

# Structural and optical properties of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ thin films\*

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**Abstract:**  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films were deposited on glass substrates by a vacuum coevaporation method. The structural, compositional, and optical properties of as-deposited  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  films were investigated using X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), and optical transmittance spectrum. The thin films are hexagonal in structure, with strong preferential orientation along the (002) planes. The composition of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films monitored by a quartz crystal oscillator agrees well with that obtained from XRF and XPS measurements. The optical constants, such as refractive index, single-oscillator energy, dispersion energy, absorption coefficients, and the optical band gap, were deduced by the Swanepoel's method, in combination with the Wemple and DiDomenico single-oscillator model, from the transmission spectrum of  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  thin films.

**Key words:** ternary compound; thin films; coevaporation

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## 1. Introduction

$\text{Cd}_{1-x}\text{Zn}_x\text{S}$  alloy compounds have attracted technological interest because the energy gap can be tuned and the lattice parameters can be varied<sup>[1]</sup>.  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  ternary compounds can form a continuous series of solid solutions, allowing systematic variation in the band gap of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  from 2.43 eV for CdS to 3.7 eV for ZnS by adjusting the composition<sup>[2]</sup>.

$\text{Cd}_{1-x}\text{Zn}_x\text{S}$  films have been deposited in a variety of ways: vacuum evaporation, metalorganic chemical vapor deposition, chemical bath deposition (CBD), spray pyrolysis, successive ionic layer absorption and reaction (SILAR), and the dip technique. Very little information is available on the ternary  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  system with any compositions prepared by the vacuum evaporation method.  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films, to our knowledge, have been prepared by vacuum evaporation involving three techniques, in one of which the thin films are prepared by using a mechanically alloyed mixture of CdS and ZnS<sup>[3]</sup>. Obviously, a homogenous mixture of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  is difficult to obtain, so some researchers<sup>[4]</sup> synthesized the fine powders of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  by solid state reaction, and then evaporated  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films. Torres *et al.*<sup>[5]</sup> deposited  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films by evaporation, varying the diameter of the openings of the coaxial chambers that contain the CdS and ZnS precursors. However,  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films with the desired content are not readily deposited by the evaporation mentioned above. In this work,  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films were prepared by co-evaporation of CdS and ZnS from two horizontal sources.

In solar cell systems, where CdS films have been demonstrated to be effective, the replacement of CdS with the higher band gap ternary  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  has led to a decrease in window absorption losses, and has resulted in an increase in the short

circuit current<sup>[6]</sup>. However, two problems exist in a CdTe solar cell with a  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  layer. One is the lattice parameter changing linearly with Zn content in the compound and thus resulting in a large lattice mismatch between  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  and CdTe. The other is the electrical resistivity increasing from  $< 1 \Omega\cdot\text{cm}$  to  $> 10^{10} \Omega\cdot\text{cm}$  as  $x$  increases from 0 to 1<sup>[7]</sup>. Therefore, in this study we focused on the preparation and properties of the  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films at low zinc content (e.g. 20%).

## 2. Experimental

$\text{Cd}_{1-x}\text{Zn}_x\text{S}$  films were deposited onto clean glass substrates by the vacuum co-evaporation technique to a thickness of  $\sim 300$  nm, keeping the substrates at room temperature. CdS powder (99.999% purity) and ZnS powder (99.999% purity) were evaporated on substrates from two independent horizontal sources. The deposition velocity and the thickness of the thin films were monitored by two quartz thickness monitors in order to prepare the  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  thin films. The thickness was confirmed precisely by surface profilometer. The X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the composition of the sample. The nature and structure of the sample was obtained by X-ray diffraction (XRD). Measurement of the optical transmittance was made over the wavelength range 400–2000 nm with a data interval of 1 nm.

