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Study of optical parameters of Chemical Bath deposited $Cd_{1-x}Zn_xS$ thin films

Ravangave L. S. Department of Physics, Shri sant Gadge Maharaj college Loha, Dist. Nanded (M.S.) India

Biradar U. V. Department of Physics, Mahatma Basweshewar college Latur (M.S.) India.

ABSTRACT *The Chemical Bath Deposition Method (CBD) was employed for deposition of $Cd_{1-}xZn_xS$ (x=0,.0, 0.2, 0.4, 0.6,0.8 1.0) thin films. The Chemically deposited $Cd_{1-}xZn_xS$ thin films were characterized by using UV-Visible spectrophotometer. Transmission spectra show the blue shifting of absorption edge. The maximum 78% transmittance was observed in the x=0.8 composition. The reflection in the blue portion of the incident spectrum was decreased as the Zn content increased. The $(\alpha h\upsilon)^2$ versus photon energy (hυ) curves shows tuning of band gap with Zn content. The observed band gap was 3.9 eV in the x=0.8 composition. The effect of composition on refractive index, absorption index and other optical dispersion parameters were also investigated. The calculated values of average excitation energy E_o approximately obey the empirical relation (E_o=1.2 E_g) obtained from single oscillator model.*

KEYWORDS: Chemical Bath Deposition, band gap, optical constants.

Introduction:

Now a days, Solar cell devices Plays vital role in converting solar energy into usable form. The selection of window material is often important in the fabrication of low cost, high efficiency solar cell devices. Tuttle J. R. et al.(1997) reported that cadmium sulphide (CdS) is a low direct band gap (Eg= 2.42eV) n-type semiconductor and widely used as window layer material in solar cell devices. Chavhan S. D.et al.(2008) reported that CdS absorbs blue portion of solar radiations and decrease the current density of solar cells. Addition of Zn to widely used CdS window material improves the electrical and optical properties. The CdZnS provides the wider band gap and higher optical transmittance as compared to CdS. The wider band gap and higher optical transmittance are essential requisite in solar cell applications (Chavan S. D. et al. 2005). The CdZnS is II-VI compound semiconductor potentially used as window material for fabrication of p-n junction without lattice mismatch in CdTe or $CuIn_xCa_{1-x}Se2$ solar cell devices (Ilican S. et al. 2007).

The knowledge of optical parameters such as optical band gap, reflectivity, optical transmittance, refractive index and dielectric constants etc. are essential prerequisite in using the suitable material for device applications A number of thin film deposition techniques are available. Of the most, Chemical Bath Deposition (CBD) is practically attractive because of its simplicity in comparison with other techniques, requiring vacuum conditions and complex instrumentations. Rakhshani et al. (1998)reported that the production of large surface area CdS thin films by easy and low cost techniques for industrial use, is still of great importance (CBD is fast, simple, inexpensive, non-vacuum and suitable for mass production.

The objective of the present study is to synthesize $Cd_{1-x}Zn_xS$ thin films by using chemical bath deposition technique (CBD). The prepared thin films are characterized by using UV- Visible spectrophotometer to study the effect of Zn content on the optical properties and optical constants like refractive index, extinction coefficients and dielectric constants etc. of $Cd1_{-x}Zn_xS$ thin films.

Experimental:

In order to prepare $Cd_{1-x}Zn_xS$ thin films, the aqueous solution of Cadmium Chloride $CdCl_2$, Znic Chloride $ZnCl_2$ and thiourea NH2CSNH2 were used as the precursor solutions. The stock solutions of $CdCl_2$ (0.05M), $ZnCl_2$ (0.05M) and NH_2CS-NH_2 (0.1M) were prepared. The experimental solutions with different volume proportions were taken in reaction beaker for deposition of $Cd_{1-x}Zn_xS$ thin films as shown in following table 1.

Table 1.The experimental solutions with different volume proportions

Composition x	$CdCl_2$ (ml)	$ZnCl_2$ (ml)	NH_2CSNH_2 (ml)
0.0	10	0	10
0.2	8	2	10
0.4	6	4	10
0.6	4	6	10
0.8	2	8	10
1.0	0	10	10

The pH of the solution was adjusted to 11 by adding the aqueous NH3. The reaction beaker was kept in temperature bath, maintained at constant 80 °C. Glass substrates were cleaned by 24 hr immersing in chromic acid, rinsed with acetone and distilled water.

All the chemicals and reagents used were of analytical grade. The experimental glass substrates were mounted on substrate holder and immersed in the reaction beaker. The substrate holder was rotated at slow speed (45 rpm) by means of DC geared motor for 25 to 30 minutes. The pH of the precursor, reaction temperature, rotation speed and dipping time of the substrate were kept constant throughout the experiment at optimized values.

