The Effect of Ionic Composition on Structural and Optical Properties of CdxZn1-xS Thin films Grown by Spray pyrolysis

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Abstract- In this work we prepared cadmium zinc sulphide ($Cd_xZn_{1-x}S$) thin films on glass substrate using spray pyrolysis chemical deposition technique. The effect of Cd composition on structural and optical was studied. The XRD pattern of $Cd_xZn_{1-x}S$ films shows hexagonal wartzite symmetry of CdZnS material. The XRD data confirmed that the crystallites were increased with composition of Cd^{2+} content. The intensity of (002) peak is increased for x= 0.6 and 0.8. The variation of grain size with composition was investigated from XRD data. The optical energy band gap obtained from data of the absorption spectra confirmed that the band gap is increased with Zn content in $Cd_xZn_{1-x}S$ thin films. The transmittance spectra reaveled the % transmittance was increased with increase of Zn content in $Cd_xZn_{1-x}S$ thin films.

Keywords: - Spray Pyrolysis, $Cd_xZn_{1-x}S$ thin film, Optical energy Band gap, Solar cells.

I. Introduction

CdS thin film absorbs the light energy in the blue region of the solar spectrum and have smaller optical band gap of 2.42 eV (1). For high performance of solar cell devices an appropriate window material should be necessary. CdZnS has larger band gap and convenient to made as window layer instead of CdS. The $Cd_xZn_{1-x}S$ films would advantages for application in solar cell because they also offer a wider band gap (larger than 2.5 eV) as compared to the CdS films (2). There have been many report on the deposition of CdZnS thin films with different concentration of Zn^{+2} using different methods of depositions (3,4,5). It is of great technological interest that the cadmium zinc sulphide (CdZnS) thin film have been widely used as a wide band gap window material in hetrojunction solar cells and in photoconductive devices. The synthesis and characterization of nanoparticle thin films of cadmium and zinc chalcogenides have became an area of great interest over last few years. The thin films of CdZnS have extensive applications in various optical, electronic and optoelectronic devices and especially in wide band gap photovoltaic solar cells with different polycrystalline absorber materials like CdTe (6),.

Keeping in view, more attention is being made in fabricating good quality $Cd_xZn_{1-x}S$ thin films and study the structural and optical properties of the prepared thin films.

A number of thin film deposition techniques are used for deposition of the thin films. Of the most spray pyrolysis is the practically attractive because of its simplicity in comparison with methods requiring vacuum conditions on complex equipments. It is fast, inexpensive vaccuumeless and suitable for mass production. It is basically a chemical deposition technique in which solutions of desired material are sprayed onto a preheated substrate. Continuous films are deposited onto substrate by thermal decomposition of reactants(7).

In the present investigations the spray pyrolysis technique was used for deposition of CdxZn1-xS thin films. Prepared CdxZn1-xS films are characterized with XRD, and UV-Visible spectroscopic technique for structural and optical study.

II. Materials and Methods

Aqueous solutions of CdCl2, $ZnCl_2$ and $(NH_2)_2CS$ were used as sources of cd^{2+}, Zn^{2+} and S^{2-} ions respectively. The entire chemical used in the present study and reagent used were of analytical reagent grade. For the preparation of good quality films concentration of $CdCl_2$ (0.1M), $ZnCl_2$ (0.05M) and (0.1M) NH2-CS-NH_2 were previously optimized and used as stock solutions. To obtain homogeneity of uniform deposition each solution was stirred for 5 minute before the film deposition. Deionised water was used as a solvent.

$Cd_xZn_{1-x}S$ films were deposited on ultrasonically precleaned microscopic glass substrates. With different Cd^{2+} concentrations (for x= 00, 0.2, 0.4, 0.6, 0.8, 1) using chemical spray pyrolysis technique. Here x represents the concentration in the spraying solution. The solution was spray at the rate of 1 ml per minute at optimized temperature of 573 ^{0}K, at 1 Kg/m^2 pressure. Prepared $Cd_xZn_{1-x}S$ films were characterized by XRD and UV Visible spectroscopic techniques. The structural and optical properties of the deposited films were studied using data obtained from XRD and UV-Visible technique.

