Aluminum Doped CdSe Thin Films: Structural Characterization

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ABSTRACT

Aluminum doped cadmium selenide tin films of different compositions, (0.1-1.0 mol %) deposited by dip coating method on cleaned glass substrates at room temperature. All the films are polycrystalline nature having hexagonal structure. For all the films the preferred orientation is (100). Some other orientations like (101), (110), (112) (202) (203) are also observed in the films. The values of interplanar distance, dislocation density, microstrain, lattice parameters, volume of unit cell, number of crystallites per unit area and particle size of the aluminum doped thin films were calculated and their variation with dopant concentration was studied. Interplanar distance, intensity, lattice parameters, volume of unit cell and particle size increases up to 0.25mol % of aluminum. Microstrain, dislocation density and number of crystallite per unit area decreases up to 0.25mol % aluminum concentration

KEYWORDS: *Thin films; X-ray diffraction; Chemical synthesis; Doping*

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I. Introduction

Numerous semiconducting films were synthesized for optoelectronic tools applications. Group II-VI composite, in wide-ranging and cadmium chalcogenides, particularly, have fascinated intense technical and scientific attention. CdSe is II-VI n-type semiconductor and is taken into consideration as an essential material for the advance of different optoelectronic devices [1-2]. It has direct inherent band energy of 1.74 eV that makes it an attractive material for different applications consists of light emitting diodes, solar devices, photodetectors, and other optoelectronic gadgets [3-6].

A proficient manner to decrease the resistivity and to get better properties of semiconducting substance is to dope with an appropriate impurity such as copper, silver, aluminum and indium. The dopant has revealed to improve properties in number of host crystal lattices. The electronic and optical properties of semiconductors are strongly influenced via the doping technique that provides the origin for tailoring the preferred carrier density and, therefore, the absorption, emission and transport characteristics as well. While the density of n-kind or p-kind doping becomes adequately high, the impurity combines with conduction and valence band and results in the development of band tail and band gap reduction [7-15]

Mahalingam et al [16] doped indium in the CdSe lattice. The optical study shows the presence of direct transition and a considerable decrease in band gap from 1.70 to 1.63 eV. Pawar et al [17] doped Fe in the CdSe. The efficiency and fill factor of photoelectrochemical cell is found to be improved from 0.34% and 31.12 to 1.80% and 35.78, respectively.

Optical and electrical characteristics of semiconducting films are necessary obligation for proper application in a variety of optoelectronic tools. These characteristic of such films are adequately structure responsive. Consequently, proper structural description of the films is essential. It can be well-known that the structural parameters which include crystal phase, crystallinity, grain size, lattice constant are strongly depending on the deposition situation. The structure of the films is possibly relies upon at the preparative parameters [18]. In our preceding

communiqué, we report the properties of CdSe thin films usage of trichloroacetic acid as complexing agent by dip coating technique [19]. An experimental study has been taking on in order to structurally describe chemically synthesized Al doped CdSe thin films and on this paper a few correlative effects of various structural parameters with quantity of Al dopant has been reported.

II. Experimental Detail

Cadmium sulphate octahydrate, trichloroacetic acid, aluminum trichloride, ammonia, selenium and sodium sulphite are used. Sodium selenosulphate (0.2 M) was applied as a selenium supply for synthesize of CdSe thin films. The solution was ready by refluxing 10 g selenium powder with 30 g sodium sulfite in 400mL double distilled water for 9 h at 363 K. The resultant solution became cooled, filtered to get rid of undissolved selenium and saved in the bottle.

In the synthesis of aluminum doped CdSe thin films, 10 mL of 0.2 M Cd^{+2} ions were taken in 100 mL beaker, and then it was complexed with trichloroacetic acid. 15 mL of 5N ammonia was added in the above reaction mixture. The varying concentration of aluminum from 0.01 to 1.0 mol% was used. Then 10 mL of 0.2 M sodium selenosulphate was added in the above reaction mixture. The resulting solution was diluted up to 75 mL with distilled water. The pH of the reaction mixture was found to be 10.21. The temperature of the reaction mixture was maintained at 278 K using an ice bath. Glass substrates were placed upright to some extent tilted in the reaction mixture. The temperature of the reaction mixture increases gradually to 298 K. After 4 hours, the glass substrates were detached and rinse with double-distilled water. The aluminum doped CdSe films was dried in the atmosphere.

