Structural, Morphological and Electrical Properties of chemical bath deposited $Cd_{1-X}Zn_XS$ Thin Film

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Abstract-$Cd_{(1-x)}Zn_xS$ ($0 \leq x \leq 1$) thin films with different compositions have been deposited on amorphous glass substrates by the chemical bath deposition technique. The composition Structural, Optical, Morphological and Electrical Properties were studied. The structural properties of as deposited films were studied by using X-ray diffraction technique. XRD studies reveal that the films are crystalline with cubic and hexagonal structure. Calculated lattice parameter shows good agreement with JCPDS data card. It is observed that grain size increasing with increased Zn up to x = 0.4. Further, it decreases with increasing Zn. The band gap of the thin films varied from 2.45 to 3.50 eV as composition varied from x=0 to x=1. It was observed that changes in the small amount of Zn result in marked changes in the optical band gap of CdS. The electrical conductivity decreases with rising Zn content and rising with temperature. An effort has also been made to obtain activation energy of these films which rise with rising Zn attention in CdS.

Keywords: *Thin film, $Cd_{(1-x)}Zn_xS(0 \leq x \leq 1)$, CBD method, Structural properties, optical properties, morphological properties, electrical properties.*

1. Introduction

In the present situation, petroleum products are insufficient to meet the vitality necessities of the world. What's more, consuming non-renewable energy sources has another hindering impact of discharge of ozone-harming substances driving to global warming. Elective renewable vitality sources, for example, sun power, wind power can be used to beat the vitality deficiency. Analysts are taking a shot at various innovations to tackle these renewable resources in a proficient way since the establishment of photovoltaic (PV) modules will give vitality less carbon footprint [1]**.** For a long time, silicon-based sun oriented cells dominated the market and with an increase in assembling capabilities, thin film PV cells are picking up significance [2]**.** Real deposition techniques, for example**,** sputtering[3], Metal Organic Chemical Vapor Deposition (MOCVD) [4]**,** e-beam evaporation (**5),** chemical bath deposition (CBD) [6]. have been attempted to produce thin film PV.

The chemical bath deposition (CBD) technique is right now drawing in considerable regard for the analyst as it doesn't require costly instrumentation like vacuum system and other costly hardware [6]. The transformation of sun energy into a usable shape is a plausible test to the researcher.

Group II-VI semiconductor thin films have attracted substantial attention because of their broad range of use in the fabrication of solar cells and other optoelectronic devices[7]**.** Group II-VI semiconductor compound they by and large display extensive band gaps, making them prominent for short wavelength applications in optoelectronics [8].

II-VI compounds can formed ternary and quaternary compounds with an immediate primary band gap assignment over the whole amalgam creation go and with high absorption coefficients control.. CdZnS ternary thin film has been broadly utilized as a great bandgap window material in hetero intersection sun oriented cells and photoconductive gadgets [9]. CdS and ZnS frame a persistent arrangement of strong arrangements, Cd Zn S. The band-gap vitality of Cd1-xZnxS can be controlled in the scope of the parallel band gap. Additionally, in heterojunction solar cells utilizing CdTe, CuInSe , and CuGaSe , the utilization of CdZnS rather than CdS can prompt an expansion in photocurrent by giving a match in the electron affinities of the two materials[11]. In order to diminish the imperfection density, the optical and electrical properties of CdS must be improved which can be accomplished through doping. It has been accounted for before that when CdS is doped with certain cationic impurities, for example, Al,Ga, Mn, Zn, Cu, In and with certain anionic contaminations, for example, F, Cl, B and so on., its optoelectronic properties might be improved.[10]. Films deposited by CBD technique are by and large polycrystalline in structure and their properties are impacted by the deposition procedure. [7].

In our present work, cadmium acetate, zinc acetate and thiourea mixture have been used as source materials to make thin films of $Cd_{(1-x)}Zn_xS$ with different composition (x = 0.0–1.0) using chemical bath deposition technique. In our previous work, we reported that Zn doping can improve the structural and optical properties of pure CdS witch refered in refrence no.[7]

The growth, structural, optical, electrical and morphological properties of these films in relation to composition 'x' are reported and discussed. Also discussed the relation between energy band gap(eV) and composition parameter(X). And discussed relation in between Grain size and composition.

