

Optical and Morphological Studies of Chemical Bath Deposited Nanocrystalline $Cd_{1-x}Zn_xS$ Thin Films

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ABSTRACT

Cadmium Zinc Sulfide, $Cd_{1-x}Zn_xS$ thin films were deposited by chemical bath deposition technique at bath temperature of 75°C. The morphology of the films was analyzed by scanning electron microscope, the optical constants of the films were estimated from the transmission and reflection spectra of the films in the wavelength range of 300 - 900 nm. The films had a transmittance between 75% and 85% and optical band gap in the range 2.8 - 3.4 eV. The dependence of the refractive index of the films on the wavelength was investigated using the single oscillator model, from which the dispersion parameters were determined. The high frequency dielectric constant ϵ_L and the ratio of the carrier concentration to the effective mass N/m^* were estimated based on the Spitzer and Fan model. Both ϵ_L and N/m^* show a decrease in value with increase in Zinc content.

Keywords: Chemical Bath Deposition; $Cd_{1-x}Zn_xS$; Scanning Electron Microscope

1. Introduction

Ultrathin semiconductor nanoparticle thin films have attracted growing interest for both fundamental research and technical application due to their size-dependent electronic properties that has lead to a wide range of technological applications as functional layers in electronic and optoelectronic devices, solar cells, photoelectrodes, photocatalysts, and sensors [1]. Nanocrystalline binary and ternary semiconductors of Groups II-VI have potential applications in many technical fields, including photoluminescence, solar cells and photovoltaic applications [2-4].

CdS alloyed with ZnS form a continuous series of solid solution $Cd_{1-x}Zn_xS$ for the whole range of x, giving rise to a systematic variation of band gap of $Cd_{1-x}Zn_xS$ from 2.43 eV for CdS to 3.7 eV for ZnS. Besides, replacing CdS with the higher energy gap ternary $Cd_{1-x}Zn_xS$ has led to a decrease in window absorption loss, and has resulted in an increase in the short circuit current in thin film CdS window-based solar cells [5]. Also $Cd_{1-x}Zn_xS$ and related ternary compounds are promising materials for high density optical recording and for blue or even UV laser diodes applications based on the structure of $Cd_{1-x}Zn_xS$ which exhibit fundamental absorption edges that can vary from green to UV [6,7].

A number of film deposition methods such as chemical bath deposition (CBD), spray pyrolysis, vacuum evaporation, chemical vapor deposition, and sputtering have been used for preparing $Cd_{1-x}Zn_xS$ films [2,8-11].

In this work, the effect of Zn content on the optical properties and morphology of $Cd_{1-x}Zn_xS$ thin films deposited by chemical bath deposition technique are presented.

2. Experimental

$Cd_{1-x}Zn_xS$ thin films were deposited on Menzel-glazer glass slides. The chemicals used were cadmium acetate ($Cd(CH_3OO)_2$) of 0.015 M, zinc acetate ($Zn(CH_3COO)_2$) of 0.015 M and 0.05 M thiourea ($SC(NH_2)_2$). The concentration of ammonium acetate (NH_4CH_3COO) used as buffer was 0.3 M, while ammonia solution (NH_3OH) concentration was 0.8 M. All chemicals were of analytical-grade. A Bath temperature of 75°C was used.

A 100 ml beaker was used as container for the reacting chemicals; this was immersed in a water bath. Solutions of cadmium acetate, zinc acetate, ammonium acetate and thiourea were first mixed together in the 100 ml beaker, heated to 75°C and stirred vigorously.

Ammonia solution was then added and substrates immersed vertically. The concentrations and the amount of chemicals used are given in **Table 1**. The substrates had

earlier been washed with detergent, rinsed in deionized water, soaked in nitric acid, degreased in ethyl alcohol and then rinsed in deionized water. The reacting bath was agitated throughout the period of deposition. The deposition was carried out for 45 minutes after which the coated substrates were removed and washed in de-ionized water to remove loosely adhered Cd_{1-x}Zn_xS particles. The samples were labelled T1, T2 and T3 based on the three volumes of Zn(CH₃COO)₂ used.

The normal incidence optical transmittance of the films was measured in the scanning mode using the double beam α -Helios UV-Vis spectrophotometer, so modified to take a solid sample. The measurements were taken from a wavelength of 300 nm to 900 nm. The films morphologies were analyzed with a CARL ZEISS MA 10 scanning electron microscope (SEM).

