

## Optical characterization of the $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$ thin films deposited by spray pyrolysis method

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$\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films have been deposited onto glass substrates by the spray pyrolysis method at a 275°C substrate temperature. The average optical transmittance of all the films was over 65% in the wavelength range 450–800 nm. The optical absorption studies reveal that the transition is direct with band gap energy values between 2.47–3.04 eV. The optical constants such as refractive index, extinction coefficient and dielectric constants have been calculated for these films. The dispersion parameters such as  $E_o$  (single-oscillator energy) and  $E_d$  (dispersive energy) have been discussed in terms of the Wemple–DiDomenico single-oscillator model. The 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.

Keywords: thin film, spray pyrolysis, optical constants, band gap energy.

### 1. Introduction

The II–VI compounds, especially CdS, CdSe, CdTe,  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ,  $\text{Cd}_x\text{Zn}_{1-x}\text{S}_y\text{Se}_{1-y}$ , etc., are of great interest because they are potential candidates in many practical applications, such as solar cells [1–3], optical detectors [4], field effect transistors [5], and optoelectronic devices [6, 7]. The development of low-cost solar cells depends on the exploitation of films and thus CdS, CdSe or CdTe films obtained under various experimental conditions require comprehensive electrical characterization [8].

A number of film deposition methods, such as chemical deposition [9, 10], vacuum evaporation [8, 11, 12], chemical vapour transport [13–15], and chemical spray pyrolysis [16–19] have been used for preparing II–VI compounds.

The chemical spray pyrolysis method for the production of thin solid films is a good method for the preparation of thin films suitable for scientific studies and for many technological and industrial applications. This method was used for the preparation of thin films of the important II–VI semiconductors.

The study of optical absorption has proved to be very useful for elucidation 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 indices of optical materials is of considerable importance for applications in integrated optical devices such as switches, filters and modulators, *etc.*, where the refractive index of a material is the key parameter in the design of a device.

The knowledge of real and imaginary parts of complex refractive index as a function of wavelength is necessary to make effective use of these materials for optoelectronic devices [20–22], particularly as an antireflective coating [23]. The variation of refractive index with doping also provides the means to tailor the refractive index to any desired value required for use in filters [24].

In the literature available we have not found data for optical parameters of spray pyrolyzed  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films. Thus, the aim of this study is to investigate optical properties of  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films to calculate optical constants, such as refractive index, extinction coefficient and dielectric constant, and the dispersion parameters such as  $E_o$  (single-oscillator energy) and  $E_d$  (dispersive energy).

## 2. Experimental

### 2.1. Materials

The spray pyrolysis method is particularly attractive because of its simplicity. It is fast, inexpensive, vacuumless and is suitable for thin film production. The spray pyrolysis method used is basically a chemical deposition method in which fine droplets of the desired material are sprayed onto a heated substrate. A continuous film is formed on the hot substrate by thermal decomposition of the material droplets [25].

The  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  ( $x = 0, 0.2, 0.4, 0.6$ ) thin films were deposited by spraying an aqueous solution containing  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $(\text{NH}_2)_2\text{CS}$  and  $\text{H}_2\text{NC}(\text{Se})\text{NH}_2$  0.01 M. The films were deposited onto glass substrates at a 275°C substrate temperature. The temperature of the substrate was controlled by an iron-constantan thermocouple. The spray rate employed was 3 ml/min and kept constant throughout the experiment. Nitrogen was used as carrier gas. After deposition, the films were allowed to cool at room temperature. The preparation parameters of  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  films and the spray pyrolysis deposition system were described in detail elsewhere [26–28]. The thickness of all the thin films deposited was measured by weight difference method using a sensitive semi-microbalance.

### 2.2. Optical measurements

The optical absorption spectra of  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films at room temperature were recorded on a Shimadzu UV-2450 PC UV-VIS scanning spectrophotometer in the wavelength range 190–900 nm.

