Semiconductors, 2022, Vol. 56, No. 5

Main effects of oxygen centers in $A^{II}B^{VI}$ optics

© N.K. Morozova[1], I.I. Abbasov[2]

[1] National Research University „Moscow Power Engineering Institute“,
111250 Moscow, Russia
[2] Azerbaijan State Oil and Industry University,
AZ1010 Baku, Azerbaijan
E-mail: MorozovaNK@mail.ru

Received December 26, 2021
Revised January 10, 2022
Accepted January 10, 2022

On the basis of the studies carried out, it is shown in the work that the influence of oxygen on the optical properties of $A^{II}B^{VI}$ crystals is determined by three main effects. This is the formation of a system of bound excitons accompanying the presence of high oxygen concentrations at stacking faults — a long-wavelength shift by hundreds of meV of the absorption edge, and the third effect is determined by the emergence of broadband „self-activated“ SA luminescence in the near-edge region of the spectrum. This work introduces the concept of a non-uniform distribution of isoelectronic oxygen centers in the bulk of crystals, both due to their predominant segregation at stacking faults and in layer of stacking faults. To analyze the optical data, we used the capabilities of the method for constructing band models, which collects extensive and multilateral information about specific samples. A refined models of the CdS(O) and ZnSeSe(O) multizone with stacking faults is presented. The paper describes the conditions and the possibility of joint and separate observation of these features in the spectra of different crystals $A^{II}B^{VI}$ and using them to create lasers.

Keywords: band model, bond excitons, additional absorption edge AAE, point defects, stacking faults, band anticrossing theory (BAC), laser effect.

DOI: 10.21883/SC.2022.05.53427.9793

1. Introduction

In previous years, the role of oxygen in the optics of $A^{II}B^{VI}$ crystals was considered mainly from the point of view of the dependence of self-activated SA emission on the presence and concentration of oxygen. An anomalous long-wavelength shift by hundreds of meV of the additional absorption edge of crystals, in which an increase in the oxygen content was assumed, was also revealed.

Our investigations of the edge luminescence of CdS, ZnS and ZnSe also revealed a group of narrow bands due to bound excitons (BE_{ex}) at oxygen centers in layers of stacking faults (SF) [1–7].

As the excitation density increased, stimulated emission and a laser effect were observed.

In this review report, an attempt is made to concentrate the final results obtained on the basis of a more detailed analysis of the conditions and the possibility of joint and separate observation of these features in the spectra of $A^{II}B^{VI}$ crystals.

2. Materials and methods of experiment

Mainly the results of studying CdS, ZnS and ZnSe crystals grown from the gas phase are considered. The work is based on the study of a group of crystals with a deviation from stoichiometry specified during growth and a known content of dissolved oxygen at the level of $10^{20}\,\mathrm{cm}^{-3}$.

In this case, real CdS(ZnS) single crystals grow from the gas phase in the central part of the homogeneity region of the compound. For zinc selenide, samples grown by the CVD method with a large excess of selenium and an oxygen concentration of $10^{20}\,\mathrm{cm}^{-3}$, which was facilitated by coactivation with copper [5], are presented.

The homogeneous distribution of oxygen at the level of $10^{20}\,\mathrm{cm}^{-3}$ is explained by its compensation by stacking faults, which are usually found in all single crystals.

For studying the photo and cathodoluminescence (CL) of crystals, various techniques were used with a change in the intensity of excitation of CL and pulsed excitation, methods of local shooting in a scanning electron microscope (SEM). Photoluminescence was studied with a step change of $\sim 30\,\mathrm{meV}$ in the excitation energy in the region of the fundamental absorption edge. The data of absorption and reflection spectra were used.

3. Concluding discussion of the experimental data

In fig. 1, the main effects determining the role of oxygen are presented by the example of CdS (O) in band models of a crystal with stacking faults. The construction is based on the principles of the band anticrossing theory (BAC) [4,8–10].

