

Optical Properties of Pure and Eu Doped ZnSe Films Deposited by CSVS Technique

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Pure (ZnSe) and europium doped (ZnSe:Eu) zinc selenide films were evaporated onto glass substrates using the close-spaced vacuum sublimation (CSVS) technique at different deposition conditions (substrate temperature). The fundamental optical parameters such as optical density, extinction coefficient, refraction index, real and imaginary parts of optical dielectric constant, band gap were evaluated in transparent region of transmittance and absorbance spectrum. Optical spectroscopy analysis shown that in both cases deposited films had a high level of transmittance values (55-65 % for ZnSe films and 80-90 % for ZnSe:Eu films). Moreover, evaluated values of the films optical band gap were in the range of $E_g = (2.63-2.69)$ eV for ZnSe films and $E_g = (2.77-2.81)$ eV for ZnSe:Eu for films with increasing of the films substrate temperature. Fourier-transformed infra-red (FTIR) analysis of deposited ZnSe and ZnSe:Eu films shown that all investigated samples are well-crystalline and identified vibrations are typical for II-VI semiconductors.

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1. INTRODUCTION

In recent years II-VI semiconductors film compounds pay a higher attention of researchers due to its unique physical characteristics and their potential usage in a wide range of instrumental applications, such as: absorption (CdTe, CdSe), window (ZnS, ZnSe, CdSe, CdTe) and conduction or buffer (ZnO) layers of high-efficiency solar cells [1], light-emission diodes (LED's) [2], irradiation detectors [3], scintillators [4], etc. Among them zinc selenide (ZnSe) film, due to its wide band gap ($E_g = 2.70$ eV) is an attractive compound for optoelectronic devices usage [5].

In II-VI compounds the incorporation of rare-earth elements (Eu, Sm, etc.) leads to improve their physical properties, such as improving their characteristics in optoelectronics applications [6]. Among these rare-earth elements Eu^{3+} ion doping is intensively researched due to its specific spectral characteristics. Moreover, Eu ions incorporation in II-VI compounds allows increasing their physical characteristics [6]. So, the aim of our investigation is to study the optical properties (refraction, extinction indexes, real and imaginary part of optical dielectric constant, optical band gap) of ZnSe:Eu and pure ZnSe films and to investigate the Eu incorporation on ZnSe films on their optical properties.

Nowadays, there are the different techniques for fabrication ZnSe films: thermal evaporation [7], pulsed laser deposition [8], chemical bath deposition [9], spray pyrolysis [10], pulsed laser ablation [11], electrochemical deposition [12], molecular beam epitaxy [13], magnetron sputtering [14], close-spaced vacuum sublimation (CSVS) [15]. The last method due to the technical features of evaporator, allows to obtain fine-crystalline stoichiometric films in conditions approach to the thermodynamic equilibrium. Moreover, this technique is comparable low-cost and simplify [16, 17].

Presently, the optical properties of ZnSe:Eu films have not been completely investigated. This fact stipulated the aim of our study presented in this paper.

2. EXPERIMENTAL DETAILS

ZnSe and ZnSe:Eu films were deposited onto ultrasonically cleaned glass substrates by CSVS technique from pure ZnSe (purity was 99,99 %) and Eu incorporated ZnSe (the Eu percentage was 0.1 %) powder (the powders were synthesized by Institute for Single Crystals NAS of Ukraine, Kharkiv, Ukraine) by VUP-5M vacuum equipment at a residual gas pressure $P = 5 \cdot 10^{-3}$ Pa under the following evaporation conditions: constant temperature of evaporator ($T_e = 1073$ K for ZnSe; $T_e = 1123$ K for ZnSe:Eu), substrate temperature was varied in both cases in the range of $T_s = (373-573)$ K, time of evaporation was $t = 1$ min. The powders were evaporated from the molybdenum boat. The vapor transport was provided in the cylindrical enclosed volume. To achieve the vapor condensation the walls of enclosed volume are heated. The substrate temperature was changed by the substrate heater and controlled by the thermal couples and proportional-integral-derivative controller TRM-10 (Oven Corp., Moscow, Russian Federation) [16]. A detailed description of this technique is presented in [18].