The absorption coefficient  $\alpha$  at frequency  $\nu$  of radiation was calculated using the formula:

$$\alpha(\nu) = 2.303 \frac{A}{d} \quad (1)$$

where  $d$  is the film thickness and  $A$  is the optical absorbance. Also,  $\alpha(\nu)$  is related to the optical transmission  $T$  and reflection  $R$  as follows [29]:

$$\alpha(\nu) = \frac{1}{d} \log \left\{ \frac{(1-R)^2}{2T} + \frac{(1-R)^2}{[(2T)^2 + R^2]^{1/2}} \right\} \quad (2)$$

and the refractive index was obtained from

$$n = \frac{1+R}{1-R} + \left[ \frac{4R}{(1-R)^2} - k^2 \right]^{1/2} \quad (3)$$

where  $k$  is the extinction coefficient which is related to the absorption coefficient and the wavelength as:

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

On the other hand, the real and imaginary parts of dielectric constant of the films can also be estimated if the refractive index and extinction coefficient are known. The real and imaginary parts of dielectric constant can be expressed by the following relations [30]:

$$\varepsilon_1 = n^2 - k^2 \quad (5)$$

and

$$\varepsilon_2 = 2nk \quad (6)$$

### 3. Results and discussion

The transmission spectra of CdZn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>2</sub> ( $x = 0, 0.2, 0.4, 0.6$ ) thin films of thickness ~600 nm are shown in Fig. 1. For  $x = 0, 0.2, 0.4, 0.6$  selenium contents, the average transmission values are 78.53%, 74.17%, 77.78% and 63.65% in the wavelength range 450–800 nm. The transmission of CdZn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>2</sub> thin films is influenced by the selenium contents. It is noticed that the CdZnS<sub>2</sub> thin film has higher transmission values in the visible range of spectrum.

The optical absorption edge is determined by the optical absorption method, which is simple and provides for the explanation of some features concerning the band

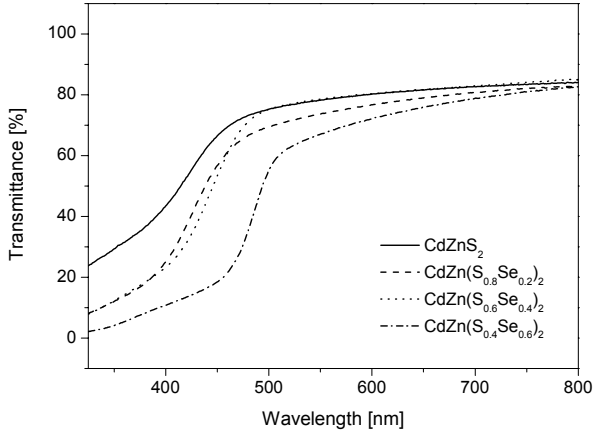


Fig. 1. Optical transmission spectra of the  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films.

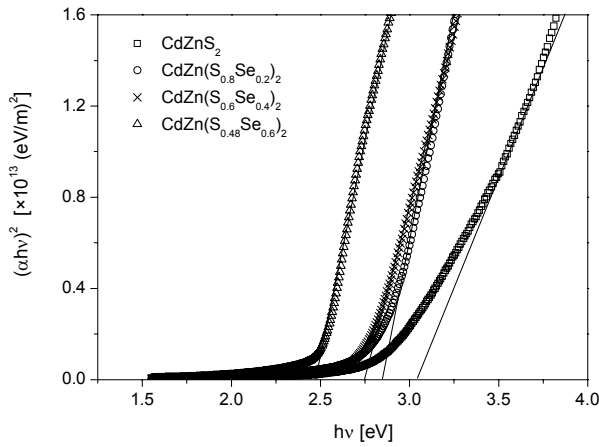


Fig. 2. Plots of  $(\alpha h\nu)^2$  vs. photon energy of the  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films.

structure of the films. The optical absorption edge was analyzed by the following equation [31]:

$$\alpha h\nu = A(h\nu - E_g)^m \quad (7)$$

where  $A$  is a constant,  $m$  values are  $1/2$  and  $2$  for direct and indirect transitions, respectively. The curves of  $\ln(\alpha h\nu)$  versus  $\ln(h\nu - E_g)$  were plotted using the  $E_g$  value to determine the value of  $m$  and it was found about  $1/2$  from the slope of these curves. Therefore,  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films appear to be a material which has a direct band gap. The variation of  $(\alpha h\nu)^2$  with photon energy for  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films is shown in Fig. 2. It has been observed that the plots of  $(\alpha h\nu)^2$  versus  $h\nu$  are linear over