The model is based on the following features of oxygen in $A^{II}B^{VI}$ [1]: 1) oxygen is always present in $A^{II}B^{VI}$ compounds, which is confirmed by analyzes and

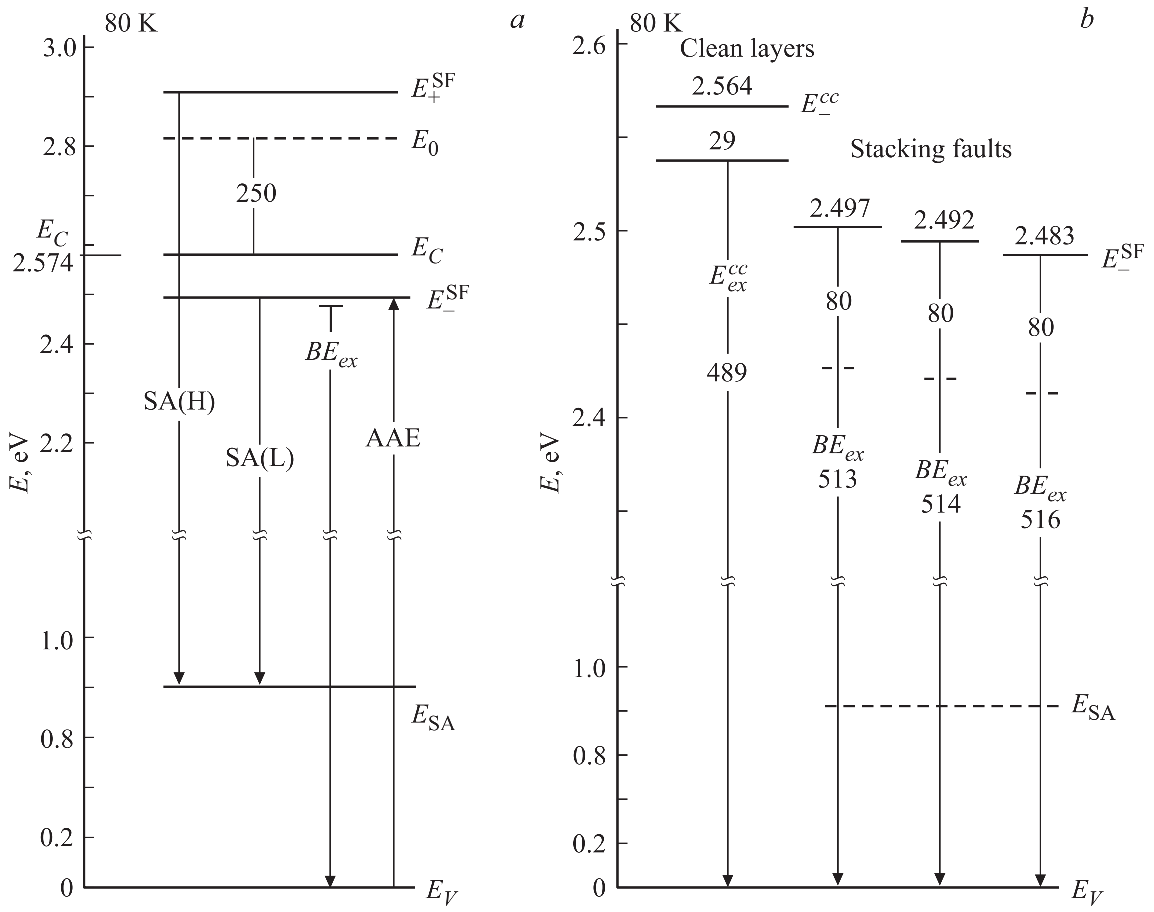

Figure 1. Band models of CdS(O) crystals: *a* — model for CdS with $[O_S] \sim 10^{20}\,\text{cm}^{-3}$, emission and absorption bands due to SA centers are highlighted, *b* — multizone of the same crystal for the edge emission spectrum. Deep levels of recombination of E_{SA} self-activated SA radiation are noted [2]. The positions of the E_+^{SF} and E_-^{SF} levels in the stacking faults SF are given on the assumption that the subband shift is linear and corresponds to 90 meV by 1 mol% ($2 \cdot 10^{20}\,\text{cm}^{-3}$) O_S [1].

substantiated thermodynamically; 2) compensation of the volume mismatch of the oxygen centers O_S^* (or oxygen complexes) by the lattice is carried out due to the formation of stacking faults; 3) the presence of O_S in increased concentrations at stacking faults is accompanied by a change in the band structure of the crystal in accordance with the BAC theory [8–10].

