

Self-Activated Luminescence In ZnS – ZnSe System From Positions Of The Band Anticrossing Model

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Abstract – Spectra cathodoluminescence CVD-samples of the ZnS-ZnSe system, grown in the entire range of compositions are investigated. Reorganization of spectrum at dissolution of oxygen in the lattice under influence of high pressures and temperatures treatment is confirmed. Dependence of the self-activated luminescence on composition sulfoselenides is revealed. The explanation to these features is given on the basis of calculations of intrinsic point defects (IPD) equilibrium, which influence in the position of the Fermi level at a deviation from stoichiometry ZnSe and ZnS. Areas in which bands self-activated luminescence SA and SAL ZnS-ZnSe system can be observed depending on IPD type and concentration of oxygen in the lattice are appreciated. Interpretation of spectra is given for the first time on basis of the band anticrossing model initiated isoelectronic impurity of oxygen. Results can be used for the semi-quantitative control of compound for similar crystals A_2B_6 over the content of dissolved oxygen and deviation from the stoichiometry

Properties of A_2B_6 alloys, widely used in optoelectronics, essentially depend on the presence of a background impurity of oxygen. Currently, there is sufficient experimental material proving that self-activated luminescence is connected to intrinsic point defects (IPD) complexes with oxygen. These complexes can be divided into different kinds [1] determined by type and charge within the homogeneity area. In [1] on the example ZnS, ZnSe and CdS the possibility of appearance of 3 types of self-activated bands, designated as: I (SA) – at excess of metal, II (SAL) – in area stoichiometry and III – at significant excess of metalloid is shown. These bands amplify (and are observed only) at the presence of the background impurity of oxygen. The defects known from calculations and the principle of volumetric compensation determine the structure of oxygen complexes. The stabilizing role of oxygen in structure of complexes with IPD has explained many contradictory facts.

New literature data, about the position levels of IPD in the band gap ZnS and ZnSe, allows to refine the diagrams of defect formation [2]. In the present work, a concrete comparison of the IPD equilibrium

(represented in [2]) with the features of spectra cathodoluminescence (CL) of the ZnS-ZnSe system from positions of the band anticrossing model was carried out. The multilevel system of absorption, which appears because of the presence of isoelectronic impurity oxygen, strengthens the emission intensity through the predominant channels of recombination.

Being electro-neutral, oxygen at interaction with IPD on the basis of compensation of volume's discrepancy and electro-negativity difference, forms complexes ($\{O \cdot Zn_i \cdot V_{Zn}^{//}\}^0$ (I), $\{O \cdot Zn_i \cdot V_{Zn}^{//}\}^{\times}$ (II) и $\{O \cdot Zn_i \cdot V_{Zn}^{//}\}^{\bullet}$ (III)) which define the bands of self-activated luminescence [1]. In Figure 1 are shown the observed change of the self-activated bands I, II and III in ZnSe, in according to the shift of the stoichiometry. It is evident that with decrease of Se there is a reorganization of the self-activated luminescence bands: III (740 nm) \rightarrow II (490 nm) \rightarrow I (600–605 and 635 nm). Within the homogeneity area there are only 3 possible IPD recharges, which determine the charge of the complexes and, as a consequence, the position of their levels in the band gap. The charge state of the center should depend on the surrounding accommodating lattice: on the charge state and the type and concentration of the IPD that influence the Fermi level.

Early, self-activated luminescence of compounds A_2B_6 was not considered on positions of the band anticrossing model that is necessary due to the presence of oxygen [3]. Therefore, in order to define the possible splitting of the conduction band in the ZnS-ZnSe system we had studied the self-activated luminescence in samples containing oxygen, obtained by chemical vapor deposition with excess Zn – SA(I), near to the stoichiometry – SAL(II) and the band III characteristic for large Se excess (Fig. 1).

In Fig. 2, taking into account the presence of oxygen and our experimental data the energy model of self-activated luminescence for ZnS and ZnSe is shown. The SA luminescence, which is observed if the compound has excess Zn in the lattice (Fig. 1, curve 1) is defined as transitions: $E_C \rightarrow E_{SA}$, and $E_{Zn_i} \rightarrow E_{SA}$ (L and L_{Zn_i} in Fig. 2). The last arise at an appreciable deviation from a point $\Delta C=0$ to the side excess of zinc. On the inset of Fig. 1 these spectra are shown, observed after annealing samples ZnSe in zinc vapors.