## 3. Results and discussions

### 3.1. Structure and composition

Figure 1 shows an X-ray diffraction spectrum of  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  thin films obtained by using  $\text{CuK}\alpha$  ( $\lambda \approx$

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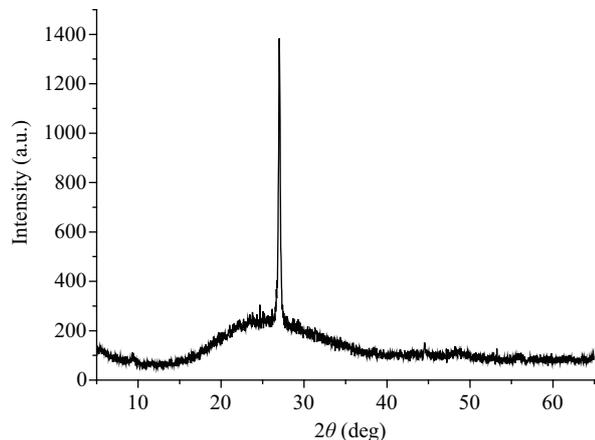


Fig. 1. XRD pattern of as-deposited polycrystalline Cd<sub>0.8</sub>Zn<sub>0.2</sub>S thin films.

0.154184 nm) radiation, where only one diffraction peak with a 2θ value between 26.38° and 28.37° is present. The absence of diffraction peaks associated with CdS and ZnS shows that the films are single phase materials. An inspection of the peak position indicates that the ternary Cd<sub>1-x</sub>Zn<sub>x</sub>S (with low Zn content) peak obtains a nearly binary CdS value. And the structure of the thin films is a hexagonal (wurtzite) phase with a very strong preferential orientation along the (002) planes<sup>[1, 4, 5]</sup>.

The experimental *d* value for the composition of the Cd<sub>1-x</sub>Zn<sub>x</sub>S system is determined using Bragg's relation by taking the value from the peak of the XRD pattern. Since the lattice constants of Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films follow the Vegard law, the composition of Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films can be determined by

$$x_{\text{Cd}_{1-x}\text{Zn}_x\text{S}} = \frac{a_{\text{Cd}_{1-x}\text{Zn}_x\text{S}} - a_{\text{CdS}}}{a_{\text{ZnS}} - a_{\text{CdS}}} \times 100\%, \quad (1)$$

where  $a_{\text{Cd}_{1-x}\text{Zn}_x\text{S}}$ ,  $a_{\text{CdS}}$ ,  $a_{\text{ZnS}}$  are, respectively, the lattice constants of Cd<sub>1-x</sub>Zn<sub>x</sub>S, CdS, and ZnS<sup>[8]</sup>. From the *d* value of the X-ray diffraction shown in Fig. 1, the lattice constant can be calculated as follows,

$$d = \frac{a_0}{\sqrt{\frac{4}{3}(h^2 + hk + k^2) + \left(\frac{a_0}{c_0}\right)^2 l^2}}. \quad (2)$$

Therefore, from Eqs. (1) and (2), one can obtain the lattice constant of Cd<sub>0.8</sub>Zn<sub>0.2</sub>S thin films  $c_0 \approx 0.58$  nm, and the composition of Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films  $x \approx 0.29$ . The composition of the thin films obtained from the Vegard law ( $x \approx 0.29$ ) is higher than that determined from the quartz crystal oscillation method ( $x = 0.2$ ). This may be ascribed to the determination of the *d* value at a low angle, where it is difficult to accurately determine the peak positions of the thin films, in the XRD pattern.

To accurately determine the composition of the Cd<sub>1-x</sub>Zn<sub>x</sub>S alloys, X-ray fluorescence spectra of Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films were also carried out. Table 1 shows the composition of the Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films from XRF using the fundamental parameter (FP) method.

From Table 1, one can obtain the composition of the Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films  $x = 0.195$ . The composition of the