2. Experimental details

$Cd_{(1-x)}Zn_xS$ ($0 \leq x \leq 1$) thin films were deposited on glass substrates with different Zn concentrations (for x = 0, 0.2, 0.4, 0.6, 0.8 and 1) using chemical chemical bath deposition technique. Here x represents the Zn parameters in the bath solution as also in the films. Aqueous solutions used as sources for Cd^{2+}, Zn^{2+} and S^{2-}, as $Cd(CH_3COO)_2\ 2H_2O$, $Zn(CH_3COO)_2\ 2H_2O$ and $CS(NH_2)_2$ are used respectively. The entire chemical used in the present study and reagent used were of analytical reagent grade. Substrate cleaning plays an vital role in the fabrication of thin films. Substrate cleaning and preparation of $Cd_{(1-x)}Zn_xS$ thin films. One of the film preparing (x=1) which is ZnS we prepare (10ml) $Znso_4$ + (4ml)TEA(tri either ammain) in a glass beaker and sterred well for 2min. And (10ml) Thaoria+(10ml) NH_3 + (4ml)NaOH all solution mixed in a beaker and add the deionized water to fill the beaker up to 150ml. Therefore, the glass slides were rinsed with washing powder and again rinsed in acetone before the deposition of the films. The cleaned substrate was kept dipped in deionized water before use. The well-cleaned glass substrates were slowly diped into the bath vertically after obtaining the homogeneous solution. The desired pH value, 9 to 11 was achieved by the addition of aqueous ammonia solution proportionally into the mixture in the chemical bath. The temperature of the mixed solution was maintained at 75^0C using a constant temperature under continuous stirring. The films were prepared under continuous stirring for 1 h. The deposited films were cleaned several times with de-ionized water. After that film was drying in sun and air.

3. Result and discussion

3.1 Structural analysis

Structural study $Cd_{(1-x)}Zn_xS$ ($0 \leq x \leq 1$) thin films were deposited by the chemical bath deposition technique. XRD study reveals that the film is crystalline with cubic and hexagonal structure. It is observed that grain size increasing with increasing Zn in composition x up to(x = 0.0 to 0.4) further it decreases with decreasing Cd upto (x= 1) as shown in the graph fig.1 and its corresponding peak value.

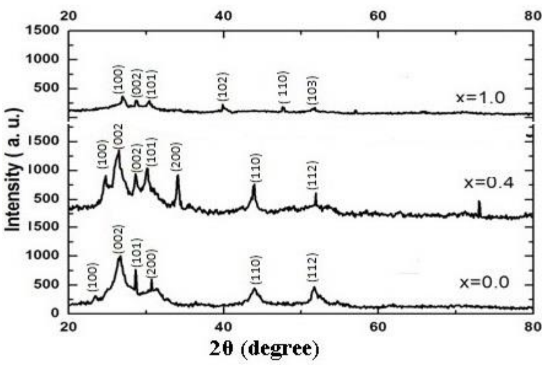


Fig. 1 XRD Spectra of Cd(1-x)ZnxS Synthesized for ($0 \leq x \leq 1$)

The XRD pattern of the $Cd_{(1-x)}Zn_xS$ ($0 \leq x \leq 1$) as shown in fig.1 diffraction indicate presence of prominent peak (100), (002), (101), (200), (110) and (112) plane of x=0.0 (CdS) material show cubic and hexagonal in structure. The intensity of (002) peak increased with increasing Zn at (x=0.0 to 0.4) and peak (100), (002), (110), (102), (110) and (103) plane of x=1.0 (ZnS) material show that hexagonal in structure. The intensity of (100) peak decreased with decreasing cd at (x=0.6 to 1). The standard crystallographic data for CdS and ZnS were taken from JCPDS card no. 80-0006 and 36-1450 respectively which is a good agreement.