III. Results and Discussion

3.1 Structural characterizations

Al doped CdSe films were characterized by using a Philips PW- 1710 diffractometer in 2θ range from 20^0 to 80^0. The chalcogenides of cadmium normally show the duality in their crystal structure. They can be formed with either cubic or hexagonal structure [20-21]. The X-ray diffraction (XRD) spectra of Al doped CdSe thin films deposited on glass substrate are shown in Fig. 1. The broad hump that is observed in the background of XRD is due to the amorphous glass substrate and as well probably because of a little amorphous phase there in the films. The spectra for pure CdSe (JCPDF card no. 19-191, JCPDS card no. 8-459) were used for identification purpose. The XRD pattern shows a large number of peaks indicating the polycrystalline character of the films. The examination of spectrum indicated that all the films have hexagonal structure in the whole range of compositions studied. The cubic phase of CdSe has not been observed. The analysis of XRD patterns in terms of h k l planes, two theta, intensity, interplanar distances, particle size, lattice parameters, volume, microstrain, dislocation density, number of crystallite per unit area have been done by considering hexagonal structure and is displayed in table 1 and table 2.

All films show (100) most intense peak. Along with (100) plane, (101), (110), (112) (202) (203) planes were observed. All the composition (except 0.01mol%) shows one peak around 2θ equal to 30^0 might be due to impurities of selenium was detected and can be indexed to hexagonal phase of selenium (JCPDS-73-0465). The peak intensity and crystallinity of the films were found to increase with aluminum doping concentration up to 0.25 mol%. For higher aluminum doping concentration, the thin films are likely to reduce crystallinity. Such performance could be explained on the basis of surface adsorption of aluminum ions over a growing film preventing further growth of the microcrystal. Thallium, silver, antimony, have obtained the alike kind of outcome on doping in host lattice [22-24]. From the position of different peaks and by the Bragg's condition,

$$n\lambda = 2d \sin\theta \text{--------} 1$$

d values for all the peaks was determined. All the aluminum doped films shows peak occur approximately at the same d value with a little modification. The interplanar distance increases gradually up to 0.25% mol aluminum concentration. The variation of d value of (100) plane against mol% is shown in Fig. 2. The constancy in the d value of prominent peaks shows that due to aluminum doping, the lattice of host material is neither shrinking nor expanding. Thus addition of aluminum ion does not alter the cell regularity. The lattice parameter was determined by using the formula [25];

$$(1/d^2) = (4/3)\,(h^2+k^2+hk/a^2) + (l^2/c^2) \text{--------} 2$$

The lattice constant a and c were determined for all the thin films. The values of lattice constant initially increase, reach a maximum at 0.25mol % aluminum and then show a decreasing trend. There is a change in lattice constants for the deposited thin films over the bulk values, which suggests that films grains are strained. This may

be due to change of nature and concentration of the native defects [26]. The change in lattice constant with mol% of dopant is shown in Fig. 3. The volume of the cell has been determined using equation

$$V = a^2c \text{------------} 3$$

As the lattice parameter increases up to 0.25mol% of aluminum, the volume also increases. The change in volume was very slight. The variation of volume with dopant concentration is represented in the Fig. 4. The crystallite size in the films has been considered applying Scherrer's method using full width at half maximum [27]

$$D = K\lambda / \beta\cos\theta \text{---------} 4$$

The particle size was determined for all the samples. The particle size of the films corresponding to (100) hexagonal reflection have been found to increases up to 0.25mol% of Al. But the variation is particle size within the dopant concentration is not very significant. With increase of dopant concentration the crystallinity of the films improves substantially. The particle size was confirmed by using Williamson-Hall plot.

$$[\beta\cos\theta/\lambda = (K/D) + \varepsilon\sin\theta/\lambda] \text{-----------------} 5$$

