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The effects of substrate temperature on refractive index dispersion and optical constants of $CdZn(S_{0.8}Se_{0.2})_2$ alloy thin films

Saliha Ilican[a], Yasemin Caglar[a], Mujdat Caglar[a], Fahrettin Yakuphanoglu[b,*]

[a] Anadolu University, Faculty of Science, Department of Physics, 26470 Eskisehir, Turkey
[b] Firat University, Faculty of Arts and Sciences, Department of Physics, 23169 Elazig, Turkey

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ABSTRACT

The effect of substrate temperature on optical properties of $CdZn(S_{0.8}Se_{0.2})_2$ thin films deposited onto glass substrates by the spray pyrolysis method has been investigated. The average optical transmittance of the films was over 74% in the visible range. The optical absorption studies reveal that the transition is direct with band gap energy values between 2.86 and 2.92 eV. The optical constants such as refractive index and dielectric constant of the films were determined. According to variation of the substrate temperature, the important changes in absorption edge, refractive index and the dielectric constant were observed. The refractive index dispersion curves of the films obey the single oscillator model and oscillator parameters changed with substrate temperature. The most significant result of the present study is to indicate that substrate temperature of the film can be used to modify in the optical band gaps and optical constants of $CdZn(S_{0.8}Se_{0.2})_2$ thin films.

1. Introduction

The II–VI semiconductor compounds such as CdS, CdSe, CdTe, $Cd_{1-x}Zn_xS$ films have widely contributed to the phenomenal growth of their applications in scientific, technological and industrial applications like solar cells [1,2], optical detectors [3], field effect transistors [4] and opto-electronic devices [5,6]. A number of film deposition methods like chemical deposition [7,8], vacuum evaporation [9–11], chemical vapour transport [12–14], and chemical spray pyrolysis [15–18] have been used for production the II–VI compounds. Among these methods, the spray pyrolysis, which has the advantages of low cost, easy-to-use, safe and can be implemented in a standard laboratory, has been known to be suitable for many scientific studies and technological applications. This method is based on the preparation of solutions of some salt of the material whose films is to be prepared.

The $CdZn(S_{1-x}Se_x)_2$ alloy thin films have an important property like tuneable of the energy gap, it is therefore, an important candidate for opto-electronic devices and tandem solar cells. In the literature, there are a few reports about CdZnSSe. Most of them are related to using in ZnSe-based laser diodes [19,20]. Only Chavhan et al. [21] reported the growth and characterization of $CdZn(S_{1-x}Se_x)_2$ alloy film using the solution growth technique and in our previous study [22], it was reported the optical properties of the $CdZn(S_{1-x}Se_x)_2$ films depend on the different x concentrations. The study of optical absorption has proved to be very useful for explanation of the electronic structure of these materials. It is possible to determine indirect and direct transition occurring in band gap of the materials by optical absorption spectra. The data transmittance can be analyzed to determine optical constants such as refractive index, extinction coefficient and dielectric constant. The evaluation of refractive indexes of optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, etc., where the refractive index of a material is the key parameter for device design.

We have evaluated that the substrate temperature of thin films can be used to modify optical band gap and optical constants of thin films, because the optical constants of thin films depend on the deposition parameter such as the substrate temperature during the deposition process. Therefore, in present work, we have investigated the effect of the substrate temperature on the optical properties of $CdZn(S_{0.8}Se_{0.2})_2$ films to modify optical constants of the films.

2. Experimental

The spray pyrolysis method is basically a chemical deposition technique in which fine droplets of the desired material are sprayed onto a heated substrate. Continuous films are formed on the hot substrate by thermal decomposition of the material droplets.

$CdZn(S_{0.8}Se_{0.2})_2$ thin films were deposited onto glass substrates by spray pyrolysis method at 225, 275 and 300 °C substrate temperatures. 0.01 M solution of cadmium chloride dehydrate ($CdCl_2{\cdot}H_2O$), zinc chloride ($ZnCl_2$), thiourea ($(NH_2)_2CS$) and selenurea ($H_2NC(Se)NH_2$) were used as starting materials. The temperature

* Corresponding author. Tel.: +90 424 2730000; fax: +90 424 2330062.
E-mail address: fyhan@hotmail.com (F. Yakuphanoglu).