For CdS(ZnS) crystals, which usually have a composition close to stoichiometry with a small excess of metal, SA centers are typical. According to [1], these are complexes of intrinsic defects and oxygen $\{O_S^*Cd_i^\bullet V_{Cd}^{//}\}^{/}$.

In the left part of the diagram (Fig. 1, *a*), the self-activated luminescence and absorption bands in crystals with $[O_S] \sim 10^{20}\,\text{cm}^{-3}$, due to SA centers, are marked. In accordance with the BAC theory, two bands of self-activated luminescence of cadmium sulfide (SA(H) 600 and SA(L) 720 nm) are determined by two transitions to deep levels of centers recombination: $E_+^{SF} \to E_{SA}$ and $E_-^{SF} \to E_{SA}$ [1].

Oxygen SA centers also determine the second effect — the additional absorption edge (AAE). In fig. 1 this corresponds to transitions $E_V \to E_-^{SF}$.

The edge emission spectrum CdS BE_{ex} is shown separately on the right side of the diagram (Fig. 1, b). This part of the diagram is based on the experimental data described in detail in [2]. In clean layers $[O_S] \sim 2 \cdot 10^{19}\,\text{cm}^{-3}$. According to [2], the emission band of clean layers CdS E_-^{cc} determines the laser effect at high excitation intensities.

The spectrum of bound excitons of CdS arises due to transitions from the subband, created by SA centers at stacking faults, to the valence band $E_-^{SF} \to E_V$ (Fig. 1, *b*). The set of bands CdS(O) edge luminescence is determined by the annihilation of excitons from different regions, which differ somewhat in their oxygen content. This corresponds to studies of the structure of the SF layers in the SEM (see below). As an averaging for all closely spaced levels of bound excitons BE_{ex} Fig. 1, *b* gives the designation of the bottom of the subband of the entire stacking fault layer — E_-^{SF}.

The values of oxygen concentrations on the SF, calculated from the spectra of the green edge luminescence of CdS(O), reveal a relatively narrow range of crystal compositions for