The plot of $\beta\cos\theta/\lambda$ against $\sin\theta/\lambda$ for all thin film which is a straight line. The reciprocal of intercept on the y-axis gives the average particle size. The particle size determined using both methods are identical. The W-H plot is shown in Fig. 1. The variation of particle size with dopant concentration is shown in Fig. 5. The microstrain developed in the thin film was calculated using formula [28];

$$\varepsilon = \beta\cos\theta/4 \text{---------------------------} 6$$

The microstrain for all the thin films was calculated. The observed value of microstrain was found to be decreases up to 0.25 mol% of aluminum and then gets increased. The change in microstrain is irregular and random. The variation of microstrain with dopant concentration is shown in the Fig. 6. The dislocation density was determined for all thin films using the equation

$$\delta = (1/D^2) \text{------------} 7$$

Fig. 7 shows the variation of dislocation density of thin films with dopant concentration. It indicates decrease in dislocation density with dopant concentration up to 0.25 mol%. In polycrystalline thin films dislocated atoms occupy the regions near the grain boundaries. It is therefore confirmed that in thin films containing smaller particle size the number of dislocation density is more. The number of crystallites/ unit area can be obtained using the relation [29]

$$N = (t / D^3) \text{---------} 8$$

Where t = thickness of a sample. The calculated N values are in the range of 2.077-1.465 x 10^{15} /m^2 for dopant concentration up to 0.25mol %. After 0.25mol % the value gets increases. Fig. 8 indicates the variation of number of crystallites/ per unit area against dopant concentration.

IV. Conclusion

Aluminum doped CdSe thin films have been synthesized by using dip coating method. The varying concentration of aluminum from 0.01 to 1.0 mol% was used. The structural studies was done using x-ray diffraction pattern. Polycrystalline character as well as a hexagonal structure having (100) plane as the preferred orientation was observed. From x-ray diffraction pattern a variety of structural factors has been estimated and is reported in this paper.

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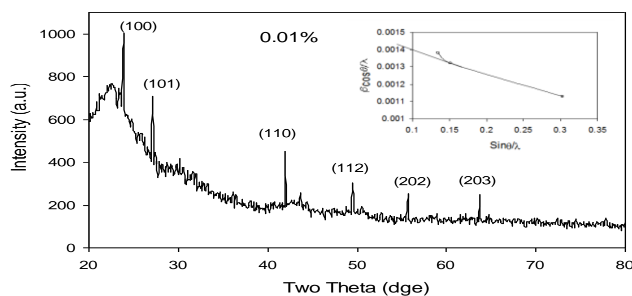
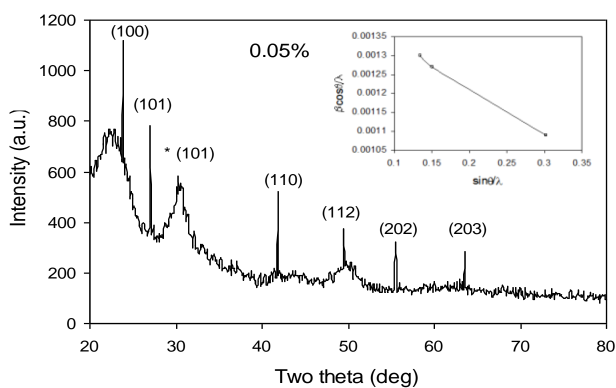
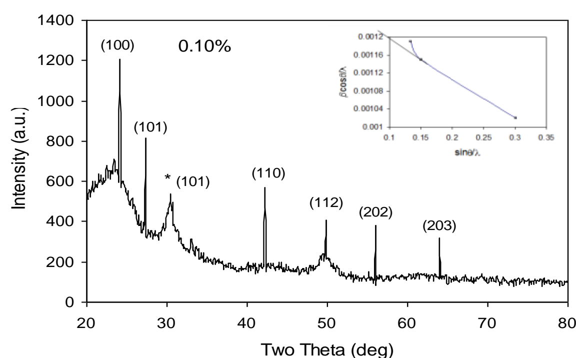
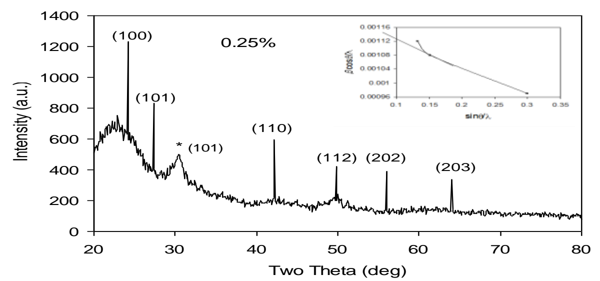