Composition 'x'	Material	lattice constant (A°)		average grain size(nm)	band gap
	$Cd_{1-x}Zn_xS$	a	c	D (nm)	
X= 0.0	CdS	4.17	6.80	20	2.45
X= 0.4	$Cd_{0.6}Zn_{0.4}S$	4.11	6.71	29	2.75
X= 1	ZnS	3.80	6.20	18	3.50

Table no. (1) Structural parameters of $Cd_{1-x}Zn_xS$ thin films.

Table.1 shows the lattice parameters a and c for hexagonal (Eq. (1)) and cubic (Eq. (2)) calculating using the following equation [11-13]. Lattice parameter is calculated CdS for (X=0.0, 0.4) and ZnS for (X= 1.0) value from each XRD because of to determining synonyms content of ZnS and CdS.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) \tag{2}$$

Where d is interplanar distance, a and c are lattice constants, and h, k, and l are the Miller indices of the plane.

The grain size 'D' of the samples was obtained by using 'Scherrer's formula [14, 15].

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{3}$$

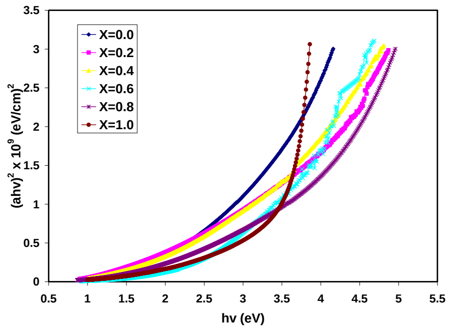
Where λ is the wave length of X-ray used (1.54 nm C_uK_α line), β is the broadening of the diffraction peak measured at half of its greatest intensity (FWHM) and θ is the Braggs angle. The calculated grain size is as shown in fig.1

3.2 optical analysis

The optical analysis of the $Cd_{(1-x)}Zn_xS$ thin films for ($0 \leq x \leq 1$). The optical studies exposed that the films were the direct type of transition thin film are highly absorptive, which anxiety the optical band gap to be determined using the following relationship

$$\alpha = \frac{A}{h\nu}(h\nu - Eg)^{\frac{1}{2}} \qquad (4)$$

where ‘A’ is a constant and ‘hν’ is [11,12] the radiation energy. The experimentally observed values of $(\alpha hm)^2$ plotted against hm is shown in Fig.(2) for a different composition.



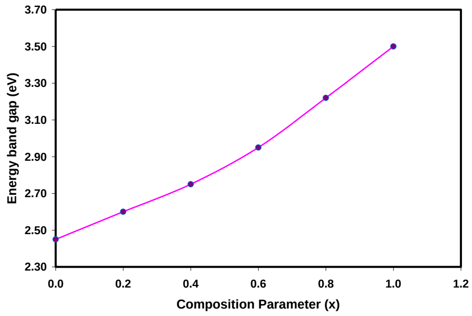


Fig. No. (2) shows that graph $(ah\nu)^2$ versus hν.
Fig. No.(3) shows the graphical representation of energy band gap eV with composition(x)

Estimated values of the energy gap were 2.45, 3.75 and 3.50 ev for samples $Cd_{(1-x)}Zn_xS$ (for x = 0, 0.4, and 1) respectively. Energy Band gap of the $Cd_{1-x}Zn_xS$ compound increased upon increasing the Zn content as shown in fig.(2). The optical band gap is diverse from 2.45 to 3.50 eV. The band gap varies with varies of the composition of x is shown in fig. (3). It represents the non-linear variation of optical band gap Eg of CdZnS over the range of composition ‘x’. It is show that amount of Zn in $Cd_{1-x}Zn_xS$ thin film greatly affects the optical band gap of CdS thin film. The nature of this variation in the band gap, energy may be useful to design a suitable window material in the fabrication of solar cells.