III. Results and Discussion

i. Structural properties

The XRD spectra of prepared CdxZn1-xS thin films are recorded using Regacu Miniflex II diffractometer and displayed in Fig. 1 a to f. All the peaks assigned to (100), (002) , (101), (102) (110), (103), and (200) orientations of hexagonal phase of CdxZn1-xS The intensity of (002) of XRD patterns for composition x=0.6 and x=0.8 was significantly increased as compared to intensity of (002) peak for other compositions. Y. Raviprakash et al.(2009) were reported earlier the hexagonal plane symmetry of CdxZn1-xS for $CdCl_2$ and $ZnCl_2$ based CdxZn1-xS thin films (8). The observed diffraction patterns are in good agreement with the standard crystallographic data for the CdS and ZnS metals of JCPDS card 02-0549 and 80-0007. The (002) diffraction peak gives the 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 photovoltaic solar cells (9). The lattice constant a and c for hexagonal planes of the CdxZn1-xS thin films are calculated from XRD data using the following equation.

$$1/d^2 = 4/3\,(h^2+hk+k^2)/a^2 + l^2/c^2 \quad \ldots\ldots (1)$$

The values of lattice constant observed to vary as composition of cadimium(from x=0 to1). The variation of lattice parameters versus temperature is given in table 1, and displayed in fig. 2. The value of lattice constant 'a' and 'c' varies with composition from 0.377 to 0.4037 nm and 0.652 to 0.688 nm respectively. The increase in values of lattice parameters with composition of Cd confirmed the increase of uite cell size.
The grain size was calculated from XRD data using Sherrie's formula (10).

$$D=0.94\,\lambda/\beta\cos\theta \quad \text{----- (2)}$$

Where λ is the wave length of X-ray used (1.54 nm Cuk_α line), β is the broadening of the diffraction peak measured at half of its maximum intensity (FWHM) and θ is the Braggs angle. Table 1 shows the variation of grain size with Cd composition and presented in fig 3. It is observed that the grain size of the CdxZn1-xS increased with increase in Cd composition. The average grain size is observed increased from 3.4 to 14 nm.

ii. Optical Characterization

The optical absorption of the CdxZn1-xS films for x=0.0, .2, 0.4, 0.6, 0.8, and 1 were recorded using Systronic Ddouble beam UV-Visible spectrophotometer 2201 in the wavelength range 350 to 900 nm. The absorption spectra are presented in fig. 4. The spectra have been used to evaluate the absorption coefficient (α), energy band gap (E_g) and nature of transition involved. Optical energy band gap (E_g) can be calculated using absorption coefficient (11).

$$\alpha=\frac{A}{h\upsilon}(h\upsilon-Eg)^{1/2} \quad \text{-------------3}$$

A is constant, h**ν** is photon energy. Thickness of the CdS films was estimated by weight difference method using

$$t = m/\rho A \quad \text{---------------------} \quad (4)$$

Where m is the mass of the film deposited on the substrate, A is area of the deposited film on the substrate and ρ the density of the bulk material. The variation of film thickness with concentration was shown in Table 1.

The spectra shows that the absorption edges are blue shifted. Blue shifting of the absorption edge confirmed that the crystallites in the films decreased with composition of Zn. The experimental values of $(\alpha h\nu)^2$ plotted against hν for different composition is shown in Fig. 5. All the films show high absorption coefficient ($\alpha=10^{12}$ cm^{-1}). The linear portion of the curve extrapolated to $(\alpha h\nu)^2 = 0$ gives the value of optical energy band gap (E_g). The optical band gap E_g obtained at $(\alpha h\nu)^2 = 0$ was vary from 2.42 to 3.49 eV. (121). The 3.49 eV maximum energy band gap is observed Cd0.0Zn1.0S. The increase of band gap can prevent the window absorption losses. The variation of optical band gap with composition is shown in Table 1. and displayed in Fig.6.