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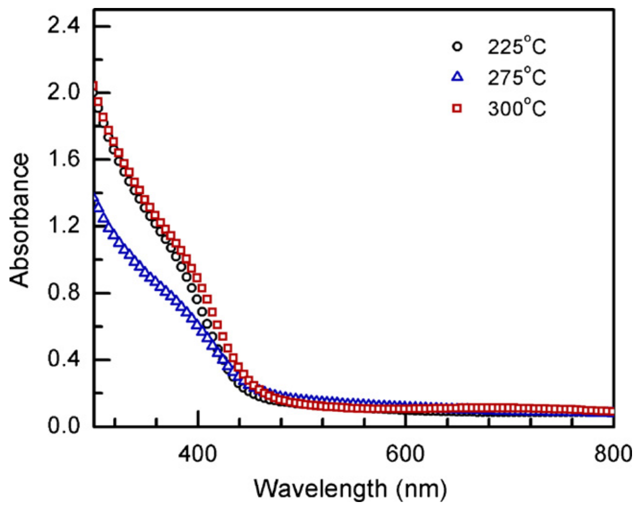

Fig. 1. Absorbance spectra of the $CdZn(S_{0.8}Se_{0.2})_2$ thin films deposited at different substrate temperatures.

of substrate was controlled by an iron–constantan thermocouple. The spray rate employed was 3 ml/min and kept constant throughout the experiment. The ultrasonic nozzle to substrate distance was 28 cm. Nitrogen was used as carrier gas, at 0.2 bar pressure. The depositon time was 30 min. After deposition, the films were allowed to cool at room temperature. The adhesion of the films onto the substrates was quite good.

The optical absorption spectra are recorded from 190 to 900 nm wavelength using SHIMADZU UV-2450 UV–vis spectrophotometer at room temperature.

3. Results and discussion

3.1. Optical absorption edge of the thin films

The absorbance spectra of $CdZn(S_{0.8}Se_{0.2})_2$ thin films is shown in Fig. 1. The optical absorptions in the ultraviolet region are larger than those in the visible region. While the optical absorptions in the visible region were almost same, those in the ultraviolet region changed little with increasing the substrate temperature. The transmittance spectra of the thin films are shown in Fig. 2. The transmission through the film is relatively low at below band gap region, indicating high concentration of defects, free carriers. The transmittance decreases abruptly in the short wavelengths. A sharp decrease in the transmittance was observed at about 430 nm,

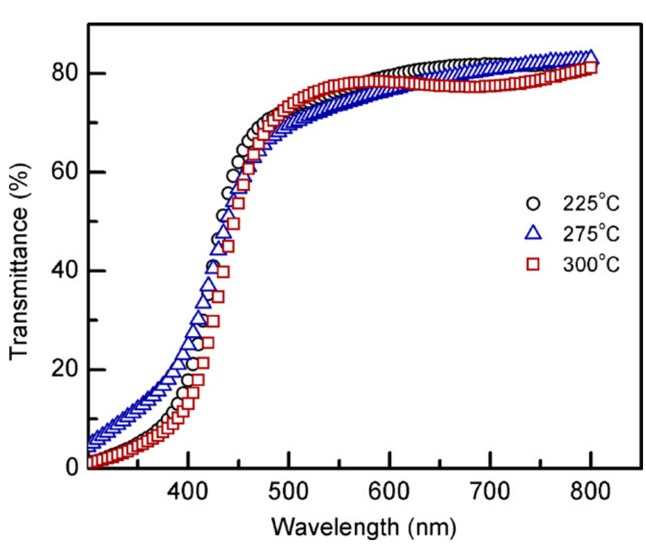

Fig. 2. Optical transmission of the $CdZn(S_{0.8}Se_{0.2})_2$ thin films deposited at different substrate temperatures.