Optical study was performed by Guangdong 721G UV-Vis spectrophotometer in the range of wavelengths $\lambda = (320-600)$ nm at room temperature. Optical transmission $T(\lambda)$ and absorption $a(\lambda)$ are measured. Further spectral distributions of reflection $R(\lambda)$, extinction $k(\lambda)$, refraction $n(\lambda)$, real $\epsilon_1(\lambda)$ and imaginary $\epsilon_2(\lambda)$ part of optical dielectric constant were evaluated by the methodology described in [19].

Fourier-transformed infrared (FTIR) study was performed by Cary 630 spectrometer (Agilent Technologies, USA). FTIR spectra were obtained in a full-refraction regime (Diamond ATR appliance). The spectral range in all cases of obtained films was varied in the range of $\nu = (650-4000)$ cm^{-1} .

The films thickness of obtained films was determined by the novel technique based on "fringing effect" [20]. The films thickness was calculated by the next

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equation:

$$d = 1/2 \times n \times N / (v_1 - v_2) \quad (1)$$

where d is the films thickness; n is a refractive index of sample; N is a number of fringes within a given spectral region; v_1, v_2 are the start and end points in the spectra in cm^{-1} [21].

3. EXPERIMENTAL DETAILSES

3.1 Optical Spectroscopy Study

The transmittance $T(\lambda)$ and reflectance $R(\lambda)$ spectra of pure and Eu doped ZnSe films, obtained at different deposition conditions are presented on Fig. 1. From transmittance spectra we observed the maxima and minima of the intensities which are connect to the interference of light in thin layers. This fact allows us to fixed the homogeneity of samples. Moreover, it should be noted that transmission values of ZnSe:Eu films are significant larger (80-90 %) than in pure ZnSe films (55-65 %).

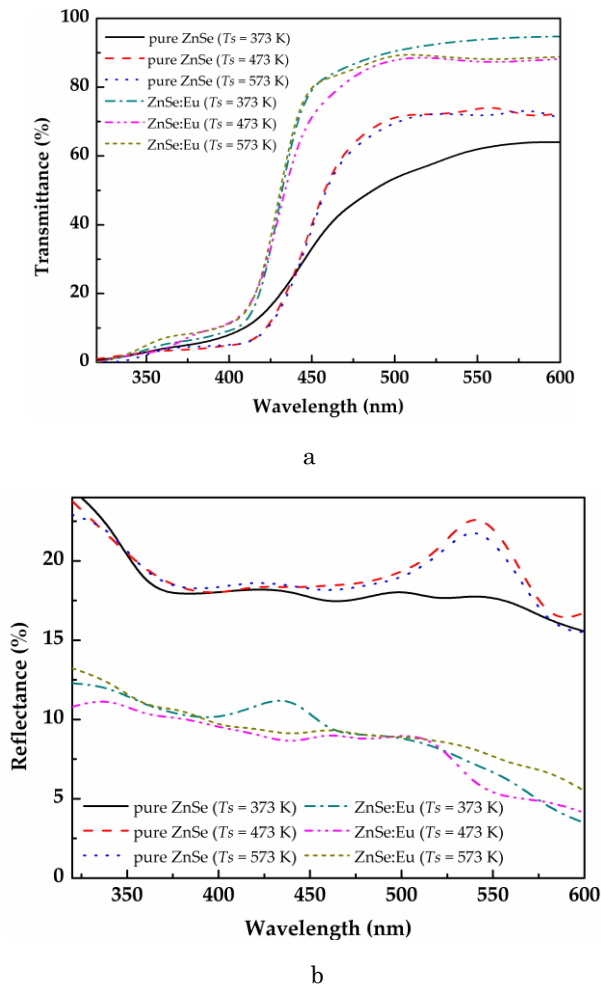


Fig. 1 – Transmittance (a), and reflectance (b) spectra of ZnSe and ZnSe:Eu films

The difference of transmittance and reflectance values of films, deposited at different substrate temperature, is due to their phase state, structural and sub-structural features of samples [22]. Similar to the $T(\lambda)$

spectra, the reflection dependencies of samples have maxima and minima values, which are also described by the interference in layers. These interference peaks confirm the films homogeneity by area.

The low values of reflections in all cases of investigated films at overall spectral ranges testify their probability of usage as an anti-reflective coating in high-efficiency solar cells.