3. Results and Discussion

3.1. Optical Properties and Dispersion Analysis

Specular yellow and adhesive Cd_{1-x}Zn_xS films were obtained for the three films. The Transmittance spectra of the films are shown in **Figure 1**. The films had a transmittance of 78%, 75% and 85% in the visible region for the samples T1, T2 and T3 respectively.

The band gaps of the films were determined from electronic absorption spectra by the direct band gap method from the intercept of the plots of α^2 versus energy $h\nu$ at $\alpha^2 = 0$, according to Tauc's relation in the strong-absorption region of the films (**Figure 2**). The composition of the ternary Cd_{1-x}Zn_xS was estimated from the expression given by the relationship [12],

$$E_g(x) = 2.42 + 0.69x + 0.62x^2$$

$E_g(x)$ is the band gap of the composition of the ternary Cd_{1-x}Zn_xS defined at x . The values of x determined from the expression are given in **Table 2** for the three films. There is an increase in band gap with increase in Zn

content x resulting from increase in the absorption edge.

The frequency dependent refractive index n of the thin films were determined from the equation [13],

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

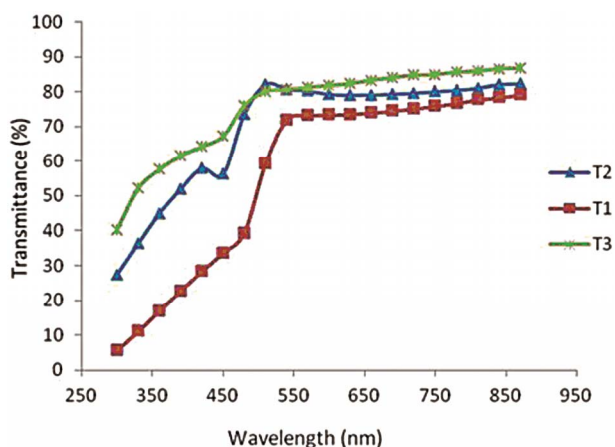


Figure 1. Transmittance spectra of the films.

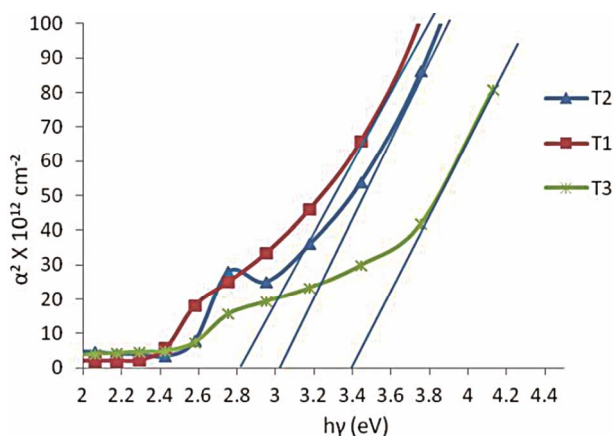


Figure 2. α^2 versus $h\nu$: Samples T1, T2 and T3.

Table 1. Concentrations and volumes of chemicals used.

Sample	Cd(CH ₃ OO) ₂ (0.0015 M)	Zn(CH ₃ COO) ₂ (0.0015 M)	SC(NH ₂) ₂ (0.05 M)	NH ₄ CH ₃ COO (0.3 M)	NH ₃ OH (0.8 M)
T1	9 ml	6 ml	12 ml	9 ml	36 ml
T2	9 ml	12 ml	12 ml	9 ml	36 ml
T3	9 ml	18 ml	12 ml	9 ml	36 ml

Table 2. Optical constants of the films.

Sample	Zn content (x value)	$E_g(x)$ (eV)	E_o (eV)	E_d (eV)	E_o/E_g	M_{-1}	M_{-3} (eV) ⁻²
T1	0.40	2.8	2.63	10.94	0.94	2.50	0.36
T2	0.56	3.0	3.22	11.91	1.1	3.73	0.36
T3	0.82	3.4	3.26	8.81	0.96	2.66	0.25

where k ($k = \alpha\lambda/4\pi$) is the extinction coefficient. The spectral dependence of the refractive index n is shown in **Figure 3**. There is a sharp rise in n for the samples T1 and T2 at absorption edge towards the shorter wavelengths of the spectrum. This sharp onset of n at the absorption band edge is attributed to Van Hove singularity in the joint density of state in the excitation of transition between two bands [14].