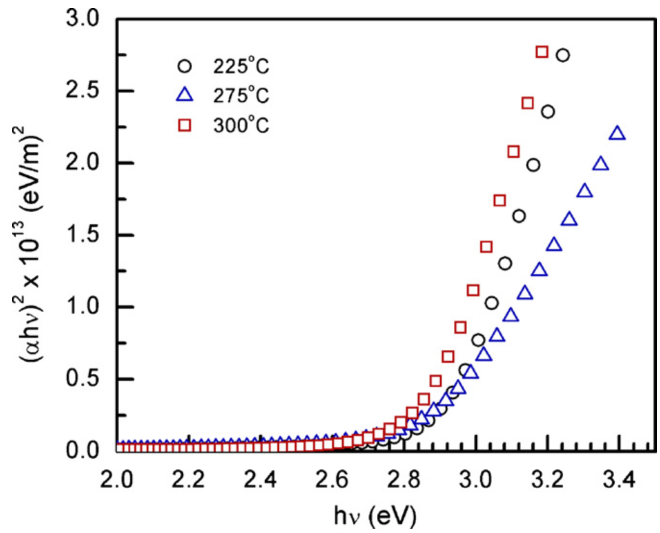

Fig. 3. The plots of $(\alpha h\nu)^2$ vs. photon energy of $CdZn(S_{0.8}Se_{0.2})_2$ thin films deposited at different substrate temperatures.

which is due to the band edge absorption. The incoming photons have sufficient energy to excite electrons from the valence band to the conduction band, resulting in strong absorption in $CdZn(S_{0.8}Se_{0.2})_2$ film. The optical absorption edge was determined by the optical absorption, a simple method that provides explanation for the features concerning the band structure of the film. The optical absorption edge was analyzed by the following relationship [23],

$$\alpha h\nu = A(h\nu - E_g)^m \tag{1}$$

where α is absorption coefficient, A is an energy-independent constant and E_g is the optical band gap. The exponent m depends on the nature of the transition, $m = 1/2$, 2, 3/2 or 3 for allowed direct, allowed non-direct, forbidden direct or forbidden non-direct transitions, respectively. Eq. (1) can be written as

$$\frac{d[\ln(\alpha h\nu)]}{d[h\nu]} = \frac{m}{h\nu - E_g} \tag{2}$$

The type of transition can be obtained by determining the value of m. A discontinuity in the $d\{\ln(\alpha h\nu)\}/d(h\nu)$ vs. $h\nu$ plot at the band gap energy, i.e. at $h\nu = E_g$ can be observed. The discontinuity at a particular energy value gives the band gap, E_g [24]. The curves of $ln(\alpha h\nu)$ vs. $ln(h\nu - E_g)$ were plotted using the E_g value to determine m value and it was found about 1/2 from the slope of plotted curves. Thus, obtained m value suggests that the fundamental absorption edge in the films is formed by the direct allowed transitions. It is well known that direct transition across the band gap is feasible between the valence and the conduction band edges in k space. In the transition process, the total energy and momentum of the electron–photon system must be conserved. Fig. 3. shows the plots of $(\alpha h\nu)^2$ vs. $h\nu$ of the films. The values of the direct optical band gap E_g are given in Table 1. The optical band gap values obtained by this method are suitable for many scientific studies and technological applications, such as gas sensors, heat mirrors, transparent electrodes, solar cells and piezoelectric devices. As seen from Table 1,

Table 1
Optical parameters of the $CdZn(S_{0.8}Se_{0.2})_2$ thin films.

Substrate temperature (°C)	E_g (eV)	E_o (eV)	E_d (eV)	λ_o (nm)	S_o (m^{-2})	n_∞
225	2.92	3.88	35.11	320.10	8.83×10^{13}	3.17
275	2.87	3.87	19.05	320.58	4.78×10^{13}	2.43
300	2.86	3.84	36.36	323.80	9.04×10^{13}	3.24

the substrate temperature leads to a decrease in optical band gaps of the films. These results show that substrate temperatures cause shrinkage in the optical absorption edge and therefore change in the band structure of the films. This suggests that the defects in thin films take place during formation of the films. It is also noted to discussion that the decrease in energy band gap increases the width of the energy bands. The decrease in the width of the energy band induces to move the band edge of the conduction band downward and that of the valence band upward [25]. It can be evaluated that substrate temperature cause a decrease in the optical band gap.