The absorption $a(\lambda)$ spectra and spectral dependence of optical density $D(\lambda)$ of ZnSe and ZnSe:Eu films are presented on Fig. 2. It should be noted that the films absorption coefficient in irradiation energies area more than optical band gap ($E_g = 2.70$ eV) reached the values of $a = (4.0-8.0) \times 10^4 \text{ cm}^{-1}$ that confirms its usage as a window layer in solar cells. Optical density dependencies $D(\lambda)$ of ZnSe and ZnSe:Eu films presented on Fig. 2b shown that these data are well correlated to transmittance spectra. At the wavelength more than “red boundary” of photoelectric effect (for ZnSe compound $\lambda_R = 457$ nm) the films optical density is intrinsic decreased from 1.50-1.75 to 0.1-0.5.

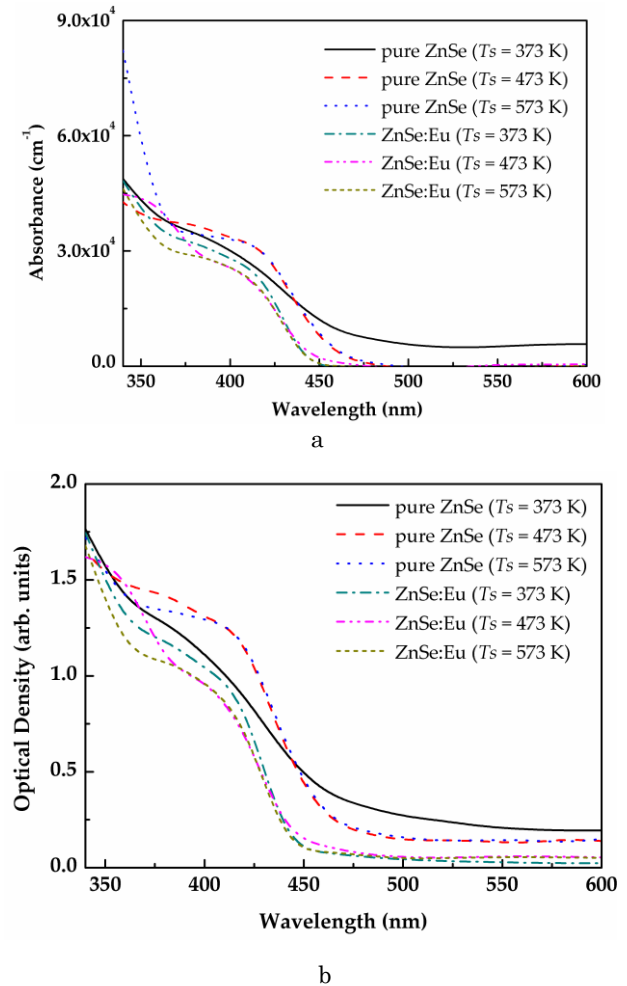


Fig. 2 – Absorption spectra (a) and optical density dependence (b) of ZnSe and ZnSe:Eu films

On Fig. 3 there are presented the spectral distributions of extinction $k(\lambda)$ and refraction $n(\lambda)$ coefficients of ZnSe and ZnSe:Eu films. We can see that the view of dependencies for ZnSe and ZnSe:Eu films is similar