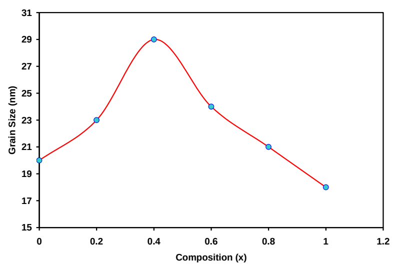


Fig. No. (4) shows graph of grain size and composition (x)

3.3 Electrical properties

The electrical conductivity of $Cd_{(1-x)}Zn_xS$ ($0 \le x \le 1$) thin films was estimated in temperature run 300– 400K utilizing Keithley DC two-point test set up in a vacuum. The variation of log(σ) with proportional temperature (1000/T) is appeared in Fig.(4) it was observed that the conductivity of $Cd_{(1-x)}Zn_xS$ ($0 \le x \le 1$) thin films result indicates that the conductivity decreases with increasing Zn content and increases with temperature. An attempt has also been made to obtain activation energy of these films which increases with increasing Zn content in CdS. This increase in electrical conductivity can be credited to increasing in grain size. The room temperature electrical conductivity of CdS and ZnS are 5.65 x 10^{-5}. and 7.28 x 10^{-5} $(\Omega\ cm)^{-1}$ respectively. The DC conductivity of a semiconductor at temperature T is given by the Arrhenius relation.

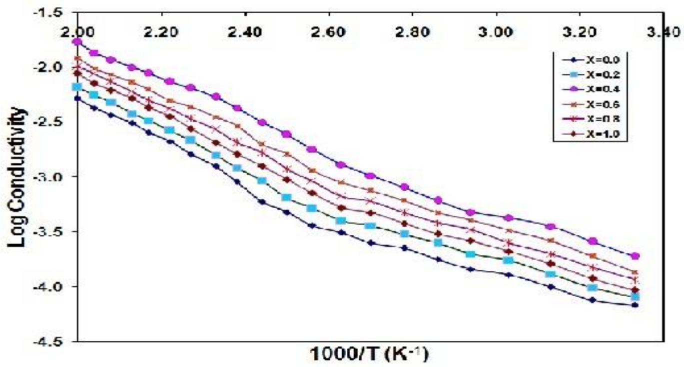


Fig.(4) shows that log(σ) vs $1000/T(k^{-1})$

3.4 Morphological properties

As taken $Cd_{1-x}Zn_xS$				As observed $Cd_{1-x}Zn_xS$		
x	**Cd**	**Zn**	**S**	**Cd**	**Zn**	**S**
0.0	**50**	**0.0**	**50**	**64.17**	**0.0**	**35.83**
0.4	**30**	**20**	**50**	**42.18**	**8.58**	**49.24**
1.0	**0.0**	**50**	**50**	**0.0**	**96.7**	**3.93**

Table no. 2) Elemental analysis of Edax

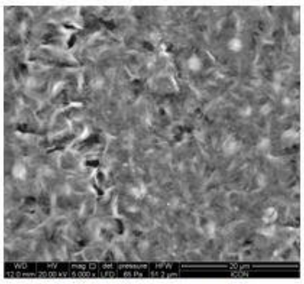


Fig.(5) SEM imege of CdS thin film

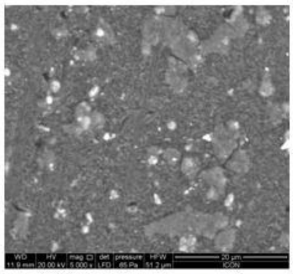


Fig.(6) SEM imege of $Cd_{0.6}Zn_{0.4}S$ thin film

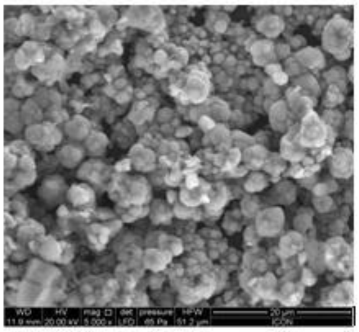


Fig. (7) SEM imege of ZnS thin film.