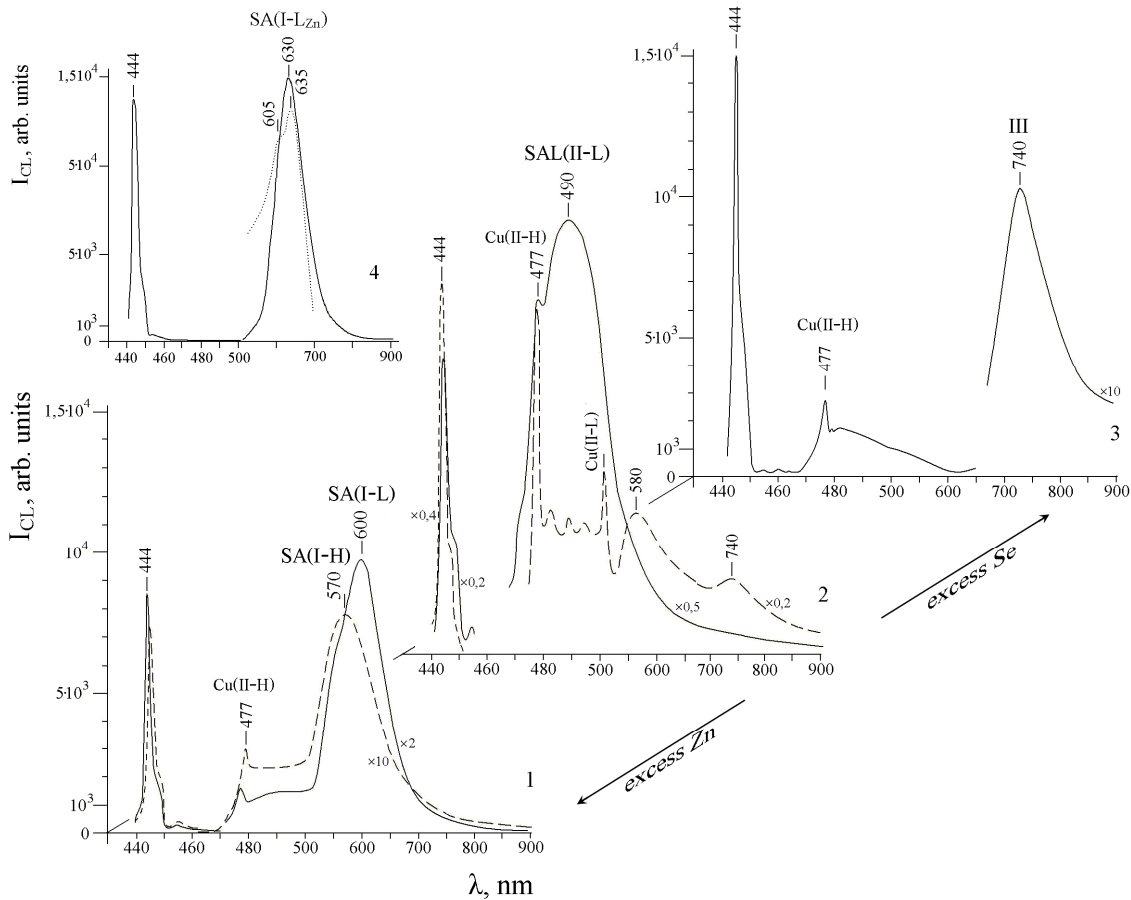


Fig. 1. Dependence of self-activated luminescence at deviations from the stoichiometry in CL spectra (80K) polycrystalline samples CVD – ZnSe. On the inset are presented samples ZnSe after annealing in zinc vapors. The concentration of oxygen [O] in the samples corresponds: $3 \cdot 10^{18}$ (3), $\leq 10^{19}$ (2), and $\geq 10^{20} \text{ cm}^{-3}$ (1,4)

The band III characteristic for large excess Se we did not investigate here because there are previous reports in the literature [4].

The change of spectrum SA luminescence, connected with an increase of dissolved oxygen concentration $[O_s]$ is shown on samples ZnSe (Fig. 1, dotted 'curve 1') after their high-temperature and pressure treatment (HIP). It was observed that with the increase of dissolved oxygen concentration, a short-wave displacement of the SA-band occurring when the transitions from the oxygen zone of localized states to levels of acceptor SA centers $E_+ \rightarrow E_{SA}$ (Fig. 2), begin to predominate. Change of spectral position of the SA peak after HIP treatment is shown also in Figure 4 by vertical arrows.