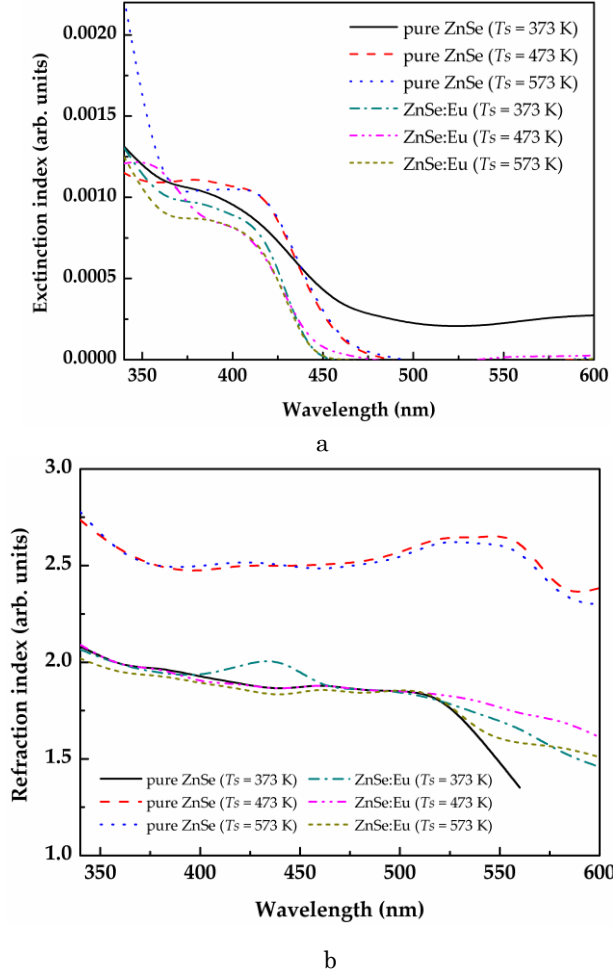


Fig. 3 – Extinction (a), and refraction (b) index of ZnSe and ZnSe:Eu films

each other. While the saturation is observed the refraction coefficients reached to $n_{\infty} = 1.74\text{-}2.53$; $k_{\infty} = 0.0001\text{-}0.0004$.

From values of k and n determined by us for all samples, we calculated the real $\varepsilon_1(\lambda)$ and imaginary $\varepsilon_2(\lambda)$ parts of optical dielectric constant by the next equations:

$$\varepsilon_1 = n^2 - k^2 \quad (2)$$

$$\varepsilon_2 = 2 \times n \times k \quad (3)$$

The calculation results are presented on Fig. 4.

As we can see from Fig. 4, the view of dependencies is similar to $k(\lambda)$ and $n(\lambda)$ characters. Their values are monotonous decreased at increasing of the wavelength. It should be noted that imaginary part $\varepsilon_2(\lambda)$ of optical dielectric constant is substantially lesser than real part $\varepsilon_1(\lambda)$. At the wavelength range $\lambda = 460$ nm these values are: for ZnSe films – $\varepsilon_1 = 3.574\text{-}6.276$; $\varepsilon_2 = 1.2 \times 10^{-4} - 4.9 \times 10^{-4}$; for ZnSe:Eu films – $\varepsilon_1 = 3.482\text{-}3.574$; $\varepsilon_2 = 1.0 \times 10^{-5}\text{-}6.0 \times 10^{-5}$. These data are well-correlated to data presented in [23].

The optical band gap determination of ZnSe and ZnSe:Eu films shown on Fig. 5. For determination the E_g for direct band gap semiconductors we used the following equation [19]:

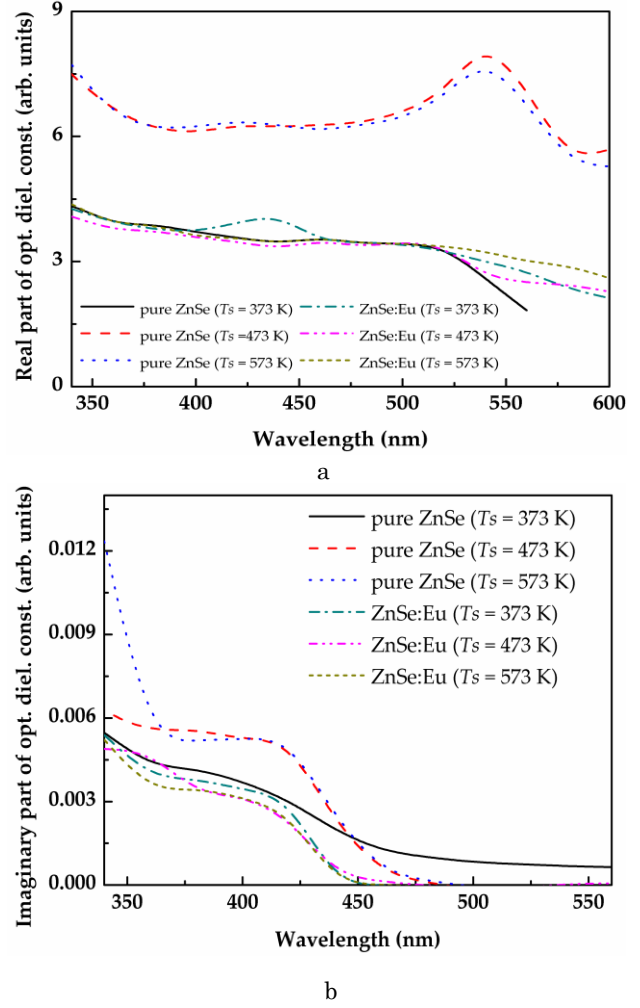


Fig. 4 – Real (a) and imaginary (b) parts of optical dielectric constant of studied films

$$\alpha h\nu = A_0 \times (h\nu - E_g)^{1/2} \quad (4)$$

where A_0 is a constant which depends on the charge carriers effective mass; $h\nu$ is a photon energy; E_g is the optical band gap.