The variation of % transmittance against wavelength for different composition x is presented in Fig. 7. It is observed that % transmittance increased with increase the Zn content in the CdxZn1-xS thin films. The % transmittance varied from 10 to 53 as x varies from 1 to 0.0.

IV. CONCLUSION

$Cd_xZn_{1-x}S$ thin film was successfully synthesized using aqueous solutions of $CdCl_2$, $ZnCl_2$ and $(NH_2)_2CS$ by spray pyrolysis technique. The XRD study revealed the hexagonal phase of the CdxZn1-xS thin films. The intensity of the (002) peak was improved for x=.06 and 0.8. The grain size is observed increased with Cd incorporation study confirmed that the CdZns compound has hexagonal phase. The (002) diffraction peak was dominant for $Cd_xZn_{1-x}S$ thin films gives the lattice matching to the Cu In_x $Ga_{1-x}Se_2$ and $CuIn(S_{1-x}\ Se_x)_2$ chalcogenised semiconductors which are used in photovoltaic solar cells. The change of lattice parameters was observed with Cd composition. Optical study confirmed that energy band gap of CdS, (direct band gap semiconductor), is increased with incorporation of Zn content. The % transmittance was observed increased with increase of Zn content of $Cd_xZn_{1-x}S$ thin films.

Table 1. The Lattice parameters, Grain size (XRD), Energy band gap, Film Thickness.

Composition x	**Lattice constants** a nm	c nm	**Grain size** nm	**Band gap** eV	**Thickness** μm
0.0	0.377	0.651	3.4	3.49	1.33
0.2	0.376	0.654	4.6	3.35	1.56
0.4	0.389	0.662	5.12	3.3	1.574
0.6	0.401	0.647	7.0	2.72	1.89
0.8	0.403	0.686	8.8	2.5	1.87
1.0	0.403	0.688	14	2.42	1.96

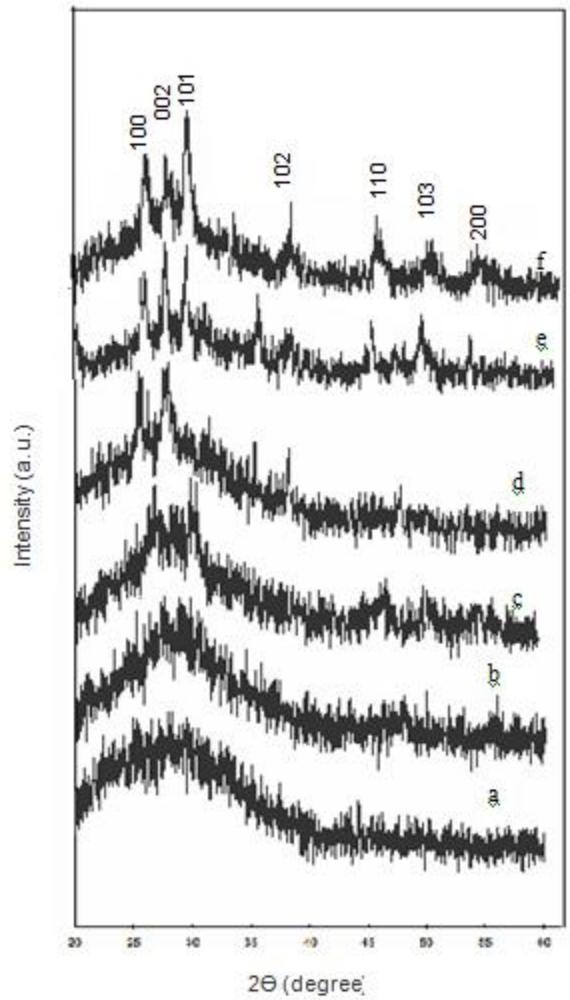

Fig. 1: XRD spectra of $Cd_xZn_{1-x}S$ for (a) x=00, (b) x=0.2, (c) x=0.4 (d) x=0.6, (e0 x=0.8 and (f) x=1

