

LUMINESCENT AND OPTICAL CHARACTERISTICS OF ZINC SULFIDE THIN FILMS PRODUCED BY CLOSE-SPACED VACUUM SUBLIMATION*

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The luminescent and optical characteristics of ZnS thin films produced by close-spaced vacuum sublimation technique (CSVs) were investigated in this work. Luminescent and optical investigations allowed determining the fluorescence centers of native defects and uncontrolled impurities.

Key words: ZnS thin films, close-spaced vacuum sublimation, photoluminescence, optical properties, native defects.

1. INTRODUCTION

ZnS is an important II–VI compound semiconductor with a large band gap. It is used as a key material for light-emitting diodes [1], cathode-ray tubes [2], thin film electroluminescence [3], and buffer layers in photovoltaic cells [4].

Last material application is caused by a transparency of ZnS thin films to practically all wavelengths of the solar spectrum, besides it is a “Cd-free” and “low-cost” material.

Chemical bath deposition (CBD) is the commonly used method for production of ZnS layers. Even though cells with the ZnO/CBD-ZnS/CIGS structure have high efficiencies ($\eta=18,6\%$) [5], manufacturing companies have sought alternatives to the CBD deposition technique [4]. It occurs, because the CBD – ZnS film includes a large amount of oxygen in the form of Zn(OH)₂ and ZnO [6]. It is considered that close-spaced vacuum sublimation (CSVs) method [7] may become successful alternative to CBD-method for producing of ZnS layers with enhanced characteristics and not containing oxide phases [8]. It is besides important to know as a growth condition influence on native defects and uncontrolled impurities in ZnS films.

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The preferred characterization methods for such problem are optical absorption and luminescence. If discrete energy levels are present in the band gap, these may dominate the optical spectrum. Luminescence measurements then yield information about the energetic positions of the electronic states in the gap. Such localized states can be due to various types of imperfections like vacancies, interstitial atoms, and atoms at surfaces and grain boundaries. It is often difficult to determine the exact energy positions of these states, because they may be very close in energy.

Luminescence in bulk solids with wide band gaps has been investigated for a long time [9–11]. However, thin films of such materials became of interest just recently. As reported before ZnS has a band gap of 3,68–3,8 eV zinc-blend (ZB) or wurtzite (WZ) at 300 K. This corresponds to ultraviolet (UV) radiation for optical interband transition, with a wavelength of $\lambda=336$ nm. Wide-band gap semiconductors are ideal materials for studies of discrete states in the gap.

In this paper, we report the results of our research on luminescent and optical properties of ZnS thin films produced by CSVS technique under various substrate temperature T_s .

2. EXPERIMENTAL

ZnS thin films were deposited on cleaned glass substrate by CSVS method. The powder of the stoichiometric compound was used as a source material. Charge of ZnS has WZ structure with small portion of the ZB phase. During the thin films deposition evaporator temperature was $T_e = 1473$ K. A substrate temperature was changed in a ranges $T_s = 393$ – 893 K. The system was then pumped down to a base pressure of $5 \cdot 10^{-3}$ Pa. The thickness (l) of as-deposited films was measured between 6–8 μm using the interference technique and by the cross-section microphotography.

Luminescent properties was investigated used by electrical fluorometer MPF-4 Hitachi in the range of wavelengths $\lambda = 360$ – 710 nm under 4,7 K and 77 K temperature. As excitation source we used the xenon lamp ($\lambda = 325$ nm). The low temperature investigations defined with the helium refrigerator. The luminescence spectra processing was performed by ORIGIN program.

Optical properties of the films were investigated by double-beam spectrophotometer in the range of wavelengths $\lambda = 320$ – 520 nm under room temperature. Spectra of optical transmission $T(\lambda)$, absorption coefficient $\alpha(\lambda)$, refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ of zinc sulfide were measured, too. Further, spectral distributions of the absorption coefficient $\alpha(\lambda)$ of were calculated from the $T(\lambda)$ spectra in the range of strong light absorption using the Lambert's expression: $\alpha = -\ln(T)/l$.

3. RESULTS AND DISCUSSION

3.1. OPTICAL STUDY

Transmission spectra $T(\lambda)$ of ZnS films are shown in the Fig.1. As one can see, under radiation wavelengths larger than $\lambda=(350-360)$ nm (the photon energies are less than E_g of the material) the significant increase of the layers transmission coefficient is observed. In the range $\lambda=(440-470)$ nm this coefficient is somewhat smaller and then again increases. At $\lambda>(490-500)$ nm all the investigated films have a very high transmission coefficient up to 85–95%. The analysis shows that the maximal value of the optical transmission have the ZnS films obtained at the substrate temperature $T_s = 373$ K, the minimal value corresponds to the $T_s = 573$ K. The various crystallographic and phase structure of the samples grown under different conditions causes the difference in their transmission coefficient [8].