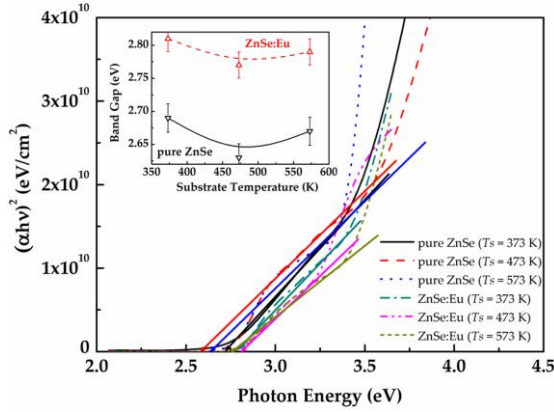
Fig. 5 shows the plot of $(\alpha h\nu)^2$ versus the photon energy $h\nu$ (Tauc plot [24]). The further extrapolation of the linear part of the curve on the $h\nu$ -axis allows to calculate the band gap of the samples.

In case of pure ZnSe films the optical band gap, while the substrate temperature was increased from 373 K to 573 K (Fig. 5 inset), was some decreased from 2.69 eV to 2.63 eV, and after that some increased to 2.68 eV. This effect may be connected to the changing of stoichiometry in films [16]. Similar view is observed also for ZnSe:Eu film. There the variation of E_g was: 2.81-2.77-2.79 eV. The larger values of band gap for ZnSe:Eu films are connected to the incorporation of Eu^{3+} ions onto the cubic lattice of ZnSe compound or to the phonons interactions [6].

The general results of optical study are presented on Table 1.

Table 1 – Optical characteristics of ZnSe and ZnSe:Eu films

T_s , K	k	n	ϵ_1	ϵ_2	E_g , eV
pure ZnSe					
373	3.26×10^{-4}	1.890	3.574	1.23×10^{-3}	2.69
473	9.17×10^{-5}	2.505	6.276	4.62×10^{-5}	2.63
573	9.98×10^{-5}	2.476	6.130	4.91×10^{-4}	2.68
Eu doped ZnSe					
373	1.84×10^{-5}	1.866	3.482	1.22×10^{-4}	2.81
473	3.28×10^{-5}	1.873	3.507	1.19×10^{-4}	2.77
573	9.21×10^{-6}	1.890	3.574	1.21×10^{-4}	2.79

**Fig. 5** – Tauc plots for determination of the films optical band gap. Inset shows the band gap vs substrate temperature dependencies

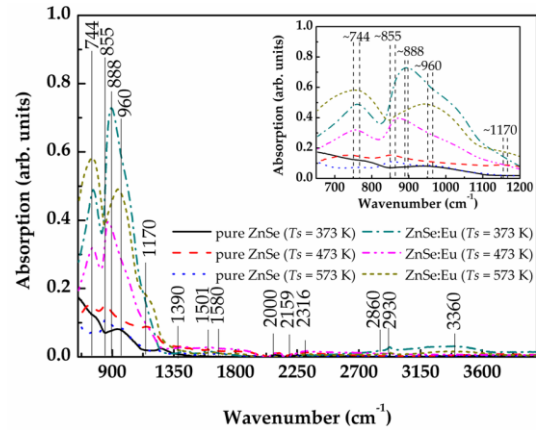
3.2 FTIR Study

FTIR analysis is an important method to determine the main functional groups and bonding or stretching interactions in semiconductor compounds. Fig. 6 shows FTIR spectra of pure and Eu doped ZnSe films. At frequencies $\nu = 742-748 \text{ cm}^{-1}$ in all samples are observed a characteristic bending Zn-Se vibration mode whereas a typical stretching Zn-Se vibration mode is observed at $\nu = 855-858 \text{ cm}^{-1}$ for ZnSe films ($T_s = 473-573 \text{ K}$) and

ZnSe:Eu ($T_s = 473 \text{ K}$); at $\nu = 1170-1171 \text{ cm}^{-1}$ for ZnSe films deposited at $T_s = 473 \text{ K}$ and ZnSe:Eu films ($T_s = 473 \text{ K}$). Moreover at frequencies $\nu = 888 \text{ cm}^{-1}$ only for ZnSe:Eu samples is observed a peak which in our point of view corresponds to Eu_2O_3 interactions. Other peaks are observed at $\nu \sim 955, 1390, 1500, 1580, 2000, 2160, 2315, 2860, 2930$ and 3360 cm^{-1} . The detailed assignments of these peaks are presented on Table 2.