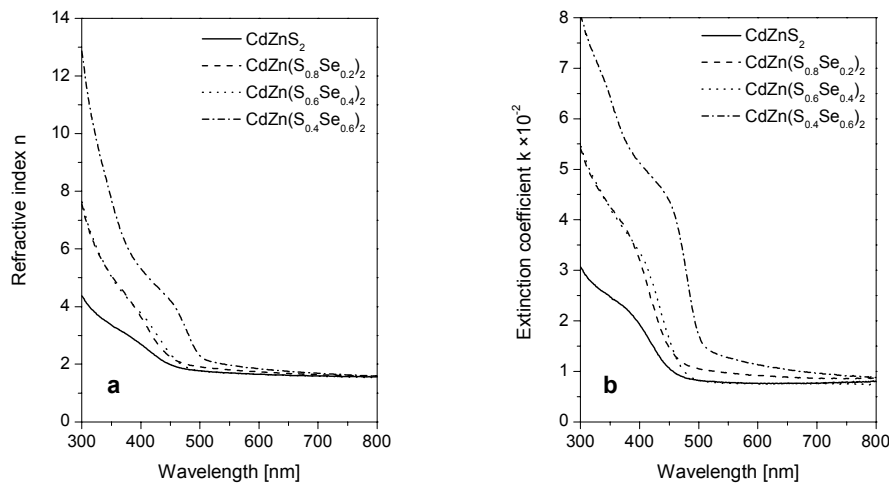
Table. Direct energy band gaps and the optical constants for the CdZn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>2</sub> thin films.

Material	$E_g$ [eV]	$E_o$ [eV]	$E_d$ [eV]	$M_{-1}$	$M_{-3}$ [eV <sup>-2</sup> ]
CdZnS <sub>2</sub>	3.04	4.250	13.759	3.237	0.179
CdZn(S <sub>0.8</sub> Se <sub>0.2</sub> ) <sub>2</sub>	2.87	3.903	19.556	5.010	0.329
CdZn(S <sub>0.6</sub> Se <sub>0.4</sub> ) <sub>2</sub>	2.74	3.887	19.055	4.902	0.324
CdZn(S <sub>0.4</sub> Se <sub>0.6</sub> ) <sub>2</sub>	2.47	3.559	24.647	6.925	0.547

a wide range of photon energies indicating the direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis give the energy band gaps. The direct band gaps for all the films were determined. With increasing selenium content, the energy band gap of CdZn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>2</sub> thin films decreases. This general trend is the agreement with that obtained by FENG *et al.* [31]. The direct band gaps  $E_g$  are given in the Table.

The calculated values of refractive index  $n$  and extinction coefficient  $k$  were plotted as a function of the wavelength, as shown in Fig. 3. We also calculated the imaginary and real parts of dielectric constant as it is directly related to the density of states within the energy gap of the films. The real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the dielectric constant of the films are shown in Figs. 4a and 4b, respectively. It is seen that both, real and imaginary parts of the dielectric constant, decrease with increasing wavelength. The real and imaginary parts follow the same pattern and it is seen that the values of real part are higher than those of the imaginary parts. Increasing selenium content causes important changes in these optical constants.

The single-oscillator parameters were calculated and discussed in terms of the Wemple–DiDomenico model. The dispersion parameters of various materials were investigated by using this model, as reported in [32–35]. This model describes

Fig. 3. Variation of refractive index  $n$  (a) and extinction coefficient  $k$  (b) with wavelength.