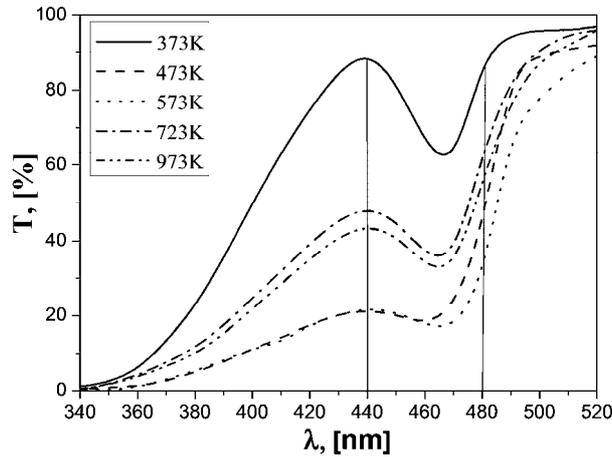


Fig. 1 – Transmission spectra of ZnS films obtained under various substrate temperatures T_s (shaded area – conditioned the zinc (sulphur) vacancies, probably).

The spectrum has an additional line of absorption $\lambda=(440-480)$ nm. It can be explained absorption of light on zinc vacancies, which are dominating in ZnS [11]. Presence of zinc vacancies is confirmed also with luminescent researches, see below.

To determine the optical band gap E_g of zinc sulfide we have applied the common expression valid for direct-gap and indirect-gap semiconductors:

$$\alpha h\nu = A(h\nu - E_g)^m, \quad (1)$$

where A is a constant depending on the effective mass of the charge carriers in the material, $h\nu$ is incident photon energy, α is an absorption coefficient, m is determined by the mechanism of photon absorption in the semiconductors; for direct materials

(ZnS is a direct – gap compound) $m=1/2$. Therefore, the extrapolation of linear part $(\alpha hv)^2 - hv$ – dependence down to interception with the energy axis enables to determine the optical band gap of the semiconductor (Fig. 2).

As demonstrates Fig. 2, the band gap values of the layers obtained at different substrate temperatures is varied. As the substrate temperature increases from 473 K to 973 K the band gap changes from $E_g=3,39$ eV to $E_g=3,59$ eV respectively.

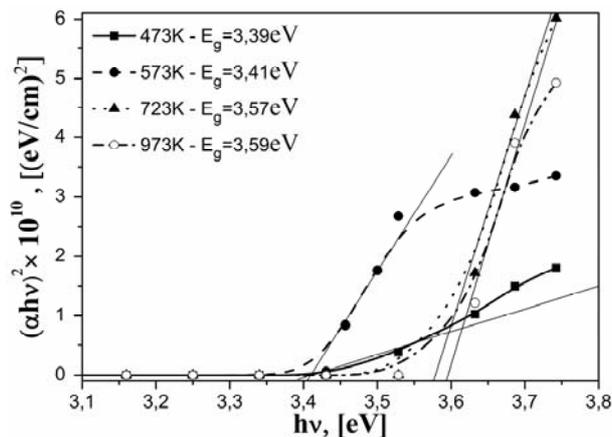


Fig. 2 – $(\alpha hv)^2 - hv$ dependencies of ZnS films obtained under various substrate temperatures T_s .

These results are in a good agreement with the data obtained for ZnS layers at $T_s=(473-623)$ K by method of close-spaced sublimation – $E_g = (3,42-3,61)$ eV [14], at $T_s=(573-773)$ K by pyrolysis – $E_g = (3,2-3,52)$ eV [15] and are somewhat lower than the data for single crystals zinc sulfide ($E_g = 3,68$ eV for the ZB phase) [16]. Increase of the ZnS films band gap under increasing the growth temperature is similar to that what we have observed.

3.2. LUMINESCENT STUDY

The photoluminescence (PL) spectrums of ZnS thin film deposited at different temperatures (Fig. 3, a–b) under the excitation with a wavelength of 325 nm indicates: at $T_s = 393$ K – two peaks at $\lambda_1=396$ and $\lambda_3=478$ nm. Lines dominating thus $\lambda_1=396$ nm, this peak are dissymmetric.

The line with $\lambda = 478$ nm also is present in the spectrums from a film with $T_s = 613$ K, here it is most intensive. At increase the condensation temperature T_s of ZnS films the luminescence spectrums essentially varies. There is a considerable quantity peaks which overlap one another. The most intensive from them situated in a range $\lambda=(560-620)$ nm. The spectrum peaks fragmentation was performed by ORIGIN program. Some results of peaks processing (for sample with $T_s=393$ K) are showed in Fig. 4.