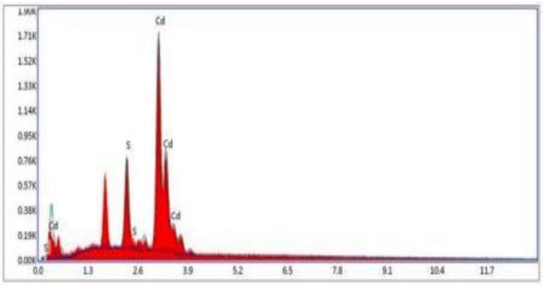


fig. 8 A . Edax of CdS thin film

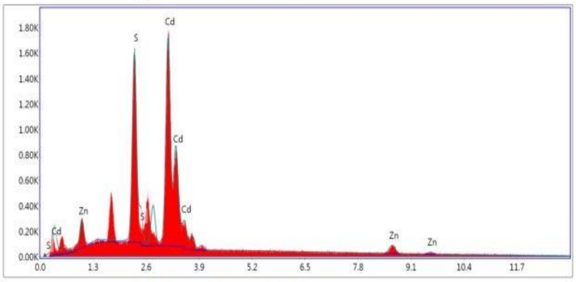


fig. 8 B. Edax of $Cd_{0.6}Zn_{0.4}S$ thin film

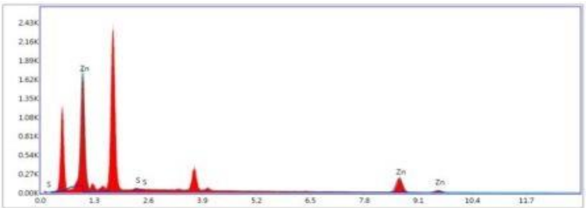


fig. 8C. Edax of ZnS thin film

Fig.(6) $Cd_{0.6}Zn_{0.4}S$ is consistently covering the substrate with no obvious pinholes giving better stage to development of CdS and ZnS layer. In Fig (7) the films appear to be smooth, opaque and uniform without any pinholes or splits. For the ZnS film the surface appears to be composed of tightly packed grains unified with each other and surface appears smooth with fully covered nano sized grains of unequal sizes. Fig. (5) shows the surface is smooth and tightly bounded with just like algae. Table no.2) Shows elemental analysis of Edax images of Fig 8 A, B, C.

4. Conclusion

$Cd_{(1-x)}Zn_xS$ ($0 \leq x \leq 1$) thin films have been prepared by the chemical Bath deposition technique. XRD studies showed that the films are crystalline with cubic and hexagonal structure. It is observed that grain size increases with increased Zn in (0.0-0.4) further it decreasing with decreasing Cd in (0.6-1). the band gap of the thin films varied from 2.45 to 3.50 eV as composition varied from x = 0.0–1.0. It was observed that changes of little amount of Zn results in noticeable changes in the optical band gap of CdS .In the entire compositions, (002) peak increased with increasing Zn up to (x=0.0 to 0.4) and further (100) peak decreased with decreasing cd up to (x= 0.6 to 1) the (002) and (100) diffraction peak was well-known which gives lattice matching to the chalcogenide semiconductor such as $CuIn_xGa_{1-x}Se_2$ and $CuIn(S_{1-x}Se_x)_2$, which are used in photo-voltaic devices [16-19]. The optical band gap varies from 2.45 to 3.50 eV. The electrical conductivity of the deposited films has been demonstrated that every one of the film have progressed from phonon-assisted hopping conduction through the impurity influence band to grain limit restricted conduction in the conduction/valence band.

References:

[1] Perry, S., Klemeš, J., & Bulatov, I. (2008). Integrating waste and renewable energy to reduce the carbon footprint of locally integrated energy sectors. Energy, 33(10), 1489-1497. doi:10.1016/j.energy.2008.03.008.

[2] Hegedus, S. (2006). Thin film solar modules: the low cost, high throughput and versatile alternative to Si wafers. Progress in Photovoltaics: Research and Applications, 14(5), 393-411. doi:10.1002/pip.704.

[3] Gupta, A., & Compaan, A. D. (2004). All-sputtered 14% CdS⁄CdTe thin-film solar cell with ZnO:Al transparent conducting oxide. Applied Physics Letters, 85(4), 684-686. doi:10.1063/1.1775289.

[4] Nouhi, A., Stirn, R. J., Meyers, P. V., & Liu, C. H. (1989). High-efficiency CdTe thin-film solar cells using metalorganic chemical vapor deposition techniques. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 7(3), 833-836. doi:10.1116/1.575850.