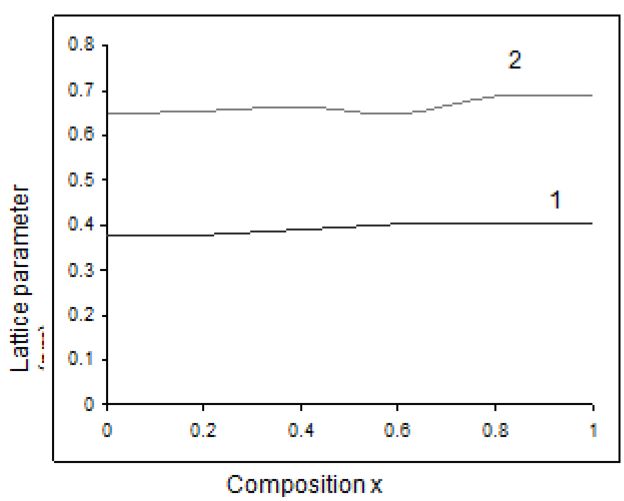

Fig. 2: The varation of lattice parameters with composition x 1. Lattice constant 'a', 2 lattice constant 'c'.

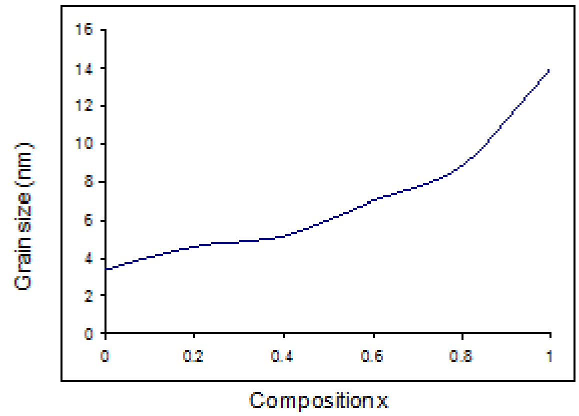

Fig. 3: Variation of grain size with composition of CdxZn1-xS

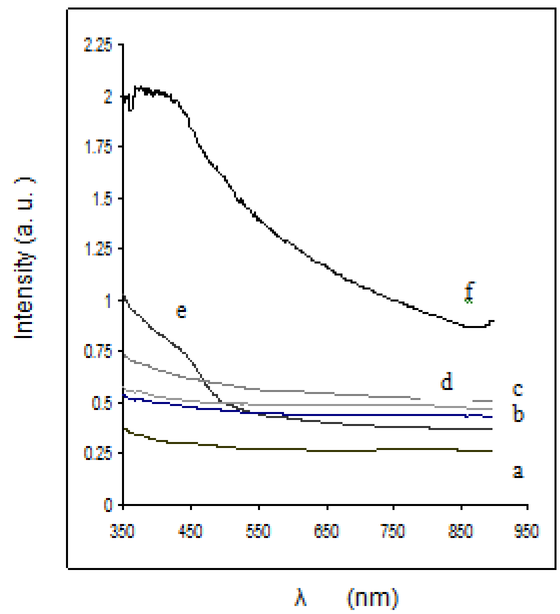

Fig.4: The absorption spectra of $Cd_x Zn_{1-x} S$ for (a) x=1.0, (b) x=0.8 (c) x=0.6 (d) x=0.4 (e) x=0.2 (f) x=0.0