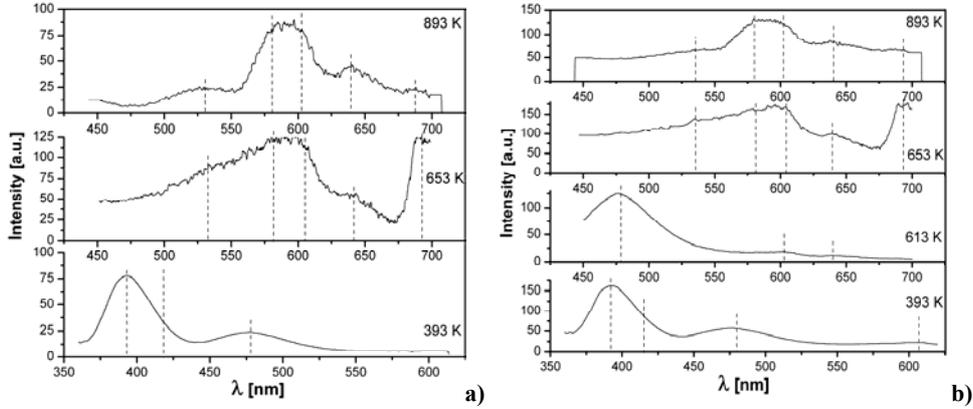
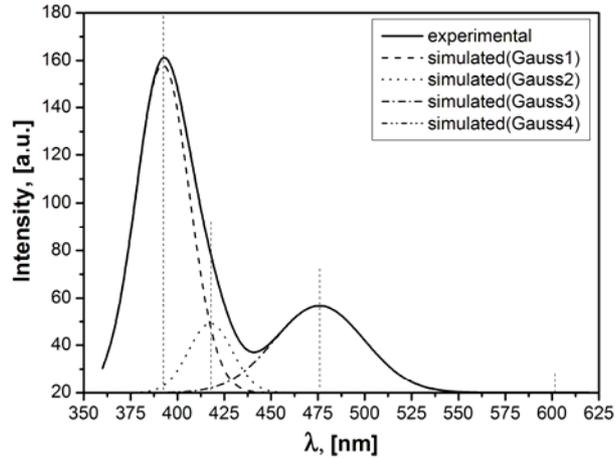


Fig. 3 – PL emission spectrums (a – at 4,7 K; b – at 77 K) of ZnS films obtained at different condensation temperature T_s .

Fig. 4 – PL emission spectrum (at 77 K) of ZnS film obtained at $T_s = 393$ K with simulated peaks fragmentation.



Vertical lines in Fig. 3, 4 showed the peaks positions, these values are summarized in Table 1.

It is considered that a radiation takes place as a result of transition an electron from the conduction band on the local level near by valence band. Then the optical depth of occurrence of level the defect (ΔE) from a valence band is equals to:

$$\Delta E_n = E_g - E_n, \quad (2)$$

where $E_g = 3,68$ eV – optical band gap ZB ZnS, $n = 1, 2, 3, \dots n$ – peaks number.

As the ZnS films preliminary were not doped it is considered that lines on spectra are caused to native defects, complexes of native defects and uncontrollable impurities. Concentration of uncontrollable impurities in initial charge didn't exceed $N = 10^{14} \text{ cm}^{-3}$. With use of the literature data we transacted identification of

the localized centers (Table 1). Apparently from the table good correlation of results with data for bulk crystal ZnS is observed. Dominating defects in ZnS films by the results of researches are: at low temperature condensation – V_{Zn}^- , at high temperature condensation – V_S . It is caused by a deviation of chemical composition from stoichiometric.

Table 1

Results of processing of luminescence spectrums (the **bold** select the most intensive pics)

T_s , K	Measuring range λ , nm	λ_1 , nm E_1 , eV	λ_2 , nm E_2 , eV	λ_3 , nm E_3 , eV	λ_4 , nm E_4 , eV	λ_5 , nm E_5 , eV	λ_6 , nm E_6 , eV	λ_7 , nm E_7 , eV	λ_8 , nm E_8 , eV
393	360–640	396	417	478			603		
		3,13	2,97	2,59			2,06		
613	450–720			478			603	640	
				2,59			2,06	1,94	
653	450–720				530	582	603	640	690
					2,34	2,13	2,06	1,94	1,80
893	450–720				530	582	603	640	690
					2,34	2,13	2,06	1,94	1,80
ΔE , eV exp.		0,55	0,71	1,09	1,34	1,55	1,62	1,74	1,88
Lattice defect		V_{Zn}^-	(O_s, V_{Zn}^{2-})	V_{Zn}^{2-}	Cu	V_S^{2+}	V_S^{2+}	<i>impur</i>	V_S^+
ΔE , eV ref.		0,60	0,70	1,10	–	1,40	1,40	–	1,90
Ref.		[17]	[17,18]	[11]	[19]	[11]	–	–	[11]

In luminescent spectra lines of an activator impurity (Cu) and complexes of native defects (O_s, V_{Zn}^{2-}) also are revealed.

4. CONCLUSIONS

The luminescent and optical characteristics of ZnS thin films obtained by close-spaced vacuum sublimation technique under different grow temperatures were carried out. The analysis shows that the maximal value of the optical transmission has the ZnS films obtained at the substrate temperature $T_s = 373$ K, the minimal value corresponds to the $T_s = 573$ K. Increase of the ZnS films band gap under increasing the growth temperature is similar to that what we have observed. Dominating defects in ZnS films by the results of researches are: at low temperature condensation – V_{Zn}^- , at high temperature condensation – V_S . On the basis of our researches the defect energy levels of native defects in the ZnS band gap are proposed (Table 1).

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