The thin, uniform $Cd_{1-}xZn_xS$ films were obtained at the end of the reaction process. The prepared $Cd_{1-}xZn_xS$ thin films were rinsed with deionized water to remove the loosely bound particles and annealed at 100 °C. The synthesized $Cd_{1-x}Zn_xS$ films are characterized by using UV- Visible spectrophotometer.

Two different methods were used for thickness measurements: the "Weighting difference method and the "Optical interference fringes method". The weighting difference method gives an approximate value for thickness of the prepared films. A digital balance with accuracy of (= 0.1x103 gm) was used for weighting the bulk content of deposited material on the substrate (Nathera A. et al. 2012) .

The optical band gap was determined by using relation (Jauc J. (1974):

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^n \quad \text{-- (1)}$$

where A is energy independent constant; Eg is optical band gap ; n is constant which can determine types of optical transitions. The wavelength dependence of optical constants such as extinction coefficients (k), refractive index (n), real (ε1) and imaginary (ε2) parts of dielectric constant were calculated using fowling equations: (Abeles F. 2007):

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

where R is the reflectance; and K is extinction coefficient.

$$k = \frac{\alpha\lambda}{4\pi} \text{------------------ (3)}$$

where α is absorption coefficient.

Results and discussion:

Absorbance data of $Cd_{1-x}Zn_xS$ thin films was recorded by using UV-Visible spectrophotometer (Systronics Double Beam 2201).

Figure1 is the plot of transmission versus wavelength. The transmission curves show the blue shifting of absorption edge (approximately from 450 – 350 nm). The figure 1, illustrate that, optical transmittance was maximum in the visible region (450 - 800 nm) and found increased from 5 to 78 % with Zn content. In the composition x=0.8, the observed transmittance was 78 %.

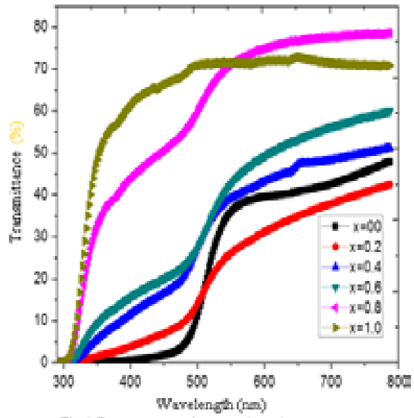

Fig 1. Percent transmittance plotted versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

Figure 2 shows the variation of optical reflection with wavelength. The reflection is found decreased from 0.02 to 0.005 (a.u.) in the visible and near infrared regions. It supports the antireflection property of the $Cd_{1-x}Zn_xS$ thin films. In the compositions x=0.8 and 1.0, the optical reflectance was significantly decreased in the blue portion of the incident spectrum. Blue shifting of absorption edge indicate the decrease in optical absorption in the blue portion of the solar spectrum. (Borse S. V. et al. 2007).

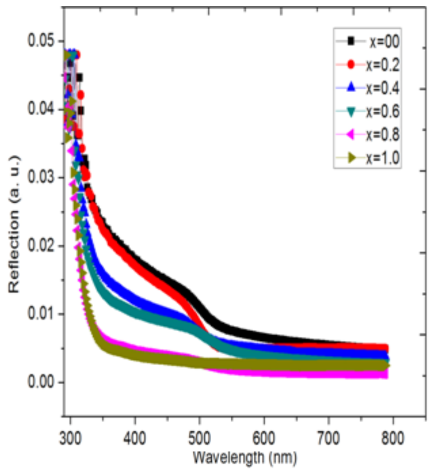

Fig.2.Reflection versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

The variation of film thickness with composition x is displayed in table 2. Thickness of the films was found decreased from 6.63 to 1.13 µm. All the $Cd_{1-x}Zn_xS$ films shows high absorption coefficient (α=10^6 cm^{-1}). The values of the direct band gap (Eg) were determined by plotting $(\alpha h\nu)^2$ versus photon energy as shown in Figure 3.

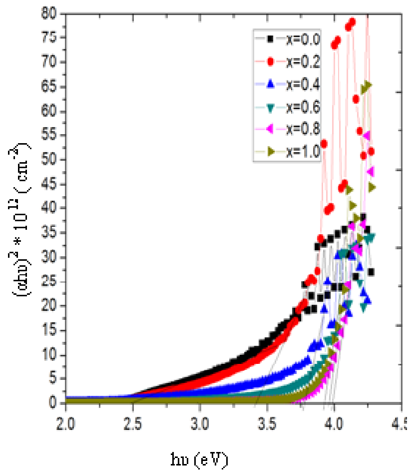

Fig.3.plot of $(\alpha h\upsilon)^2$ versus hυ of $Cd_{1-x}Zn_xS$ films.