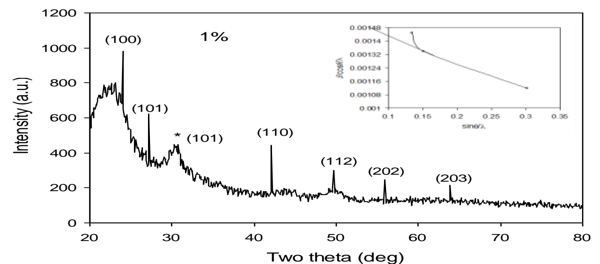


Fig. 1 X-ray diffraction pattern of CdSe: Al thin films.

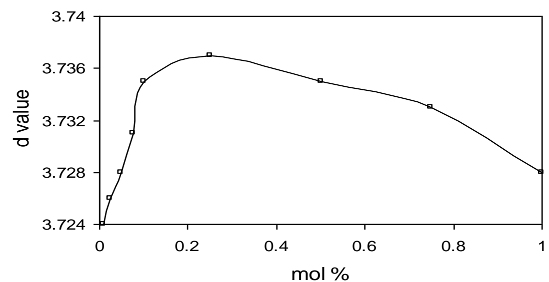
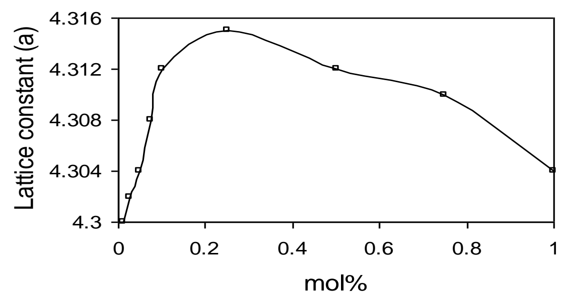


Fig. 2 Variation of interplanar distance with dopant concentration



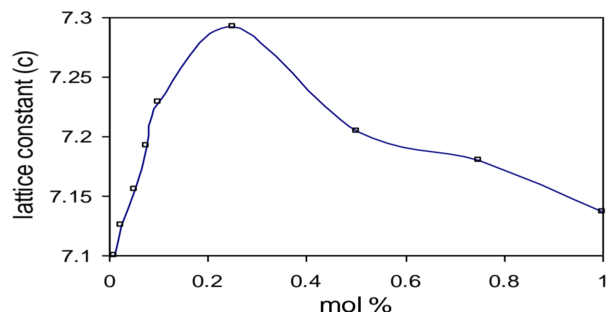


Fig. 3 Variation of lattice parameters with dopant concentration

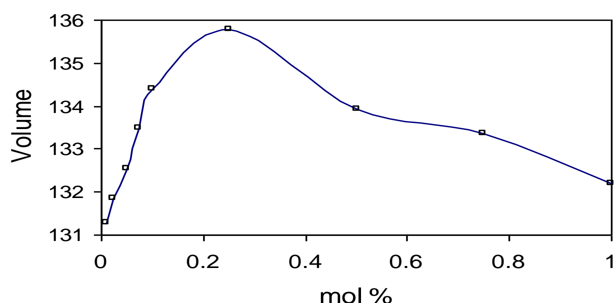


Fig.4 Variation of volume with dopant concentration

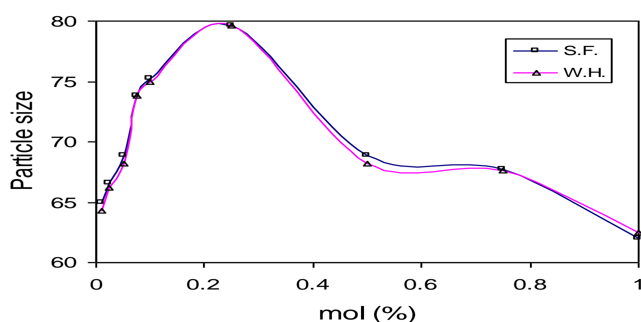


Fig. 5 Variation of particle size with dopant concentration.