[5] Mangalhara, J., Thangaraj, R., & Agnihotri, O. (1989). Structural, optical and photoluminescence properties of electron beam evaporated CdSe1−xTex films. Solar Energy Materials, 19(3-5), 157-165. doi:10.1016/0165-1633(89)90002-6

[6] Pawar, S,M., B.S. Pawar, J.H. Kim, Oh-Shim Joo,Lokhande, C.D. 2011. Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films. Current Applied Physics. 11 : 117-161

[7] Dhananjay Mugle, M.A. Barote, L. S. Ravangave and Ghanshyam jadhav. 2017. Study on the Structural and Optical Properties of Chemically Deposited Cd(1-x)ZnxS thin Films Using Chemical Bath Deposition Technique. Clay Research, Vol. 36, No. 1, pp. 28-32.

[8] https://en.wikipedia.org/wiki/II-VI_semiconductor_compound.

[9] Jubory, A. A. 2012. Study on the effect of copper doping on the structural and optical properties of Cd0.7Zn0.3S Nanocrystalline thin films prepeared by chemical bath deposition. International Journal of Scince and Technology. 2 : 707-712.

[10] Selvan, G., Abubacker, M., & Balu, A. (2016). Structural, optical and electrical properties of Cl-doped ternary CdZnS thin films towards optoelectronic applications. Optik - International Journal for Light and Electron Optics, 127(12), 4943-4947. doi:10.1016/j.ijleo.2016.02.047.

[11] Aziz, S., Rezagholipour, H., Dizaji, and Ehasani, M.H. 2016. Structural and optical properties of Cd1-xZnxS (x=0, 0.4, 0.8, 1) thin film prepered using the precursor obtained from microwave irradiation process. Optik. 127: 7104-7114.

[12] Ravangave, L. S., Brajdar, U. V. and Misal, S. D. 2012. The effect of ionic composition on structural and optical properties of CdxZn1xS thin film growth by spry pyrolesys method. International Jouranal of Scintific Reserch Journal. 10 : 193-198..

[13] Raviprakash, Y., Kasturi, V., Bangara, V. and Shivkumar, G. K. 2010. Growth structural and optical properties of CdxZn1-xS thin film grown by spry pyrolysis technique. Current Applied Physics. 10 : 193-198.

[14] F. Lisco, P.M. Kaminski, A. Abbas, K. Bass, J.W. Bowers, G. Claudio, M. Losurdo, J.M.Walls, The structural properties of CdS deposited by chemical bath deposition and pulsed direct current magnetron sputtering, *Thin Solid Films*, 582 (2015) 323–327.

[15] M. A. barote, A. A. yadav, L. P. deshmukh, E. U. Masumdar, Synthesis and characterization of chemically deposited $Cd_{1-x}Pb_xS$ thin film, *Journal of Non-Oxide Glasses*, Vol. 2, No 3, 2010, p. 151-165.

[16] M. Bouroushian, Z. Loizos, N.Spyrellis, G. Maurin, *Appl. Surf. Sci*, 115 (1997) 103.

[17] G. Laukaitish, S. Lindroos, S. Tamulevicius, M. Leskela, M. Rackaitis, SILAR deposition of Cd_xZn_{1-x} S thin films, *Appl. Surf. Sci*, 161 (2000) 396–405

[18] M. Abdel Rafea, A.A.M. Farag, N. Roushdy,"Structural and optical characteristics of nano-sized structure of $Zn_{0.5}Cd_{0.5}S$ thin films prepared by dip-coating metho, *J. Alloys Compd*, 485 (2009) 660–666 Z. Sedaghat, N.Tagavinia, M. Marandi, *Nanotechnology*, 17 (2006) 3812.

[19] M. A. barote, A. A. Yadav, R. V. Suryawanshi, E. U. Masumdar, Effect of Pb Incorporation on energy band gap of CdS thin film, *Journal of Ovonic Research*, Vol. 7, No. 3, May - June 2011, p. 45 – 50.