Extrapolating the straight line portion of the $(\alpha h\nu)^2$ versus ($h\nu$) to the zero absorption (α=0) gives the band gap (E_g).

The annealing effect shows that, band gap of CdS ($Cd_{1.0}Zn_{0.0}S$) is 2.47eV which is larger than 2.42 eV of the bulk CdS material. The variation of band gap with Zn content was shown in table 2. The band gap was increased with Zn content from 2.427 to 3.9 eV. In the composition x=0.8, the band gap was found to be 3.9 eV .

The dispersion of incident photon energy plays the important role in determining the optical property of the material.

The knowledge of variation of refractive index helps to investigate the average excitation energy (E_o) and dispersion energy (E_d) of the deposited material.

The variation of refractive index (n) and extinction coefficient (k) with wavelength of the $CdxZn_1$-xS films are presented in figures 4 and 5 respectively.

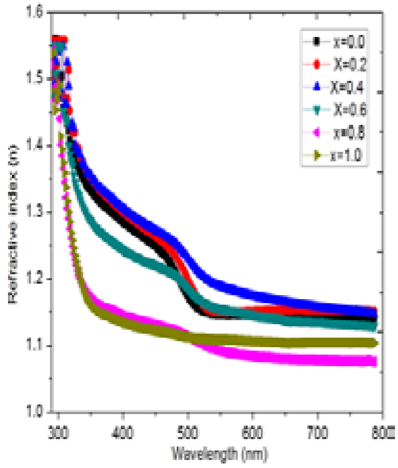

Fig.4.Plot of Refractive index (n) versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

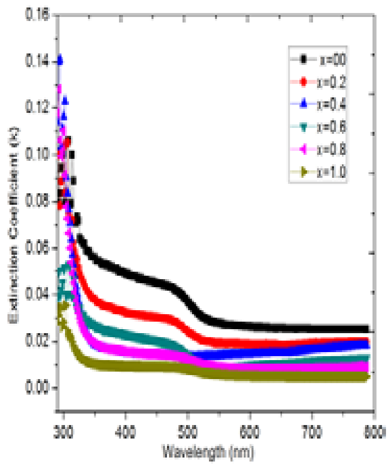

Fig.5 Plot of extinction coefficient (k) versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

The refractive index of the deposited films significantly changes with the film composition. In the low wavelength region the values of refractive index for deposited films are higher and then decreased after 350 nm. The effect of Zn content of the deposited Cd_1-xZnxS films on n and k was clearly illustrated from the figures 4 and 5. The extinction coefficient (k) shows similar nature of variation; however the k has less value as compared to n. The observed values of n and k at wavelength 450 nm were presented in table 2.

The investigation of complex dielectric constant is very important as it provides information about electronic structure of the deposited material onto the substrate. The dielectric constant is given as,

$\varepsilon(\omega) = \varepsilon_1(\omega)+i\varepsilon_2(\omega)$

where, real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of dielectric constant are related to the n and k values respectively.

The ε_1 and ε_2 were calculated using formulas (Ilican S. 2011)

$\varepsilon_{1=}n^2 - k^2$ --------- (4)

$\varepsilon_{2=}2nk$ --------- (5)

The real and imaginary parts of dielectric constant (ε) plotted versus wavelength and presented in figures 6 and 7 respectively.

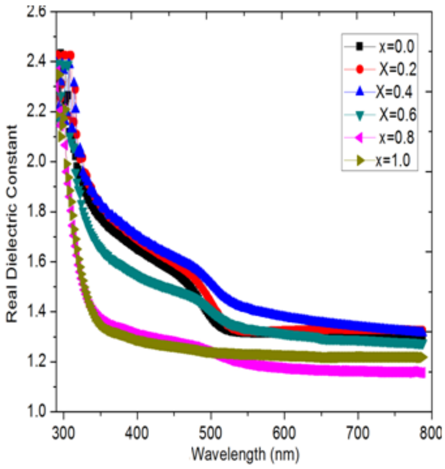

Fig.6. Plot of real part of dielectric constant(ε_1) versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