Transitions to the acceptor centers E_{SAL} predominate in samples near to the stoichiometry. CL spectra with this kind of self-activated bands are shown in Fig. 1, curve 2. The main band of SAL luminescence is at 490 nm and corresponds transitions $E_- \rightarrow E_{SAL}$. It must be noted that SAL luminescence excludes transitions $E_{Zn_i} \rightarrow E_{SAL}$ (Fig. 2) since Zn_i disappears for the stoichiometric compound [2]. As it has been shown earlier, the limit of solubility of

oxygen depends on the ensemble of IPD, reaching the maximal size at about 1.3 mol% for the area of Zn excess, and it decreases sharply approximately by an order at change of IPD type at the point of stoichiometry $\Delta C=0$. Therefore, for these samples the value of splitting ($\Delta = E_+ - E_-$) degrees, especially for ZnSe since oxygen solubility is lower than for ZnS. In the presence of background impurity Cu are also observed transitions $E_+ \rightarrow E_{Cu(II)}$ and $E_- \rightarrow E_{Cu(II)}$. It is possible to observe these transitions when the concentration of dissolved oxygen is comparable with the concentration of copper. In Figure 1 'dotted curve 2' are shown very intensive and narrow peaks luminescence at 477 and 580 nm that determines the transitions from E_+ and E_- to the acceptor level Cu(II) (Fig. 2). These transitions allow to define the value of the conduction band splitting Δ .

Figure 3 represents the results of the CL study of sulfoselenides [2, 5] grown by CVD method with Zn excess and $[O] \leq 10^{20} \text{ cm}^{-3}$. The position of the SA-band in ZnS_xSe_{1-x} for the entire range of compositions, has a shorter wave length in comparison with those heat-treated at excess of zinc (Fig. 3). The observed

Elementary processes

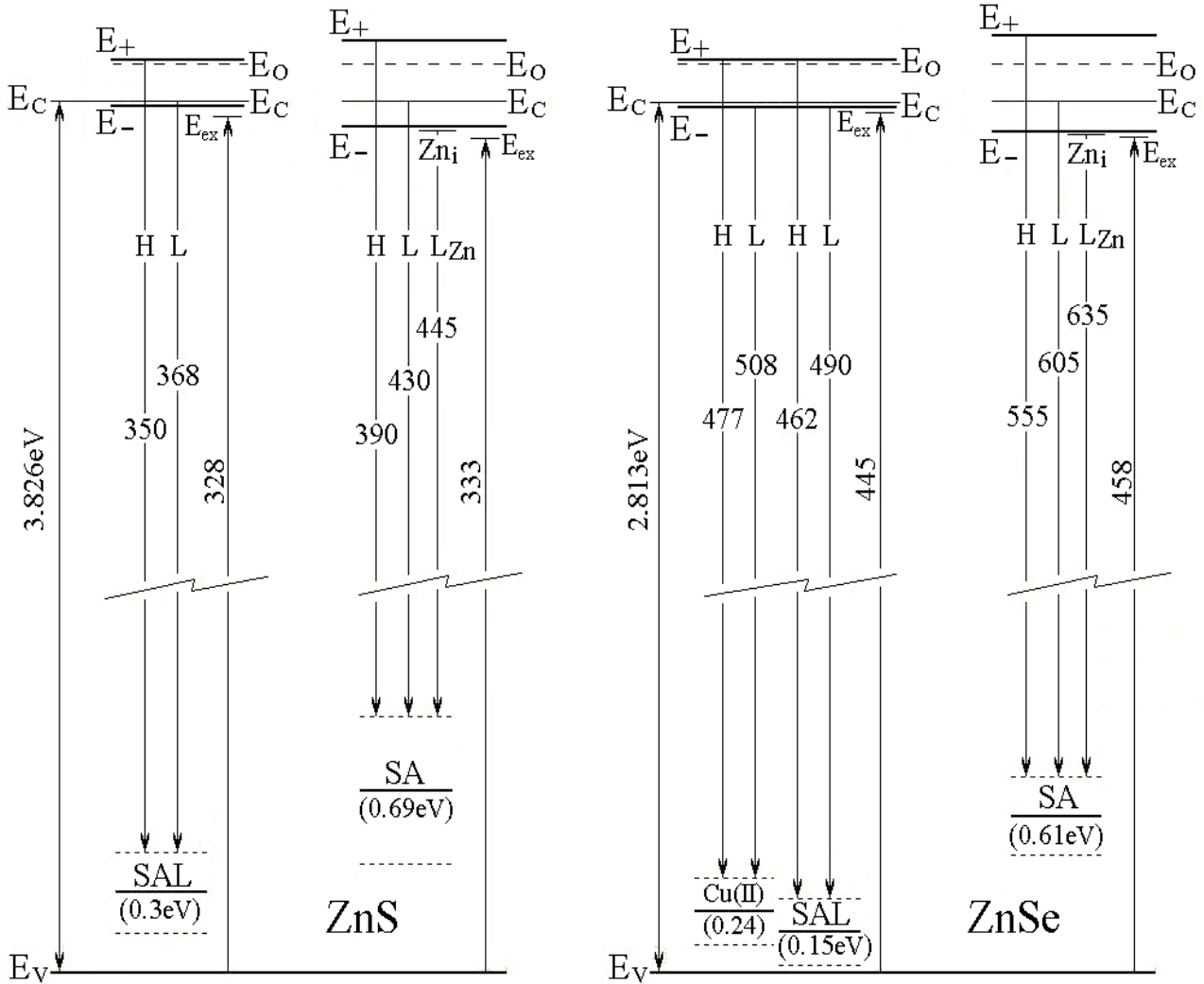


Fig. 2. Model of the self-activated transitions in the band gap ZnS·O and ZnSe·O at 80K. Wavelengths For luminescence and absorption bands are specified in nanometer. The concentration of oxygen [O] corresponds: ~ 0,1 mol % for SAL and 1 mol% for SA luminescence.

