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X-Ray Diffraction Studies of Undoped and in-Doped $Cd_{0.22}Zn_{0.78}S$ Films Deposited by Spray Pyrolysis

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Abstract

$Cd_{0.22}Zn_{0.78}S$ and In-doped $Cd_{0.22}Zn_{0.78}S$ films have been produced by the spray pyrolysis method at 275±5°C substrate temperature. This work describes the X-ray diffraction spectra of all films at room temperature. X-ray diffraction spectra of the films showed that they are hexagonal and formed as $Cd_{0.22}Zn_{0.78}S$ polycrystalline structure. Film thickness, texture coefficient (TC), grain size values, lattice constants, and d% error were calculated. Effects of Indium incorporation on these properties deposited films have been systematically investigated.

Key Words: Cadmium Zinc Sulfide, Indium Doping, Spray Pyrolysis, X-Ray Diffraction Spectra, Texture Coefficient, Grain Size.

1. INTRODUCTION

$Cd_xZn_{1-x}S$ films are of considerable interest for a variety of solar cell systems in which CdS films have been demonstrated to be effective as the large band gap window material of a heterojunction (Chynoweth and Bube, 1980). $Cd_xZn_{1-x}S$ compounds are promising materials for a variety of optoelectronic device applications, such as electroluminescent, photoluminescent and photoconductor devices and especially in photovoltaic cells with different polycrystalline absorber materials for example Cu_xS, $CuInSe_2$, CdTe and $CuGaSe_2$ (Dona and Herrero, 1995).

In-doped $Cd_xZn_{1-x}S$ films have been prepared by a variety of methods such as spray pyrolysis (Chynoweth and Bube, 1980; Uplane et al., 1996), ion beam deposition

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(Kuroyanagi, 1994), chemical spray process (Agnihotri and Gupta, 1979), solution growth (Padam et al., 1988) and chemically deposited (Lee et al., 2002; Lee et al., 2003). Among these methods, spray pyrolysis provides an easy route to fabricate films at low cost. It is also easy with this method to dope the films and to produce large area coatings. Spray pyrolysis is basically a chemical deposition technique in which fine droplets of the desired material solution are sprayed onto a heated substrate.

Undoped $Cd_{0.22}Zn_{0.78}S$ films obtained by spray pyrolysis method have also been reported (Ilican and Zor, 2003). In the present work, the effects of the Indium incorporation on the structural properties of $Cd_{0.22}Zn_{0.78}S$ films deposited by spray pyrolysis method were reported.

2. MATERIALS AND METHODS

Undoped and In-doped $Cd_{0.22}Zn_{0.78}S$ films have been deposited onto the Objekttrager pyrex glass substrates (1x11x26mm^3 and 1x11x6mm^3). The films were deposited by taking equimolar (0.05M) aqueous solutions of $CdCl_2.H_2O$, $ZnCl_2$ and $(NH_2)_2CS$ in a appropriate volume to obtain the [Cd]:[Zn] ratio 1:1 and [CdZn]:[S] 1:1. The required volume of $InCl_3$ (0.01M) solution is added to the final mixture in order to get the proper doping concentration. The starting solution was mixed thoroughly and final solution was sprayed. Aqueous solution of [CdZnS]:[In] ratio, which are 100:1, 100:2.5 and 100:5 of 0.2 at.% (atomic ratio), 0.5 at.% and 1 at.% In-doped $Cd_{0.22}Zn_{0.78}S$ films, respectively.