The dispersion of the refractive index is related to the photon energy E (λ), by the single-oscillatory model proposed by Wemple and DiDomenico which describes the dielectric response for transitions below the interband absorption edge. Below the absorption edge, refractive index dispersion can be analyzed by the single-oscillator model [15]

$$n^2(E) - 1 = \frac{E_d E_o}{E_o^2 - (h\gamma)^2}$$

where h is Planck's constant, E_o is the average excitation energy for electronic transitions and is empirically related to the optical band gap, while E_d is the dispersion energy and is a measure of the average strength of interband optical transitions and can be considered as a parameter having very close relation with the charge distribution within unit cell and therefore with the chemical bonding [16]. The increase in E_d is associated with the evolution of the thin film microstructure to a more ordered phase [17]. The parameters E_o and E_d are obtained from the intercept and slope of the plot of $(n^2 - 1)^{-1}$ versus photon energy $(h\gamma)^2$. **Figure 4** shows an extended region of linearity of the plot, and is employed to determine these values. The obtained dispersion parameters change with deposition parameters.

Based on the single oscillator model, the single-oscillator parameters E_o and E_d are connected to the imaginary part ε_i of the complex dielectric constant and the -1

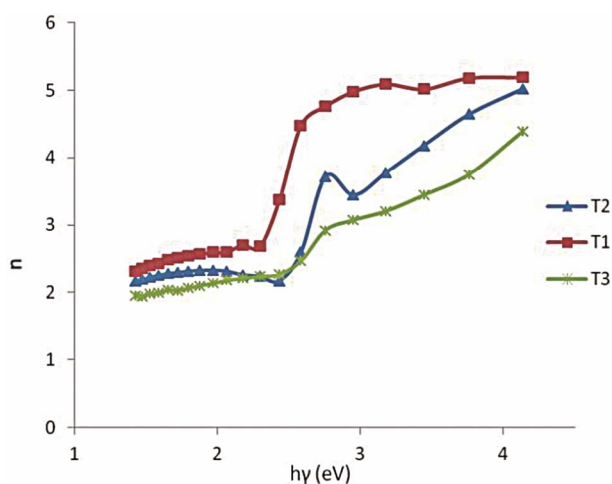


Figure 3. Variation of refractive index n with photon energy $h\gamma$ of the films.

and -3 moments of the ε_i optical spectrum can be derived from the relations [18]:

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

The determined values of M_{-1} and M_{-3} moments of the imaginary part ε_i of the dielectric constant of the samples as well the estimated values of the oscillator parameters and other values of the calculated optical parameters are summarized in **Table 2**.

The ratio $E_o/E_g \approx 1$ is obtained for all the samples with a deviation of about ± 0.1 eV. Ilican *et al.*, had obtained a value of $E_o/E_g \approx 1.2$ [19] in a similar work, using spray pyrolysis method in studying the influence of substrate temperature on the optical properties of CdZnS film. Sample T2 with $x = 0.56$ had the highest dispersion energy E_d of 11.91 eV, indicating it is of more ordered microstructure compared to samples T1 and T3.

It should be stressed that the oscillator energy E_o though very similar to the parameter used by Penn, being a measure of the energy difference between the "centers of gravity" of the valence and conduction bands [20], its value is different from the optical gap which probes the optical properties near the band edges of the material.

The refractive index at zero photon energy, also called the static refractive index n_o , given by the infinite wavelength dielectric constant $\varepsilon_o^{WD} = n_o^2$ is determined from the dispersion relation [21]

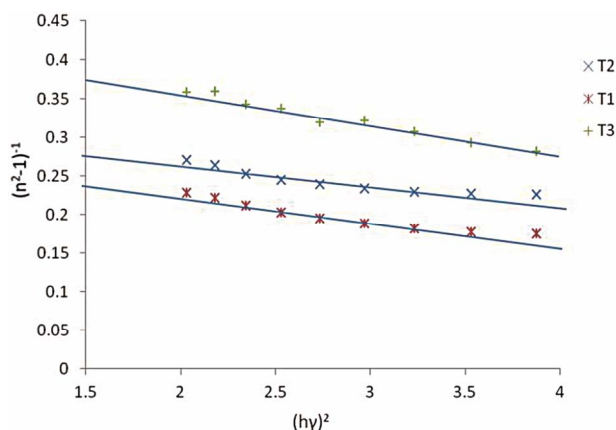


Figure 4. Plot of $(n^2 - 1)^{-1}$ versus photon energy $(h\gamma)^2$ for Cd_{1-x}Zn_xS thin films.

Table 3. Values of ε_o^{WD} , ε_L and N/m^* .