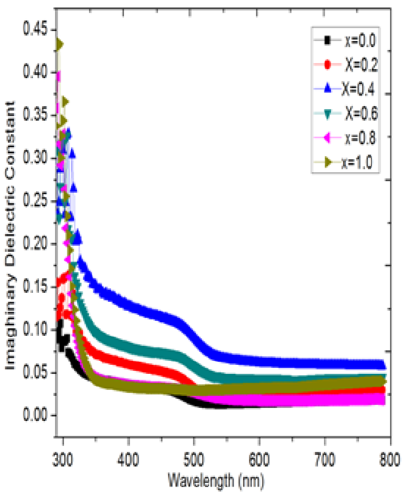

Fig.7. Plot of Imaginary part of dielectric constant(ε_1) versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

From the figures 6 and 7, it is concluded, that both ε1 and ε2 decreases from 0.45 to 0.025 and 2.4 to 1.2 respectively. The observed values of ε1 and ε2 at wavelength 450 nm were presented in table 2.

Table 2. The variation of film thickness (t) and optical constants with Zn composition (x)

x	t µm	Eg (eV)	n at 450 nm	K at 450 nm	ε1 at 450 nm	ε2 at 450 nm
0.0	6.3	2.427	1.20	0.045	1.46	0.021
0.2	4.3	3.4	1.27	0.029	1.61	0.05
0.4	2.13	3.7	1.212	0.019	1.64	0.109
0.6	2.13	3.8	1.21	0.0144	1.48	0.073
0.8	1.67	3.9	1.129	0.014	1.27	0.030
1.0	1.13	3.85	1.123	0.0091	1.25	0.030

The variation of ε1 as a function of wavelength follows the similar behavior as n whereas the variation of ε2 follows the behavior of k. The extinction coefficient (k) and ε2 are related to absorption coefficient α and hence the thickness of the deposited thin films. The change of Zn content in Cd1-xZnxS thin films causes the important change in dielectric constants.

The approximate relation between refractive index n, average excitation energy for electronic transition (E_o), the dispersion energy (E_d) and incident photon energy (hυ) was described by Wemple and DiDomenico (Wemple S. H. 1971) means of single oscillator:

$n^2 - 1 = E_d E_o / (E_o^2 - (h\nu)^2)$ ---(6)

Plot of $(n^2-1)^{-1}$ against $(h\nu)^2$ gives the oscillator parameters Eo and Ed which are determined by fitting a straight line to the points and shown in fig 8.

The values of E_o and E_d can be directly determined from the gradient $(E_oE_d)^{-1}$ and intercept on vertical axis, (E_d/E_o).

The values obtained for dispersion parameters, Eo and Ed are displayed in table 3. Table 3. Variations of oscillator

parameters with composition x.

x	Eo (eV)	Ed (eV)	M-1	M-3 (eV)-2
0.0	3.72	23.1	6.71	0.49
0.2	4.082	25.9	6.31	0.38
0.4	4.08	26	6.32	0.38
0.6	4.378	22	5.0	0.26
0.8	5.17	14.78	2.89	0.118
1.0	5.26	14	2.66	0.096

Ilican S. et al. (2006) were reported that, the oscillator energy E_o is related to lowest dierect band gap empirically by $E_o = 1.2E_g$. The calculated values of E_o satisfies the empirical relation approximately obtained from single oscillator model.

The moments M_{-1} and M_{-3} of the optical transitions can be obtained from relationships:

$(E_o)^2 = M_{-1}/M_{-3}$ --(7)

$(E_d)^2 = M^3_{-1}/M_{-3}$ ---(8)

The calculated vaues of E_o, E_d and M_{-1}, M_{-3} were found decreased with Zn content. As compared with values reported (Ilican S. et al. 2006), the obtained values of E_o, E_d and M_{-1}, M_{-3} are found higher. This may be because of technique of deposition. The values of moments of optical transitions are tabulated in table 3 shows the decreasing trend with Zn content.

The compositional and structural studies are the future scope of the work, to confirm the initial and final content of elements.

Conclusion:
The transparent $Cd_{1-x}Zn_xS$ thin films have been synthesized by low cost simple Chemical bath deposition technique. It was concluded that, Zn content changes the optical properties of the $Cd_{1-x}Zn_xS$ thin films. The film of composition x=0.80 and 1.0 gives maximum 78% transmittance. The maximum transmittance and low reflection property indicate that the prepared thin films are antireflective. The band gap shows the increasing trend with Zn content. The film composition x=0.8 shows maximum 3.9 eV band width. The variation of ε_1 as a function of wavelength follows the similar behavior as n whereas the variation of ε_2 follows the behavior of k. The values of E_o, E_d and M_{-1}, M_{-3} decreased with concentration of Zn. The calculated values of average excitation energy E_o approximately obey the empirical relation obtained from single oscillator model.

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