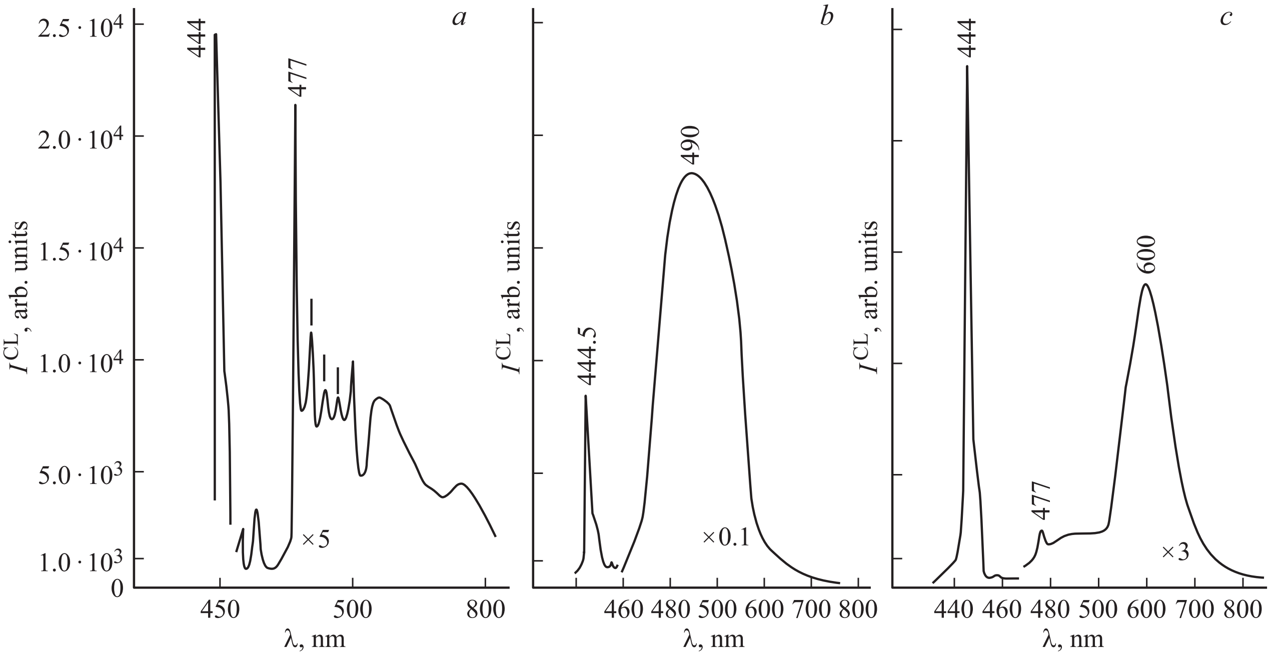

Figure 2. Changes in the CL spectra at 80 K along the length of the CVD condensate: ($a \to c$). At the entrance to the reactor — (a); with a decrease in the vapor pressure of Se and slightly oxygen in the gas phase — ($b \to c$) [3].

which the SA oxygen centers are completely compensated by own point defects [11,12].

According these works, the system of levels of localized excitons BE_{ex} at stacking faults does not change with temperature. The BE_{ex} bands were observed for CdS at the same wavelengths at both 80 and 300 K [1,2,11,12].

In contrast to the considered crystals of CdS, zinc selenide has a wide range of homogeneity [1–3] and can be obtained with a significant excess of selenium. The emission spectrum of such crystals acquires new features [1,3,5].

Figure 2 shows CVD ZnSeSe(O) samples grown with the introduction of an excess of selenium and oxygen up to 4% into the gas phase. Calculation of the equilibrium of intrinsic point defects under growth conditions showed that the range of sample compositions is shifted significantly from the „stoichiometric region" to p-type ZnSe [3].

As seen from Fig. 2, a, for ZnSeSe(O), a group of very narrow (~ 20 meV) bands with a head line at 477 nm and LO phonon repeats in the region of 477−490 nm is observed. With increased [$\mathrm{O_S}$] (Fig. 2, b), all components of this multiband ZnSeSe(O) spectrum are enhanced, overlap, and give a total broad band with a maximum of ~ 490 nm. The ~ 490 nm band is very intense and dominates in the entire 450−600 nm spectral range (Fig. 2, b).

Changes in the spectrum with a decrease in the excess of Se during the growth and enrichment of crystals with zinc are shown in Fig. 2, $b \to c$. In this case, the 490nm band decreases in intensity, its individual components stand out, in particular, 477 nm. With an excess of Zn in the crystals, the SA(L) band appears and prevails as the main, self-activated 600 nm emission.

According to [3–6], the spectral shift of these narrow lines is absent with increasing temperature. A study of the 477 nm band in pulsed CL spectra [3,7] showed that its maximum does not shift with increasing excitation intensity, when the band dominates in the spectra. In pulsed CL at an excitation density of $\geq 10^{25}\,\mathrm{cm}^{-3}\cdot \mathrm{c}^{-1}$, stimulated emission with an increase in the intensity of the 477 nm band [7].

Refinement of the position of the E_{+}^{SF} level in the ZnSeSe(O) band model according to the data of [6] made it possible to determine the nature of the narrow bands. In fig. 3 shows the ZnSeSe(O) band model with stacking faults according to the experimental data of this work.

The E_{-}^{SF} defines the position of the bottom of the conduction band in the stacking fault layer. The main band is 477 nm, according to Fig. 3, b corresponds to a bound BE_{ex} exciton. In this case, in relatively inhomogeneous stacking fault layers (Fig. 3, c), the 477-nm band belongs to the regions with the minimum [$\mathrm{O_S}$], while the 490-nm band belongs to the regions doped to the maximum with oxygen. This interpretation differs from the earlier description of these ZnSeSe(O) spectra in [1,3,5] as SA(II).