3.2. Refractive index, dispersion and dielectric constants of the thin films

In order to calculate the refractive index (n) of the films, we recorded transmittance spectra of the films and we calculated the refractive index values of the films using the following equations [26],

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \tag{3}$$

where T is the transmittance, α is the absorption coefficient, d is the thickness of thin film,

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{4}$$

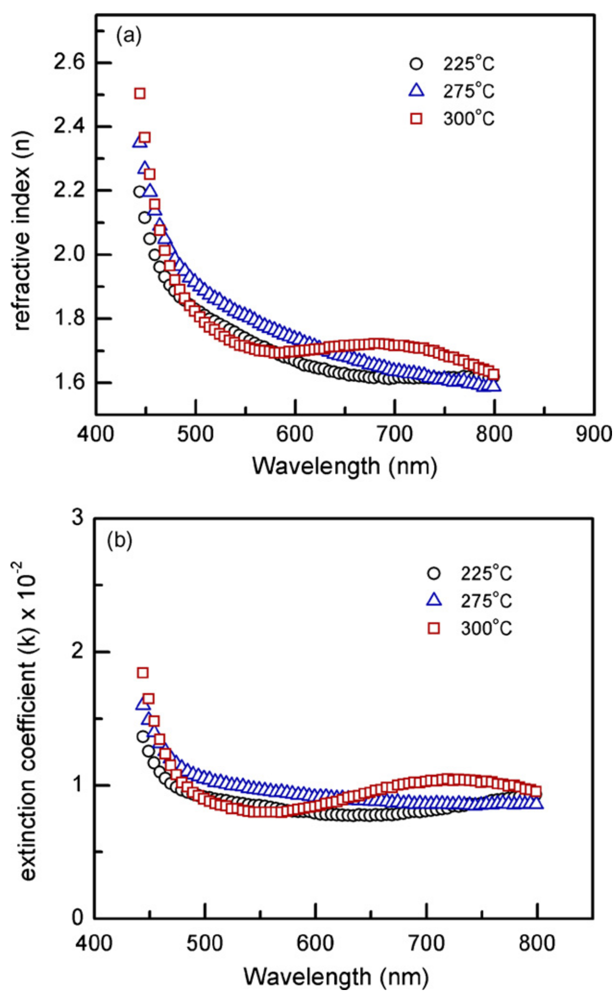

Fig. 4. The variation of (a) refractive index and (b) extinction coefficient with wavelength for the $CdZn(S_{0.8}Se_{0.2})_2$ thin films.

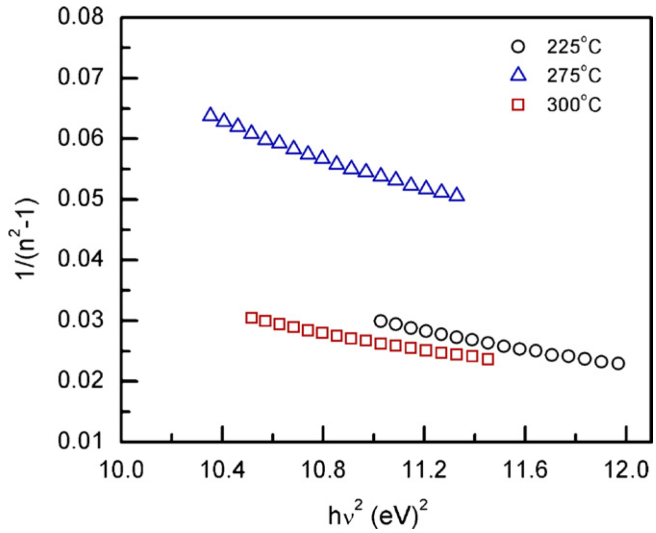

Fig. 5. Plots of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ of the $CdZn(S_{0.8}Se_{0.2})_2$ thin films.

where R is the reflectance and k $(=\alpha\lambda/4\pi)$ is the extinction coefficient. The refractive index and extinction coefficient dependence of the wavelength are shown in Fig. 4. As seen in Fig. 4, n and k values are influenced by the substrate temperature and increase with decreasing the wavelength. Therefore, they show the normal dispersion.

The dispersion plays an important role in the research for optical materials due to a significant factor in optical communication and in designing devices for spectral dispersion. The below the absorption edge, refractive index dispersion can be analyzed by the single oscillator model [27],

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \tag{5}$$

where n is the refractive index, h is Planck's constant, ν is the frequency, $h\nu$ is the photon energy, E_o is the oscillator energy for electronic transitions and E_d is the dispersion energy, which is a measure of the strength of interband optical transitions. These parameters can be easily obtained by plotting of $(n^2-1)^{-1}$ vs. $(h\nu)^2$. Fig. 5 shows $(n^2-1)^{-1}$ vs. $(h\nu)^2$ plots of films. The E_d and E_o values was calculated from the slope $(E_d E_o)^{-1}$ and intercept (E_o/E_d) of Fig. 5. The values of E_d and E_o change with increasing substrate temperature. The E_o values decrease with increasing substrate temperature. This confirms that the optical band gap of the thin films decreases with increasing substrate temperature.