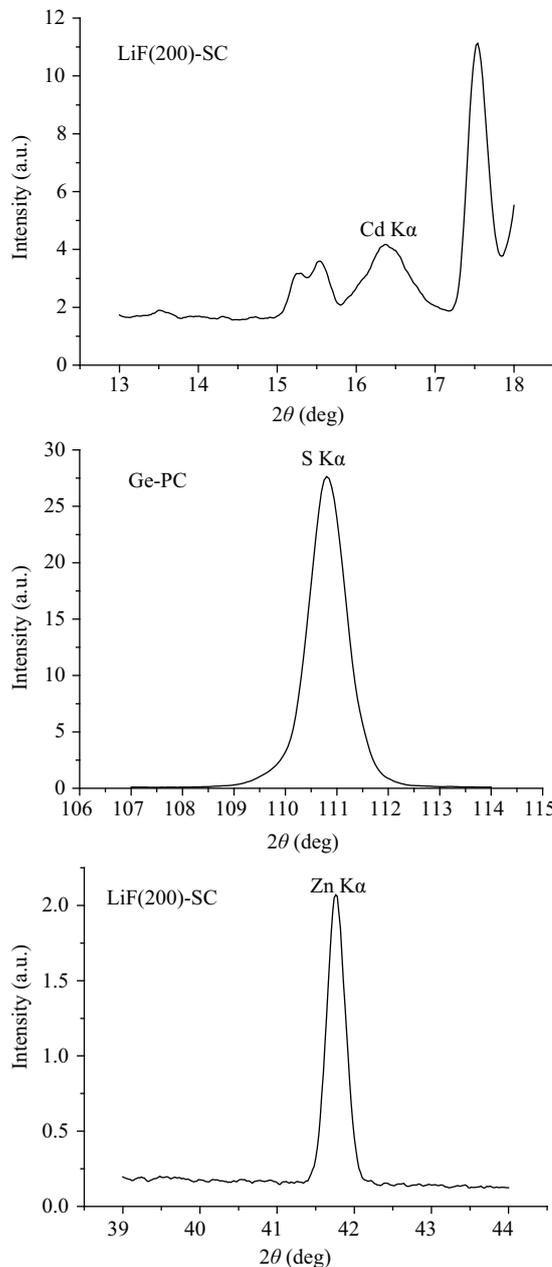


Fig. 2. XRF spectra of Cd<sub>1-x</sub>Zn<sub>x</sub>S polycrystalline thin films.

Table 1. Results of XRF for Cd<sub>1-x</sub>Zn<sub>x</sub>S polycrystalline thin films.

No.	Composition	Results (10 <sup>-7</sup> mol/cm <sup>2</sup> )	Spectral line	Intensity (kcps)
1	S	6.8056	S-Kα	27.6371
2	Zn	1.48031	Zn-Kα	2.07068
3	Cd	6.10319	Cd-Kα	4.14129

Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films determined from the quartz crystal oscillation method ( $x = 0.2$ ) agrees with that determined from the X-ray fluorescence spectra. The precision suggests that we can control the composition of Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films that were prepared by co-evaporation of CdS and ZnS.

Further, the surface composition of the Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films was observed by X-ray photoelectron spectroscopy (XPS), which was analyzed by the Gaussian-Lorentzian fitting method, as shown in Fig. 3. The binding energies of Cd3d5/2,

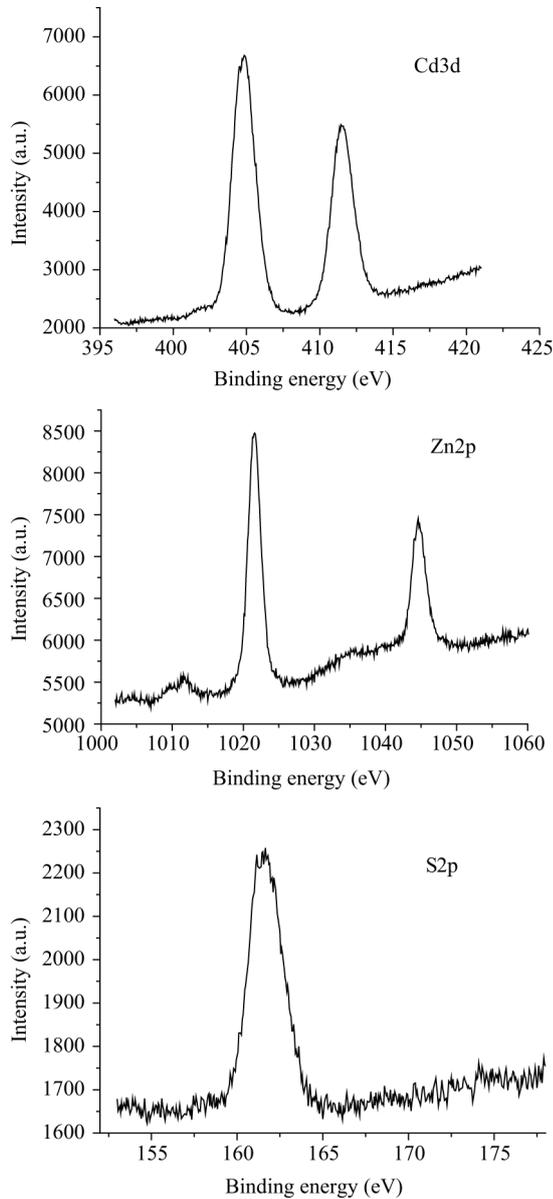


Fig. 3. Cd3d, Zn2p, S2p spectrum of Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films.