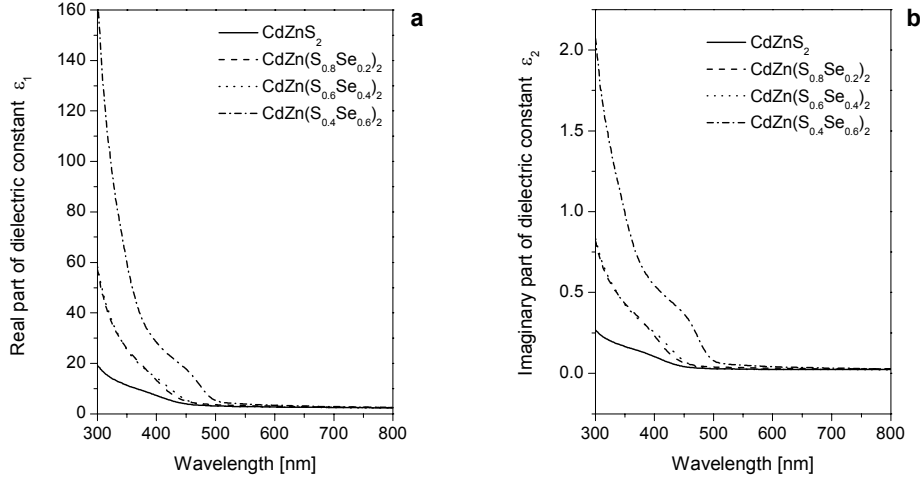


Fig. 4. Variation of real (a) and imaginary (b) parts of the dielectric constant with wavelength.

the dielectric response for transitions below the optical gap. This plays an important role in determining the behaviour of the refractive index. The dispersion data of the refractive index can be described by a single-oscillator model [36]:

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - (h\nu)^2} \quad (8)$$

where  $E_o$  and  $E_d$  are single-oscillator constants ( $E_o$  is the single-oscillator energy and  $E_d$  is the dispersion energy which is a measure of the strength of interband optical transitions). By plotting  $(n^2 - 1)^{-1}$  versus  $(h\nu)^2$  and fitting a straight line shown in

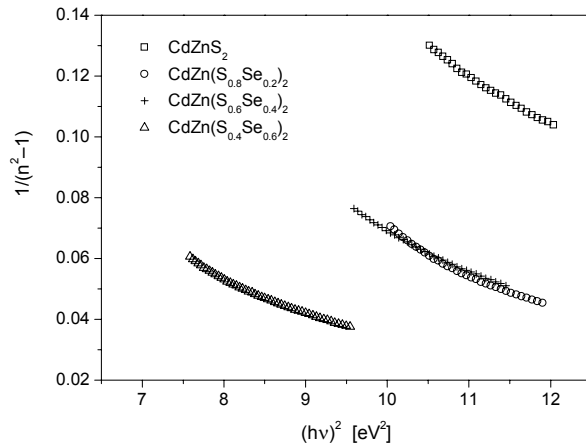


Fig. 5. Plots of  $(n^2 - 1)^{-1}$  vs.  $(h\nu)^2$  for the  $\text{CdZn}(\text{S}_{1-x}\text{Se}_x)_2$  thin films.

Fig. 5,  $E_o$  and  $E_d$  are determined directly from the gradient,  $(E_o E_d)^{-1}$  and the intercept  $(E_o/E_d)$ , on the vertical axis. Also, the long wavelength refractive index  $n_\infty$  for all the thin films was determined from the interception of the vertical axis in Fig. 5. The values of  $n_\infty$  were found to be between 2.06 and 2.82. The values of  $E_o$  decrease with increasing selenium content. The  $E_o$  and  $E_d$  values for the CdZn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>2</sub> thin films are given in the Table. The oscillator energy  $E_o$  is an average energy gap as pointed out in many references [37–40]. We found that  $E_o$  value of the films is related empirically to the lowest direct band gap by  $E_o \approx 1.36 E_g$ . This relation is in agreement with the relation ( $E_o \approx 1.4 E_g$ ) obtained with the use of a single-oscillator model [37].

The  $M_{-1}$  and  $M_{-3}$  moments of the optical spectra can be derived from the following relations:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (9)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}}$$

The values obtained are given in the Table. It is seen that  $M_{-1}$  and  $M_{-3}$  moments have a tendency to increase with an increase in selenium content.

#### 4. Conclusions

CdZn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>2</sub> ( $x = 0, 0.2, 0.4, 0.6$ ) thin films have been deposited by the spray pyrolysis method at 275°C substrate temperatures. Based on the optical investigations of the films, the following results were obtained. The spray pyrolyzed thin films show average transmission values to vary between 65 and 79%. The optical constants, such as refractive index  $n$ , extinction coefficient  $k$ , real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of dielectric constant of the films, were calculated for the films. All of these constants decrease with wavelength. The optical absorption spectra of the films under study show that the absorption spectra mechanism is due to direct transition. The optical dispersions ( $E_o$  and  $E_d$ ) using Wemple–DiDomenico model were also analyzed. In conclusion, we can state that the influence of the selenium content on the optical properties of CdZn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>2</sub> thin films is noticeable.

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