Unlike CdS, in fig. 3, b, there are no levels of SA complexes containing excess zinc. The bands of the self-activated SA emission of ZnSe ~ 540 nm (SA-H) and ~ 630 nm (SA-L) are not observed in the ZnSeSe(O) spectra. Bound excitons determine the main radiative channel $E_{-}^{\mathrm{SF}} \to E_{\mathrm{V}}$ and, at high excitation intensities, the laser effect [7]. The spectrum of a bound exciton is due to the segregation of the isoelectronic centers Ose in the complexes on the SF. The edge of the additional absorption of such crystals is shifted to the long-wave side by the amount of the E_{-}^{FS} level shift relative to the E_C (Fig. 3, b).

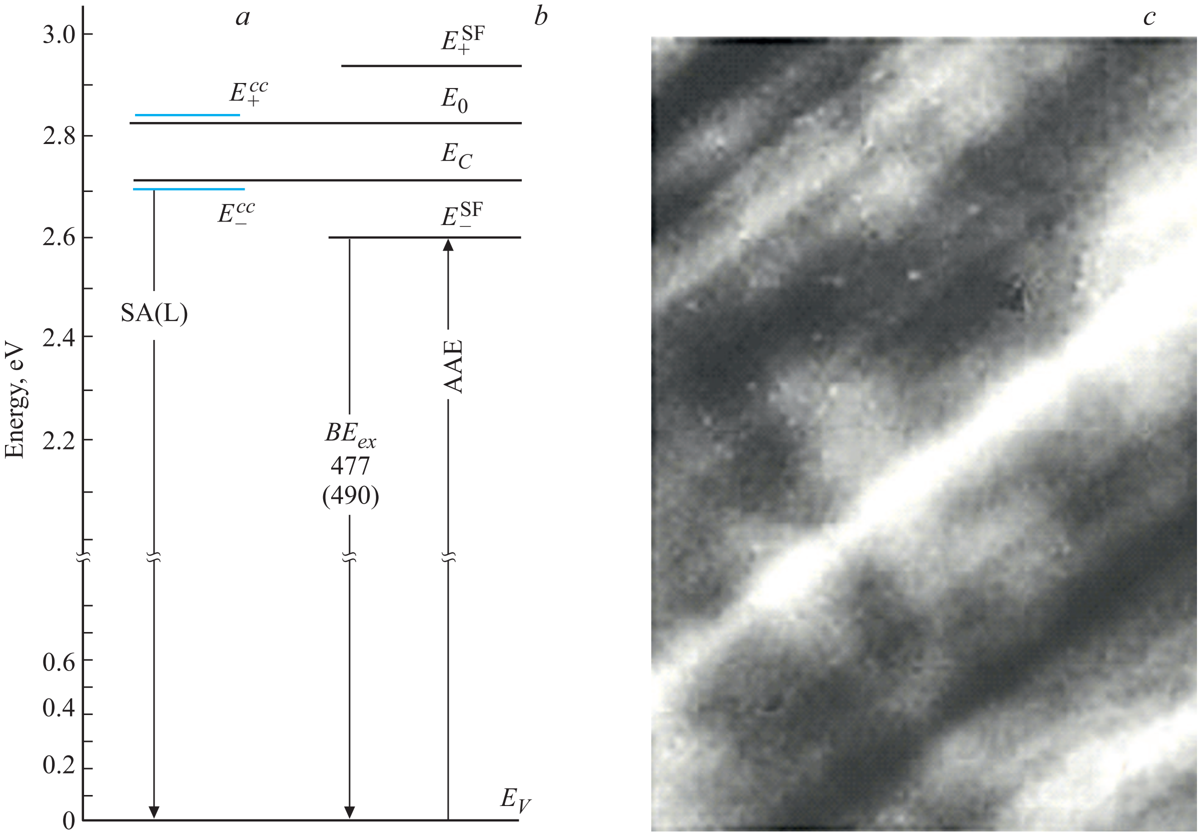

Figure 3. Multizone of a ZnSeSe(O) crystal. Pure layers — (*a*), layers of stacking faults — (*b*). The edges of the subbands of pure layers in Fig. 3, *a* are denoted as E_-^{cc} (E_+^{cc}). The subband shift for ZnSe corresponds to $\sim 100\,\text{meV}$ per 1 mol% of dissolved oxygen [1]. Figure 3, *c* shows a photo of an $A^{II}B^{VI}$ (CdS) single crystal cleavage in the compo SEM mode at ×5000 magnification. Dark areas with high oxygen content highlight layers of stacking faults.