Znp3/2, and S2p3/2 for the thin films were 404.8, 1021.6, and 161.6 eV, respectively. We used the standard sensitivity factor (Cd ≈ 3.5, Zn ≈ 4.8, S ≈ 0.54) to obtain the atomic concentrations. The atomic concentrations of the Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films were Cd ≈ 45.48%, Zn ≈ 11.96% and S ≈ 42.56%, where *x* is ~ 0.208. The composition of the thin films obtained here is consistent with the result from XRF (discussed earlier).

### 3.2. Optical properties

Figure 4 displays the transmission spectrum of Cd<sub>0.8</sub>Zn<sub>0.2</sub>S thin films and sharp absorption edges were observed. The optical transmittance of the Cd<sub>0.8</sub>Zn<sub>0.2</sub>S films is typically 60% at wavelengths beyond the absorption edge. The refractive index, *n*, thickness, *d*, absorption coefficient,  $\alpha$ , and optical band gap, *E<sub>g</sub>* were calculated from the transmission spectrum using Swanepoel's method<sup>[9]</sup>.

The approximate value of the refractive index of the Cd<sub>0.8</sub>Zn<sub>0.2</sub>S thin films, *n*, in the spectral region of medium and

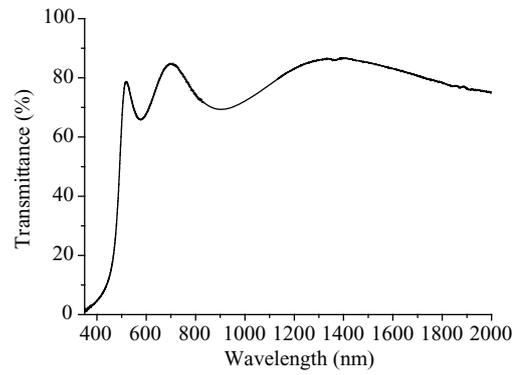


Fig. 4. Transmission spectrum for Cd<sub>0.8</sub>Zn<sub>0.2</sub>S thin films.

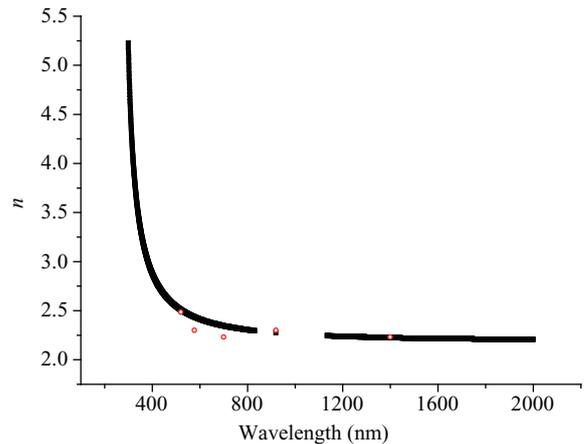


Fig. 5. Refractive index (*n*) of the Cd<sub>0.8</sub>Zn<sub>0.2</sub>S thin films.

weak absorption, can be calculated by the expression

$$n = \left[ N + (N^2 - n_s^2)^{1/2} \right]^{1/2}, \quad (3)$$

where  $N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2}$ , *T<sub>M</sub>* and *T<sub>m</sub>* are the transmission maximum and the corresponding minimum at a certain wavelength  $\lambda$ , and *n<sub>s</sub>* (= 1.54) is the refractive index of the glass substrate.

The calculated values of refractive index at different wavelengths from the transmission spectrum of Cd<sub>0.8</sub>Zn<sub>0.2</sub>S thin films are shown in Fig. 5.

To determine the film thickness, *d*, a number of thicknesses, *d'*, are calculated using the following relation,

$$d' = \frac{\lambda_1 \lambda_2}{2(n_1 \lambda_2 - n_2 \lambda_1)}, \quad (4)$$

where *n<sub>1</sub>* and *n<sub>2</sub>* are the refractive indices at two adjacent extremes of the same type at  $\lambda_1$  and  $\lambda_2$ , and the thickness, *d*, is estimated as the average value of *d'*<sup>[10]</sup>. The calculated thickness value of the Cd<sub>0.8</sub>Zn<sub>0.2</sub>S thin films is about 314 nm.