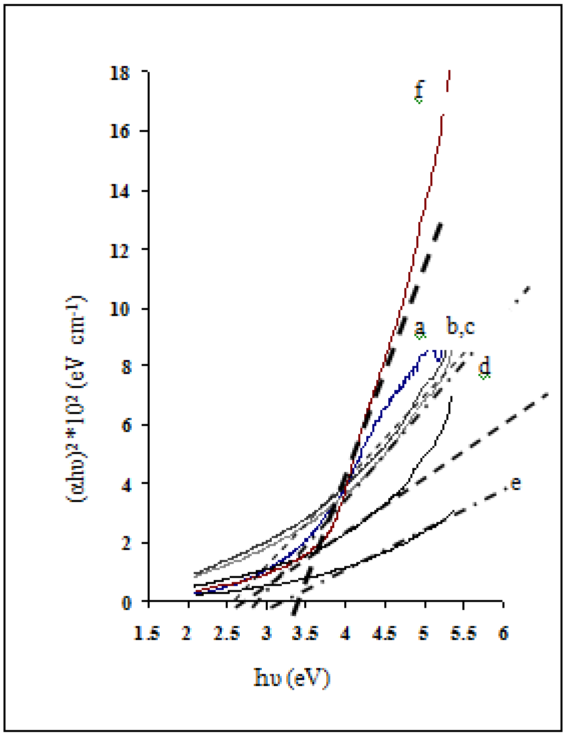

Fig.5: The plot of (αhυ)^2 versus hυ of CdxZn1-xS films with (a) x=1, (b) x=0.8 (c) x=0.6 (d) X=0.4 (e) x=0.2 (f) x=00

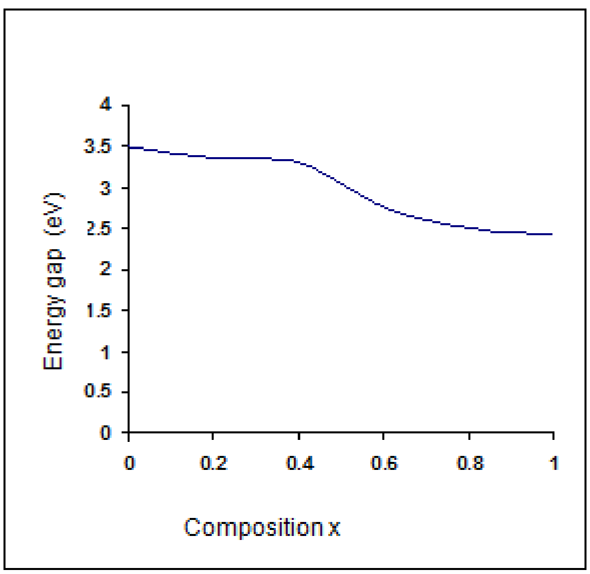

Fig. 6: Dependence of optical band gap of Cdx Zn1-x Sfilms on composition parameter x.

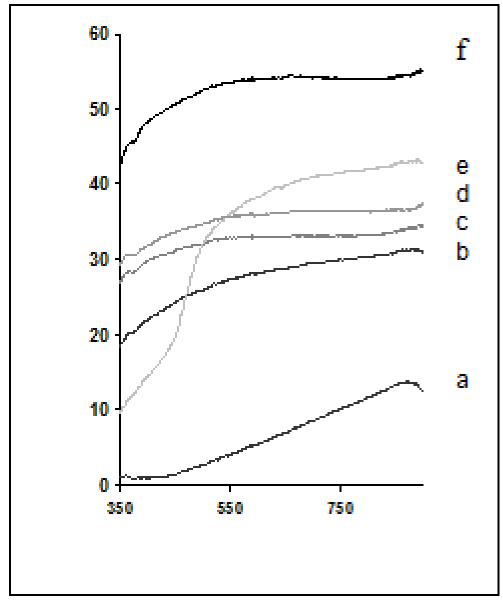

Fig.7: % transmittance is plotted against wavelength for $Cd_x\ Zn_{1-x}$ S for (a) x=1.0, (b) x=0.0.8 (c) x=0.6 (d) x=0.4 (e) x=0.2 (f) x=0.0

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