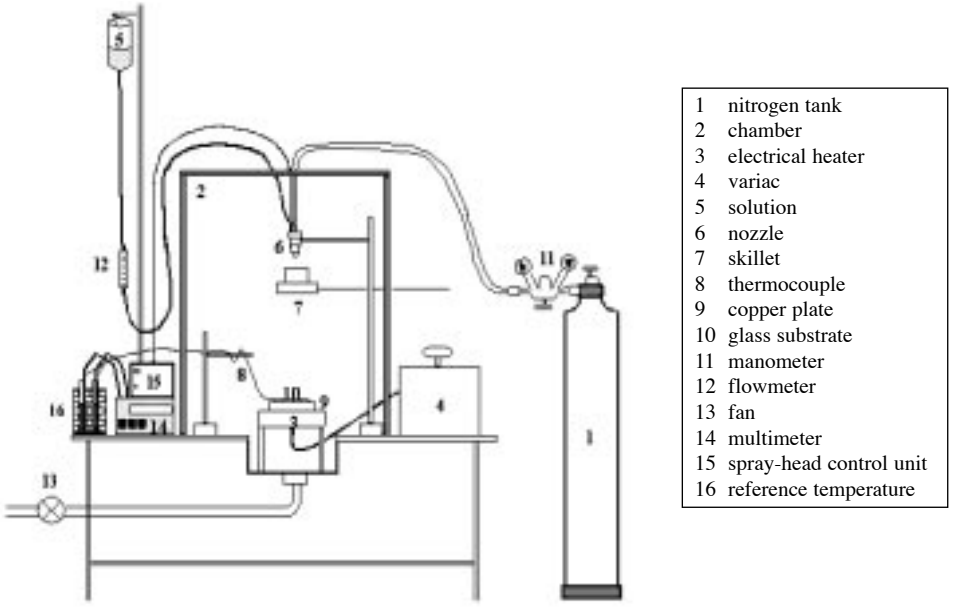

Figure 1. Schematic of The Spray Pyrolysis System Used for all The Films.

The schematic diagram of the spray pyrolysis apparatus used in this work is shown in Figure 1. The flow-rate of the solution during spraying was adjusted to be about 3.5mlmin^{-1} and kept constant throughout the experiment. Nitrogen was used as the carrier gas. The nozzle was kept vertically above the substrate plate at a distance of 28cm. The deposition time is 45 minutes for all the films. Substrate temperature was controlled by means of Iron-Constantan thermocouple and maintained at 275±5°C substrate temperature. After depositing the film, it was allowed to cool to room temperature. The adhesion of the films onto the substrates was quite good. In-doped $Cd_{0.22}Zn_{0.78}S$ films exhibited yellow colour with a slight greyish tinge. The colour of the films observed to changed from yellow to greyish yellow as Indium content was increased.

The structural properties of all the films were studied by RIGAKU RINT 2000 Series X-Ray Automatic Diffractometer using Cu:K_α radiations (λK_α=1.5405Å). The scanning angle 2θ was varied in the range of 20°-60° in steps of 2°min^{-1} for all the films.

The thicknesses of the films were measured using the weighing-method.

3. RESULTS AND DISCUSSION

In the present work all of the parameters, which are substrate temperature, deposition time, and flow-rate of the solution are kept constant and films were prepared with various Indium concentrations. The variation of film thickness with Indium concentration is given in Table 1. Weighing-method was employed for film thickness measurement using the following relation:

$$t = \frac{\Delta m}{\rho A} \qquad (1)$$

where ρ is the bulk density of material of film deposited on area A and Δm the mass of the film deposited. It is interesting to note that thickness of In-doped film increases with Indium content. This variation of thickness with doping concentration has been also reported (Uplane et al., 1996).

Table 1. The Variation of Film Thickness and Grain Size with Indium Concentration.

	$Cd_{0.22}Zn_{0.78}S$ Undoped	**$Cd_{0.22}Zn_{0.78}S$ 0.2 at.% In-Doped**	**$Cd_{0.22}Zn_{0.78}S$ 0.5 at.% In-Doped**	**$Cd_{0.22}Zn_{0.78}S$ 1 at.% In-Doped**
Thickness (μm)	7.21	2.88	3.21	3.46
Grain Size (nm) for (100)	56.50	12.92	12.53	11.34
Grain Size (nm) for (101)	90.00	10.60	54.00	14.30

X-ray diffraction spectra of the undoped, and 0.2 at.%, 0.5 at.% and 1 at.% In-doped $Cd_{0.22}Zn_{0.78}S$ films have been given in Figure 2. X-ray diffraction spectra of all the films were taken at room temperature and found to show almost similar behaviour. The peaks with

the Miller indices given belong to the $Cd_{0.22}Zn_{0.78}S$ (JCPDS file reference number Card No: 351469) film in hexagonal form.