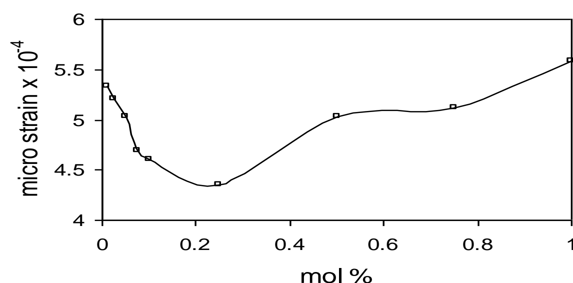


Fig. 6 Variation of microstrain with dopant concentration

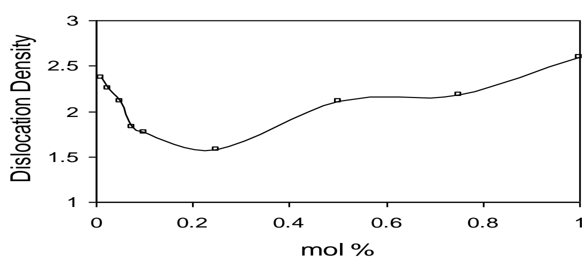


Fig. 7 Variation of dislocation density with dopant concentration.

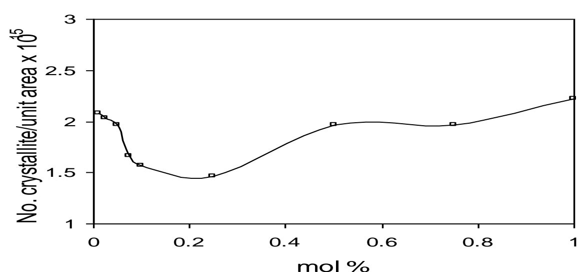


Fig. 8 Variation of number of crystallite/unit area against dopant concentration.

Table-:1 interplanar distance, hkl, intensity, lattice parameters and volume of the aluminum doped thin films.

Doping Conc. (mol%)	Observed 'd' value (Å)	Std. 'd' value (Å)	hkl	Intensity	Lattice Parameters (Å)	Volume $(Å)^3$
0.01	3.724 3.290 2.151 1.838 1.649 1.459	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	1003 710 453 304 253 248	a = 4.300 c = 7.100	131.27
0.025	3.726 3.293 2.156 1.841 1.651 1.461	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	1088 765 502 341 297 263	a = 4.302 c = 7.125	131.86
0.05	3.728 3.296 2.158 1.841 1.653 1.463	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	1121 783 524 376 321 284	a = 4.304 c = 7.155	132.54
0.075	3.731 3.297 2.159 1.843 1.656 1.465	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	1186 799 552 394 363 302	a = 4.308 c = 7.192	133.47
0.1	3.735 3.301 2.162 1.846 1.659 1.467	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	1208 813 571 406 379 319	a = 4.312 c = 7.229	134.41
0.25	3.737 3.304 2.166 1.848 1.663 1.470	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	1234 832 595 421 392 336	a = 4.315 c = 7.292	135.77
0.5	3.735 3.300 2.161 1.844 1.658 1.466	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	1192 801 569 402 371 309	a = 4.312 c = 7.204	133.94
0.75	3.733 3.297 2.157 1.842 1.656 1.463	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	1126 737 531 368 316 272	a = 4.310 c = 7.180	133.37
1.0	3.728 3.293 2.153 1.839 1.652 1.460	3.720 3.290 2.151 1.834 1.645 1.456	100 101 110 112 202 203	982 621 443 301 247 216	a = 4.304 c = 7.137	132.20

Table-:2 Particle size, microstrain, dislocation density and number of crystallite per unit area of the aluminum doped thin films.

Doping Conc. (mol%)	Particle size (nm)		Microstrain x 10^{-4}	Dislocation Density (per m^2) x 10^{14}	No. of crystallite/ unit area (per m^2) x 10^{15}
	Scherrer's formula	W-H plot			
0.01	64.98	64.28	5.333	2.368	2.077
0.025	66.59	66.17	5.204	2.255	2.032
0.05	68.82	68.18	5.036	2.107	1.963
0.075	73.84	73.77	4.693	1.834	1.664
0.1	75.21	75.00	4.608	1.768	1.568
0.25	79.64	79.64	4.351	1.576	1.465
0.5	68.81	68.18	5.036	2.112	1.964
0.75	67.67	67.66	5.121	2.183	1.968
1.0	62.01	62.50	5.589	2.600	2.222