio 0.9:0.1 leads to a complete suppression of the “red-orange” band and a substantial flare up of the “blue” one. The latter band is a sum of three sub-bands caused respectively by the recombination through DAP (e.g., $Zn_i^+Se_i^-$), the annihilation of the excitons bound at Mg centres and the interband transitions. The efficiency of the blue-band photoluminescence amounts to ~20% at the room temperature.

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