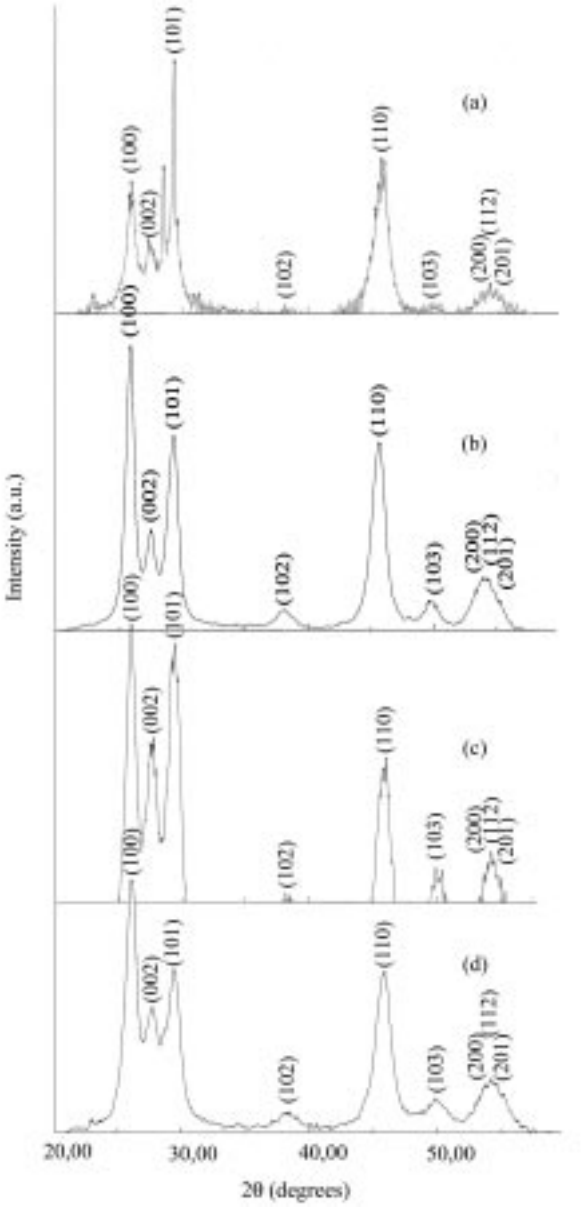

Figure 2. X-Ray Diffraction Spectra of (a)Undoped, (b) 0.2 at. % In-Doped, (c) 0.5 at.% In-Doped, and (d) 1 at.% In-Doped $Cd_{0.22}Zn_{0.78}S$ Films.

The presence of sharp structural peaks in these X-ray diffraction patterns confirmed the polycrystalline nature of the films. As shown in Figure 2.a, undoped film has (101) as the preferred orientation. This result is in good agreement with literature data (Kumar et al., 1998; Ray et al., 1998). Another major orientation present is (110), while other orientations like (100), (002) and (112), are also seen with comparatively lower intensities.

From X-ray diffraction spectra of indium doped films (Figure 2.b-d.) it is clear that all the doped films have (100) as the preferred orientation. Secondary peaks present are (101), (110), (002), (112), (103) and (102). Indium incorporation in to the compounds caused reorientation which exhibited itself as (100) preferred orientation, whereas (101) peak intensities observed to be decreased. This result is in good agreement with those reported for thin films prepared by the spray pyrolysis method (Krunks and Mellikov, 1995; Oktik et al., 1996; Riad et al., 2001; Tiburcio-Silver, 1998; Van Heerden and Swanepoel, 1997).

The experimental d-values and JCPDS (Joint Committee on Powder Diffraction Standarts) d-values are in relatively good agreement and show hexagonal structure (JCPDS file reference number Card No: 351469).

No phases related to Indium have been observed in the In-doped films.

The relative percentage error for the observed and JPCDS standart d-values for all the films are calculated using the formula (Padiyan and Marikani, 2002)

$$\text{Relative percentage error } \frac{|ZH - Z|}{Z} \times 100 \qquad (2)$$

where Z_H represents the actual d value obtained and Z is the standart d value in JCPDS card file. For all the films 2θ, d-Values, and d% error data calculated by using equation (2) are given in Table 2. The average relative percentage error is found to be 1.17%, 1.01%, 0.69%, and 0.92% for the undoped, and 0.2 at.%, 0.5 at.% and 1 at.% In-doped $Cd_{0.22}Zn_{0.78}S$ films respectively.

The lattice constants for hexagonal $Cd_{0.22}Zn_{0.78}S$ film are reported in JCPDS standart data a=3.9216Å and c=6.4050Å (JCPDS file reference number Card No: 351469). The analytical method (Cullity and Stock, 2001) for calculating lattice constants is used to calculate a and c for all the films, where it was found that for Undoped $Cd_{0.22}Zn_{0.78}S$ film a=3.9509Å and c=6.6189Å, 0.2 at.% $Cd_{0.22}Zn_{0.78}S$ film a=3.9689Å and c=6.5501Å, 0.5 at.% $Cd_{0.22}Zn_{0.78}S$ film a=3.9331Å and c=6.5643Å, and 1 at.% $Cd_{0.22}Zn_{0.78}S$ film a=3.9539Å and c=6.7341Å. These calculated values are aggrement with JCPDS data.