The spectrum of bound excitons can be observed as an independent one for certain ZnSe compositions when there is no excess of zinc and its complexes. For CdS(ZnS) or ZnSe crystals with an excess of Zn, this is impossible, since the presence of oxygen in crystals in this case is determined by SA centers, which are simultaneously responsible for broadband emission, additional absorption, and the spectrum of bound BE_{ex} excitons.

4. Conclusions

We note the following main results of the work.

1. The oxygen centers responsible for the effects in the luminescence and absorption of $A^{II}B^{VI}$ crystals have been identified. The oxygen present in complexes on stacking faults changes the band structure of the crystal, which determines the long-wavelength shift of the absorption edge by hundreds of meV and the spectrum of bound excitons. The $\{O_B\,A_i^{\bullet}V_A^{//}\}^{/}$ complexes besides form deep recombination levels that lead to the appearance broadband „self-activated“ SA-emission.

2. It is shown that self-activated crystals ZnSeSe(O), similar in composition to the *p*-type of conductivity and containing elevated oxygen concentrations in complexes with Cu, have an anomalous radiation spectrum of bound (localized) excitons that determines their optical properties.

3. Taking into account the composition and structure crystals, the band models are refined, as well as the nature of individual luminescence bands ZnSe(O) and CdS(O).

4. Conditions are described that make it possible to observe various types of emission (absorption) spectra at change in the intrinsically defective structure and composition of crystals.

5. Results are presented on the prospects of using $A^{II}B^{VI}$ crystals with different structures and compositions for semiconductor lasers.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] N.K. Morozova. *New in the optics of II–VI–O compounds (New possibilities of optical diagnostics of single-crystal systems with defects)* (LAP LAMBERT Academic Publishing, Riga, Latvia, 2021).

[2] N.K. Morozova, I.N. Miroshnikova. FTP, **55** (11), 1068 (2021) (in Russian).

[3] V.V. Blinov. *Optics of centers due to the presence of oxygen and copper in $A^{II}B^{VI}$ compounds (for example, ZnSe).* Cand. dis. (M., MEI, 2003).
[4] D.A. Mideros. Optical properties of A_2B_6 compounds with isoelectronic oxygen from the point of view of the band anticrossing theory. Cand. dis. (M., MEI, 2008).
[5] N.K. Morozova, I.N. Miroshnikova. FTP, **54** (1), 59 (2020) (in Russian).
[6] N.K. Morozova, I.I. Abbasov, E.M. Gavrishchuk, M.A. Musayev, J.I. Huseynov, A.J. Mammadova. FTP, **56** (1), 80 (2022) (in Russian).
[7] V.I. Oleshko, S.S. Vilchinskaya, N.K. Morozova. FTP, **55** (5), 403 (2021) (in Russian).
[8] W. Shan, W. Walukiewicz, J.W. Ager III, K.M. Yu, J. Wu, E.E. Haller, Y. Nabetani, T. Mukawa, Y. Ito, and T. Matsumoto. Appl. Phys. Lett., **83** (2), 299 (2003).
[9] M.A. Mayer, Kin Man Yu, E.E. Haller, W. Walukiewicz. J. Appl. Phys. **111** (11), 113 (2012).
[10] W. Walukiewicz, W. Shan, K.M. Yu, M.J. Seong, H. Alawadhi, A.K. Ramdas. Phys. Rev. Lett. 85(7). 1552 (2000).
[11] N.K. Morozova, A.A. Kanakhin, A.S. Shnitnikov. Semicond., **49** (9), 1134 (2016).
[12] A.A. Kanakhin. *Application of the model of anticrossing zones in the case of high oxygen doping CdS.* Cand. dis. (M., MPEI, 2015).