Sample	Zn content (x value)	ε_o^{WD}	ε_L	N/m^* ($10^{41} \text{ m}^{-3} \text{ g}^{-1}$)
T1	0.40	5.16	7.4	15.50
T2	0.56	4.70	5.8	6.36
T3	0.82	3.70	2.4	2.65

$$n_0^2 = 1 + \frac{E_d}{E_0}$$

The values obtained for T1, T2 and T3 are 5.16, 4.70 and 3.70 respectively.

The high frequency dielectric constant is also given by [22]

$$\epsilon_1 = \epsilon_L - \left(\frac{e^2}{\pi c^2} \right) \left(\frac{N}{m^*} \right) \lambda^2$$

where ϵ_1 is the real part of the dielectric constant, ϵ_L is the high frequency dielectric constant (or lattice dielectric constant) and N/m^* is the ratio of carrier concentration to the effective mass. The real part of the dielectric constant $\epsilon_1 = n^2$ was determined at different values of the wavelength λ in the transparent region. The plot of n^2 against λ^2 is given in **Figure 5** and shows a linear dependence of n^2 on λ^2 in the transparent long wavelength region. Extrapolating the linear part of the plot to zero wavelength gives the value of ϵ_L and N/m^* is determined from the slope. The values obtained are given in **Table 3**.

The difference between the values of ϵ_o^{WD} and ϵ_L ob-

tained is attributed to the formation of free carriers in the thin films [23]. All the parameters in **Table 2** tend to decrease with increase in Zn content.

3.2. Surface Morphology

The SEM micrographs and the corresponding 3D topographical maps of the films are presented in **Figures 6(a)-(c)**, they indicate that the surface morphology of the

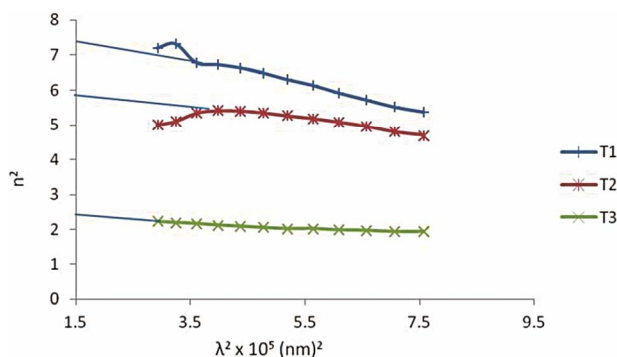
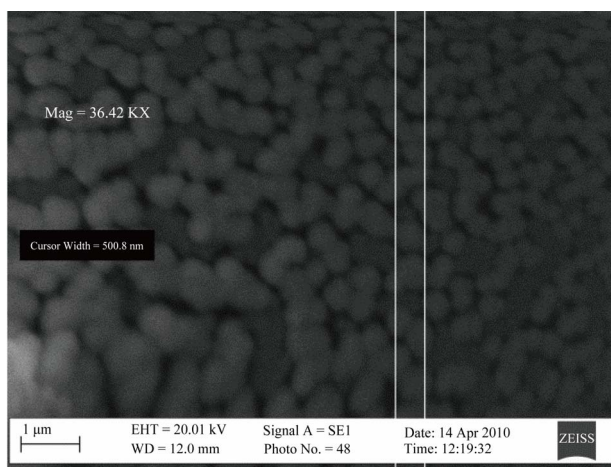
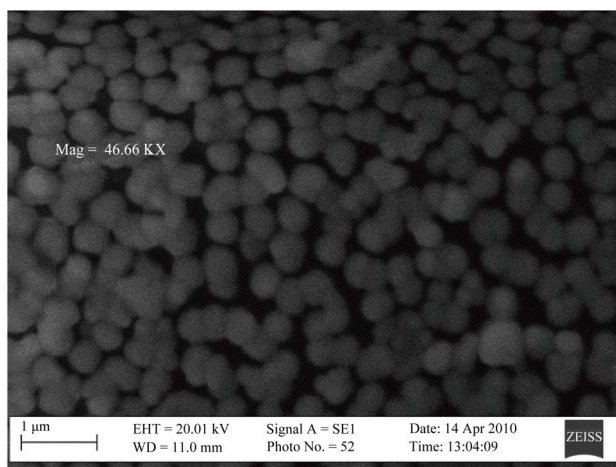
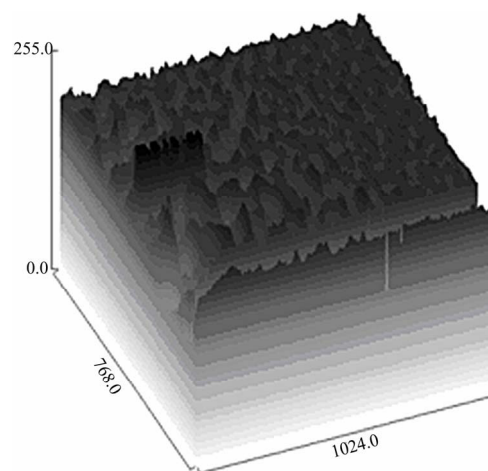