Table 2. All The Films 2θ, d-Values and Calculated d% Error.

$Cd_{0.22}Zn_{0.78}S$ Undoped In-Doped			**$Cd_{0.22}Zn_{0.78}S$ 0.2 at.% In-Doped**			**$Cd_{0.22}Zn_{0.78}S$ 0.5 at.% In-Doped**			**$Cd_{0.22}Zn_{0.78}S$ 1 at.% In-Doped**		
2θ	**d(Å)**	**d% error**	**2θ**	**d(Å)**	**d% error**	**2θ**	**d(Å)**	**d% error**	**2θ**	**d(Å)**	**d% error**
26.020	3.4216	0.75	25.900	3.4372	1.21	26.140	3.4062	0.30	26.000	3.4242	0.83
27.400	3.2524	1.61	27.540	3.2361	1.10	27.920	3.1929	0.25	27.680	3.2201	0.60
29.360	3.0395	1.25	29.320	3.0436	1.39	29.520	3.0234	0.71	29.360	3.0395	1.25
			38.090	2.3606	1.31	38.176	2.3607	1.32	38.400	2.3422	0.52
45.680	1.9844	1.19	45.620	1.9869	1.32	46.020	1.9706	0.49	45.800	1.9795	0.94
			50.120	1.8186	0.29	49.840	1.8282	1.12	49.800	1.8295	1.19
			53.900	1.6996	0.04	53.968	1.6976	0.08	53.720	1.7049	0.35
54.220	1.6903	1.03	54.320	1.6874	0.86	54.603	1.6794	0.38	54.160	1.6921	1.14
			55.200	1.6629	1.27	55.000	1.6682	1.60	55.100	1.6654	1.43

Comparisions of the X-ray results of the films indicate that better crystallinity was observed for the undoped $Cd_{0.22}Zn_{0.78}S$ film. It can also be seen from Figure 2 that the crystallinity of $Cd_{0.22}Zn_{0.78}S$ films were deteriorated with Indium incorporation.

The grain size of crystallites was calculated using a well-known Scherrer's formula (Cullity and Stock, 2001):

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (3)$$

where D is the grain size of crystallite, λ (=1.5405Å) the wavelength of X-rays used, β the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction. The values of calculated grain size for all the films are given in Table 1.

The calculated grain sizes as a function of the Indium contents are plotted in Figure 3. In this Figure the calculated grain sizes are given for both (100) and (101) reflections. A rather high fluctuation is seen when (101) reflection considered. This is most probably due to the reorientation of the crystal structure. On the other hand, when (100) reflections are considered, a homogenous grain size has been obtained due to the Indium incorporation.

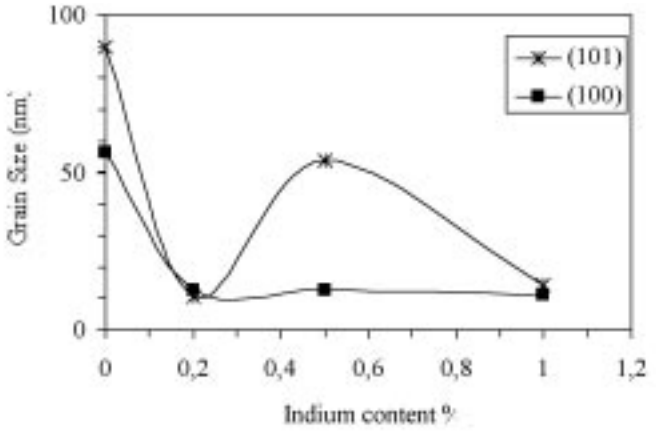

Figure 3. Variation of Grain Size with Indium Content in $Cd_{0.22}Zn_{0.78}S$ Films.

The texture coefficient (TC) represents the texture of the particular plane, deviation of which from unity implies the preferred growth. The different texture coefficient TC(hkl) have been calculated from the x-ray data using the well-known formula (Barret and Massalski, 1980)

$$TC(hkl) = \frac{I(hkl)/I_o(hkl)}{N^{-1}\sum_n I(hkl)/I_o(hkl)} \qquad (4)$$

where I(hkl) is the measured relative intensity of a plane (hkl), I_o(hkl) is the standard intensity of the plane (hkl) taken from the JCPDS data, N is the reflection number and n is the number of diffraction peaks. TC(hkl) values of all the films are presented in Table 3.