SA bands in these samples ZnS_xSe_{1-x} determine $E_C \rightarrow E_{SA}$ transitions. The observed shift of the SA band is in good agreement with the depth of the Zn_i^* levels in ZnS and ZnSe.

Influence concentration of dissolved oxygen $[O_S]$, as well as IPD (deviation from the stoichiometry); explain the dependence of changes in the spectra of self-activated luminescence on the composition of sulfoselenides reported in [4]. Thus, after HIP treatment, samples close to ZnSe show a change from SA luminescence to SAL luminescence (Fig. 3). This must correspond to the transition from excess of zinc area to stoichiometry. On the other hand, the samples similar to ZnS after HIP kept SA luminescence. This is in accordance with the IPD equilibrium (represented in [2]), where the area with excess of zinc Zn_i^* in ZnS – is wider. Therefore the samples ZnS, grown with Zn

excess at the same P_{Zn} had greater excess of Zn_i^* than ZnSe, and after its partial removal at HIP treatment remain within the limits of the same area (Fig. 3).

The analysis of spectra of reflection and absorption (and also excitation) ZnS and ZnSe with prevailing SA or SAL bands luminescence has allowed to complete the band model (Fig. 2) in crystals with dissolved oxygen. The position of the fundamental absorption edge E_- is characterized as E_{ex} (FE). Free exciton binding energy ZnS is taken by us as 40 meV, and 20 meV in ZnSe. The displacement of level E_- with increase of $[O_S]$ is determined by data in [3, 6] according to which it is 75 and 90 meV at 1mol % for cubic modification ZnS and ZnSe respectively. Position of the level of oxygen E_O above E_C is taken as 0.14 meV, according to our experimental data.

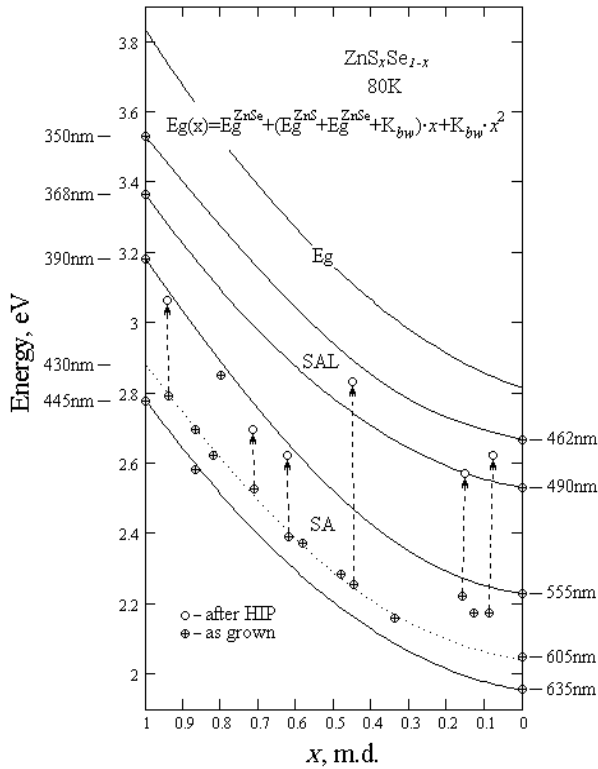


Fig. 3. The spectral position of self-activated bands luminescence in ZnS_xSe_{1-x} [2, 5].

It was estimated the values of splitting of the conduction band connected with the concentration of oxygen (in Fig. 2 at ~ 0.1 and 1 mol %). In the Figure 2, SA bands were examined for $[O_S] \sim 1$ mol %. It was

done because the maximal solubility of oxygen in the lattice is possible at excess Zn, as well as arises of the SA band luminescence. On the other hand, SAL luminescence was examined in the area of stoichiometry at concentration of dissolved oxygen 0.1 mol % that depends on the IPD type.

It is interesting the fact that excitons peaks observed in Fig.1 correspond to the free exciton of pure ZnSe. This can be explained as superposition of the CL spectra of heterogeneous samples: intense peaks for the pure areas and weaker peaks for the oxygen doped areas.

References

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