On Fig. 6 (inset) we can see the slightly shifting of peaks at various substrate temperatures. This effect may be caused by the tensile strains in ZnSe (ZnSe:Eu) films and material of substrate (glass). Similar effect is observed by us using Raman spectroscopy in [16].

It should be noted, that at frequencies more than $\nu = 1200 \text{ cm}^{-1}$ this effect is negligible. This effect may be caused by the vibrations of molecules near the film substrate [16].

**Fig. 6** – FTIR spectra of ZnSe and ZnSe:Eu films. Inset shows the low-frequency spectral range

A determination process of the films thickness is presented on Fig. 7, where we can observe the range of frequencies for all samples to calculate the thickness by “fringing” effect.

Table 2 – FTIR spectra assignment of ZnSe and ZnSe:Eu films, deposited at different substrate temperatures

Pure ZnSe			ZnSe:Eu			Assignment	[Ref.]
$T_s = 373 \text{ K}$	$T_s = 473 \text{ K}$	$T_s = 573 \text{ K}$	$T_s = 373 \text{ K}$	$T_s = 473 \text{ K}$	$T_s = 573 \text{ K}$		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}		
744	742	748	744	744	746	Zn-Se bend.	[25]
–	855	855	–	858	–	Zn-Se stretch.	[26]
–	–	–	888	–	888	Eu_2O_3	[27]
956	958	958	–	–	960	Se-O stretch.	[28]
–	1170	–	–	–	1171	Zn-Se stretch.	[29]
–	–	–	1390	1392	1389	N-NH bend.	[29]
1502	1505	1502	1501	1502	1502	C-N bend.	[28]
1580	1580	1578	1582	1580	1585	O-H bend.	[26]
1996	2000	1998	2008	2002	1998	C-N carbonile	[28]
2159	2152	2160	2148	2156	2159	C-O stretch.	[30]
–	–	–	2316	2314	2316	C-O ₂ stretch.	[28]
–	–	–	2860	2865	2862	C-H vibration	[28]
–	–	–	2930	2930	2927	Sample forming	[28]
–	–	–	3360	–	–	O-H stretch.	[28]

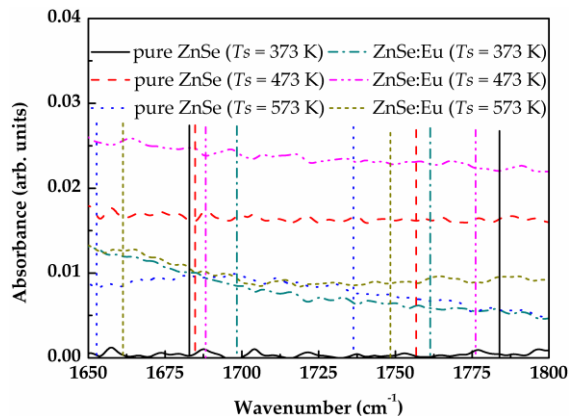


Fig. 7 – The ZnSe and ZnSe:Eu films thickness determination processing

As a results of thickness calculation it should be noted that obtained valued of films thickness are $d[\text{ZnSe}] = (420-780)$ nm; $d[\text{ZnSe:Eu}] = (280-528)$ nm. These results are well-correlated to the thickness values obtained by spectral photometer in [19].

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4. CONCLUSIONS

The optical parameters (refraction, extinction indexes, real and imaginary parts of optical dielectric constant, band gap) of polycrystalline ZnSe and ZnSe:Eu films deposited by CSVS technique have been calculated using the transmittance and absorbance spectra in the strong absorption region. The results indicated that refraction index n in all cases of deposited films at increasing of the wavelength is decreased to the saturation conditions. Calculated values of E_g took a possibility to make a conclusion about the direct transitions with band gap energies in the range of 2.63-2.69 eV for pure ZnSe films and 2.77-2.81 eV for ZnSe:Eu films.

FTIR analysis has been shown that all deposited films have a fine-crystalline nature and high level of optical quality that confirmed the results of optical study.

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