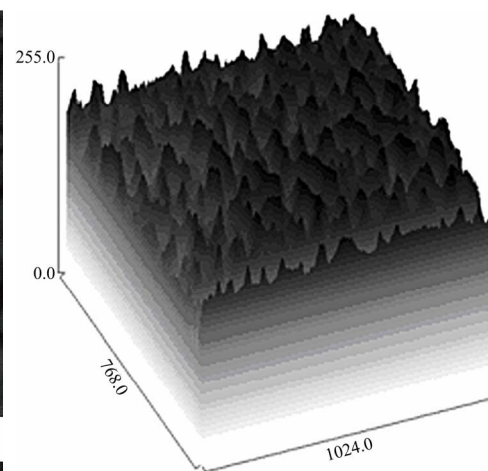
Figure 5. Plot of n^2 versus λ^2 for Cd_{1-x}Zn_xS thin films.



(a)



(b)



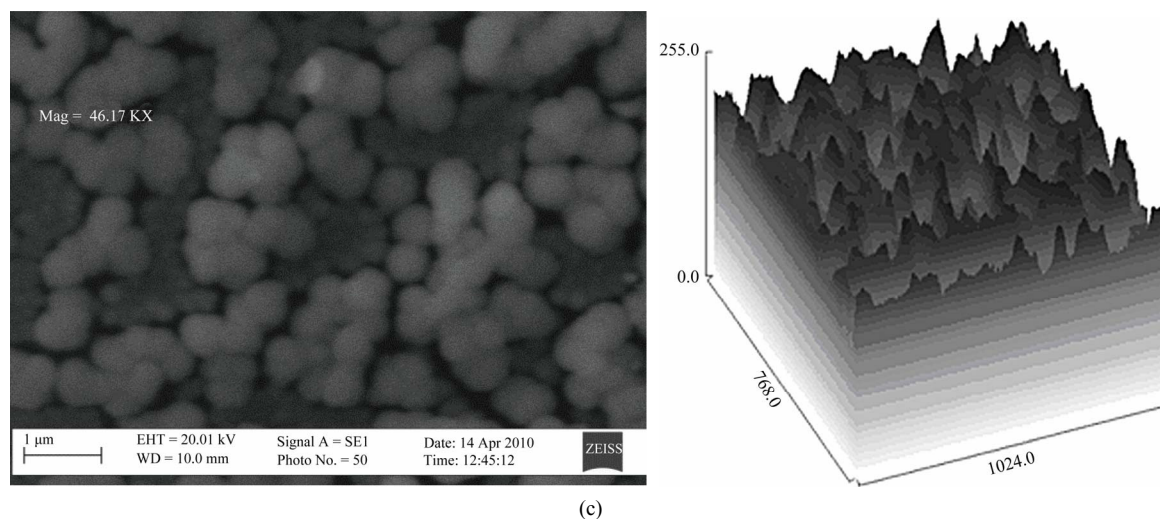


Figure 6. SEM micrograph of the films for samples (a) T1, (b) T2 and (c) T3.

films are influenced by the Zn content. The films show smooth and uniform spherical grains. The microstructure of the films are denser and more uniformly distributed for samples T1 and T2. The surface grain sizes were determined by the image analysis of several (ten) grains and the average values are 25, 11 and 13 nm for Samples T1, T2 and T3 respectively.

4. Conclusion

The effects of Zn content on optical and morphological-properties of Cd_{1-x}Zn_xS thin film deposited by Chemical Bath Deposition technique been investigated. The optical band gaps E_g of the films were found to be between 2.8 and 3.4 eV. The average excitation energy for electronic transitions E_o , the dispersion energy E_d and the M_{-1} and M_{-3} moments of the ϵ_i were determined based on the single-oscillator model. The ratio $E_o/E_g \approx 1$ for all the films. The sample with Zn content $x = 0.56$ showed a more ordered microstructure with the highest dispersion energy E_d of 11.9 eV. The high frequency dielectric constant ϵ_L and N/m^* of all the samples were observed to decrease with increase in Zn content x .

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