Table 3. Relative Intensity of The Peaks (I/I_o) and TC(hkl) Values of all Deposited Films.

	$Cd_{0.22}Zn_{0.78}S$ Undoped In-Doped		**$Cd_{0.22}Zn_{0.78}S$ 0.2 at.% In-Doped**		**$Cd_{0.22}Zn_{0.78}S$ 0.5 at.% In-Doped**		**$Cd_{0.22}Zn_{0.78}S$ 1 at.% In-Doped**	
(hkl)	**I/Io**	**TC(hkl)**	**I/Io**	**TC(hkl)**	**I/Io**	**TC(hkl)**	**I/Io**	**TC(hkl)**
(100)	52	1.028	100	2.728	100	2.174	100	2.500
(002)	29	0.573	35	0.955	64	1.391	50	1.250
(101)	100	1.976	68	1.855	94	2.043	66	1.650
(102)			7	0.191	13	0.283	8	0.200
(110)	61	1.206	66	1.800	56	1.217	64	1.600
(103)			8	0.218	21	0.457	14	0.350
(200)			18	0.491	26	0.565	20	0.500
(112)	11	0.217	18	0.491	23	0.500	22	0.550
(201)			10	0.273	17	0.369	16	0.400

The variation of texture coefficient for (101) and (100) planes with the Indium content is shown in Figure 4. It can be seen that the highest TC was in (101) plane for undoped $Cd_{0.22}Zn_{0.78}S$ film and in (100) plane for all the doped $Cd_{0.22}Zn_{0.78}S$ films. It is interesting to note that Indium incorporation causes an increase in TC(100) whereas TC(101) observed to be almost stabilized. This is also an indication for the (100) preferential orientation.

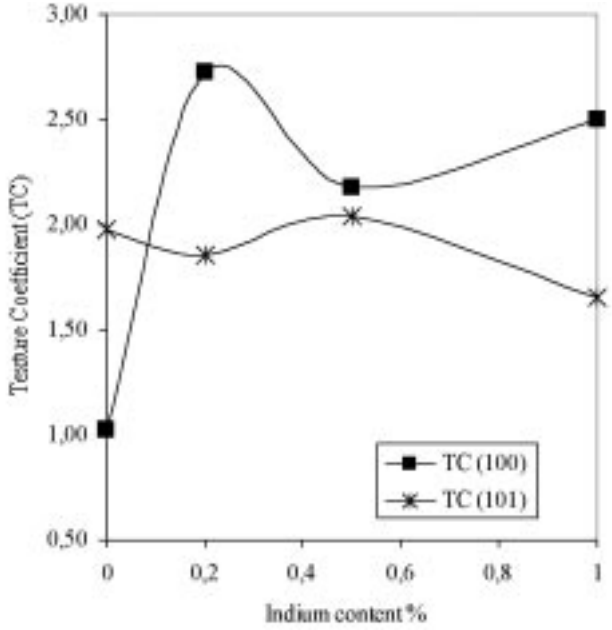

Figure 4. Variation of TC (100) and TC (101) with Indium Content in $Cd_{0.22}Zn_{0.78}S$ Films.

4. CONCLUSION

$Cd_{0.22}Zn_{0.78}S$ and In-doped $Cd_{0.22}Zn_{0.78}S$ films have been deposited by the spray pyrolysis method at 275±5°C substrate temperature. Although, Indium incorporation causes a noticeable decrease in the film thicknesses compared to the undoped one, a rather gradual increase in thickness is observed with Indium incorporation for the In-doped films. All the deposited films are polycrystalline in nature. No phases corresponding to indium oxide or to other indium compounds were detected. The crystalline nature of the films was deteriorated with Indium incorporation. Furthermore the preferential orientation of $Cd_{0.22}Zn_{0.78}S$ films also changed from (101) to (100), grain sizes decreased depending on the Indium incorporation. It was found that a drastic decrease in grain size with incorporation of Indium. Consequently, it was seen that Indium incorporation makes a significant change on the structural properties, which is grain size, preferential orientation and texture coefficient of deposited $Cd_{0.22}Zn_{0.78}S$ films. For all the films, calculated-values and lattice constants are in agreement with JCPDS data. Further work to understand the

effect of Indium incorporation on the optical and electrical properties of the undoped and doped $Cd_{0.22}Zn_{0.78}S$ films are in progress.

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