The energy dependence of *n* of semiconductor materials can be fitted to the Wemple and DiDomenico dispersion relationship that is the single-oscillator model<sup>[11]</sup>, as shown in Fig. 5,

$$n^2 - 1 = \frac{E_0 E_d}{E_0^2 - E^2}, \quad (5)$$

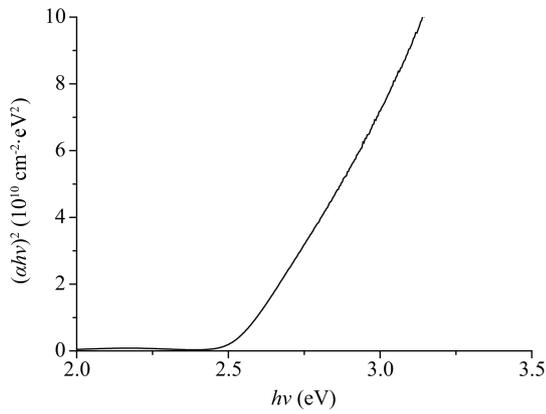


Fig. 6. Dependence of  $(\alpha hv)^2$  on photon energy  $h\nu$  for  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  thin films.

where  $E_0$  is the single-oscillator energy and  $E_d$  is the dispersion energy. By plotting  $(n^2 - 1)^{-1}$  versus  $E^2$  and fitting the data to a straight line,  $E_0$  ( $\approx 4.47$  eV) and  $E_d$  ( $\approx 16.92$  eV) can be determined from the intercept,  $E_0/E_d$  and the slope,  $-1/E_0E_d$ .

The absorption coefficient,  $\alpha$ , in the weak and medium absorption regions has been determined using the following relation<sup>[9]</sup>,

$$\alpha = -\frac{1}{d} \ln \frac{E_M - \left[ E_M^2 - (n^2 - 1)^3 (n^2 - n_s^2) \right]^{1/2}}{(n - 1)^3 (n - n_s^2)}, \quad (6)$$

where  $n_s$  is the substrate refractive index,  $d$  the thickness of the thin films, and  $n$  the refractive index of the films, and

$$E_M = \frac{8n^2n_s}{T_M} + (n^2 - 1)(n^2 - n_s^2). \quad (7)$$

In the strong absorption region,  $\alpha$  was calculated from the relation<sup>[9]</sup>

$$\alpha = -\frac{1}{d} \ln x = -\frac{1}{d} \ln \left[ \frac{(n + 1)^3 (n + n_s^2)}{16n^2n_s} T \right], \quad (8)$$

where  $T$  is the transmittance of the films in the strong absorption region.

In order to deduce the energy band gap of this transition, an analysis of the absorption spectrum of Fig. 4 was made. It was found that the spectral dependence of the absorption coefficient could be described by the following relation<sup>[12]</sup>,

$$\alpha hv \propto (hv - E_g)^m, \quad (9)$$

where  $h\nu$  is the photo energy, and the exponent  $m$  may take values 1, 2, 3, 1/2 or 3/2, depending on the electronic transitions in  $k$ -space. A linear fit was obtained for the investigated sample with  $m = 1/2$ , indicating that a direct allowed transition was involved. As shown in Fig. 6, the square of the absorption coefficients times energy,  $(\alpha hv)^2$ , obtained from the spectrum of the  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  thin films shown in Fig. 4, is plotted against  $h\nu$  to obtain the extrapolated value of about 2.59 eV for  $E_g$ .

The band gap can also be estimated from the empirical expression<sup>[13]</sup>

$$E_g(x) = 2.38 + 0.69x + 0.85x^2. \quad (10)$$

When  $x = 0.2$ ,  $E_g$  becomes 2.552 eV, which agrees well with that reported on other  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  alloy systems in thin films by Borse *et al.* ( $b = 0.85$  eV)<sup>[14]</sup>. It can be seen that there is good agreement between the two sets of  $E_g$  values.

#### 4. Conclusions

The  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  thin films were successfully deposited on glass substrates by the vacuum co-evaporation method. The structure of the thin films is hexagonal, which has very strong preferential orientation along the (002) plane. The optical constants were deduced by Swanepoel's method from the transmission spectrum of the  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  thin films. The analysis of the optical absorption data revealed that the optical band gap  $E_g$  was direct transitions and it agrees well with the empirical expression.

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