The refractive index dependence on wavelength is expressed by the following dispersion relation [27],

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1-(\lambda_o/\lambda)^2} \tag{6}$$

where λ is the wavelength of incident light. S_o is the average oscillator strength and λ_o is an average oscillator wavelength. Eq. (6) also can be transformed as

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \tag{7}$$

The parameters, n_∞, S_o and λ_o values were obtained from the slope and intercept of $(n^2-1)^{-1}$ vs. λ^{-2} curves plotted and are given in Table 1. The obtained parameters change with substrate temperature. These changes show that the film is suitable to change refractive index and oscillator parameters by substrate temperature.

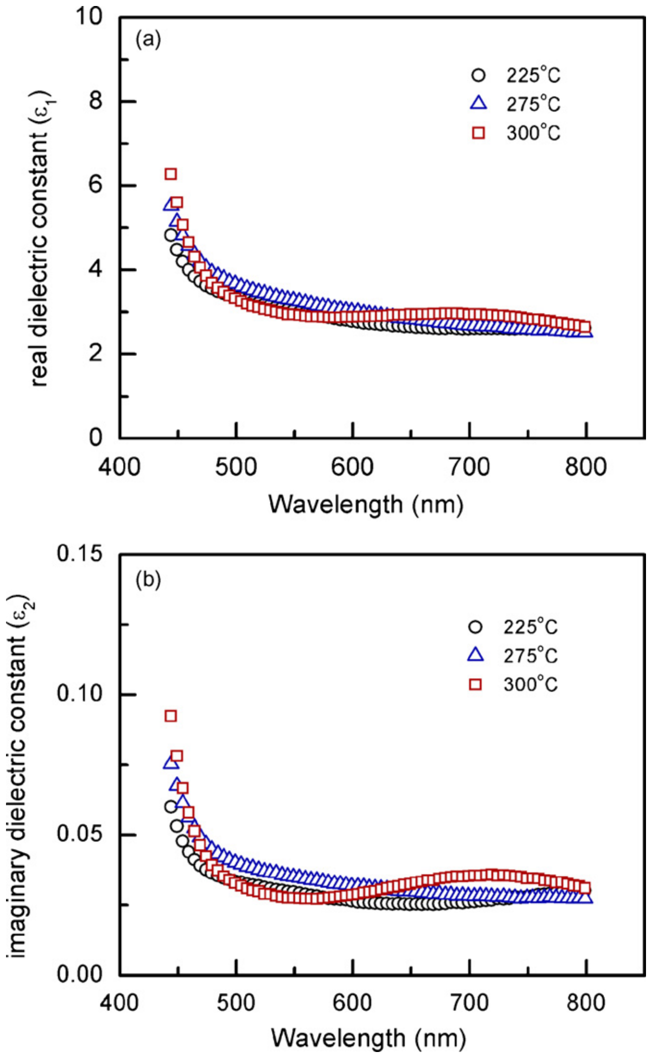

Fig. 6. The variation of real (a) and imaginary part (b) of the dielectric constant with wavelength.

The imaginary and real parts of dielectric constant of the films were also determined by the following relations [26],

$$\varepsilon_1 = n^2 - k^2 \tag{8}$$

and

$$\varepsilon_2 = 2nk \tag{9}$$

The real and imaginary parts of the dielectric constant of the films are, respectively shown in Fig. 6(a and b). It is seen that both ε_1 and ε_2 decreases with increasing wavelength. The real and imaginary parts follow the same pattern and the values of real part are higher than imaginary parts. The substrate temperature causes important changes in real part and imaginary parts of the dielectric constant of the films.

4. Conclusions

The effect of substrate temperature on optical properties of $CdZn(S_{0.8}Se_{0.2})_2$ thin films deposited onto glass substrates by the spray pyrolysis method has been investigated. The direct optical band gaps of the films were found between 2.86 and 2.92 eV. The absorption edge, refractive index and the dielectric constant of the films are influenced by the substrate temperature. The refractive index dispersion curves of the films obey the single oscillator model. The results show that the substrate temperature modifies the optical band gaps and optical constants of $CdZn(S_{0.8}Se_{0.2})_2$ thin films.

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