

# Influence of Preparation Technique on the Properties of In:CdS Thin Films

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This paper presents the results of the structural, morphological and optical analysis of In:CdS thin films prepared by chemical bath deposition and successive ionic layer adsorption and reaction techniques. X-ray diffraction patterns showed the hexagonal phase of cadmium sulfide and it has been found that the amount of atomic percentage of indium increases the intensity of the preferential orientation (002) plane in chemical bath deposition In:CdS thin films. Compositional analysis confirmed the replacement of Cd ions by In ions and morphological analysis confirmed the lesser grain size and dense morphology in chemical bath deposition In:CdS thin films. Increase in In concentration in successive ionic layer adsorption and reaction In:CdS thin films leads to an increase in the optical transmission up to 80% and the higher band gap and therefore the results of this investigation enabled to understand the significance of preparation technique.

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## 1. Introduction

Cadmium sulphide with a direct band gap of 2.42 eV is a suitable window material for CdS/CuInSe<sub>2</sub> and CdS/CdTe heterojunction solar cells [1–4]. Two basic requirements for the window material are low electrical resistivity and high optical transmittance. Even though resistivity and optical transmittance strongly depend on preparation conditions [5, 6], undoped CdS thin films generally show high electrical resistivities. Thus, it is difficult to produce undoped CdS thin films with both low resistivity and high transmittance just by controlling preparation conditions. An effective way to obtain thin films with low resistivity and high optical transmittance is to add In impurity into CdS thin films. Several researchers [7–10] have employed indium one of the more effective dopants to obtain *n*-doped CdS because the extra electron coming from the In<sup>3+</sup> ion is placed substitutionally in Cd<sup>2+</sup> sites [11] and therefore prepared by several researchers [8–11]. Doped CdS thin films are also important for the fabrication of gas sensors and photovoltaic devices [12–14]. Based on these ideas in mind the present work has been aimed to prepare In:CdS by chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) techniques and also to study the influence of preparation technique on its structural, morphological, compositional and optical properties.

## 2. Experimental details

### 2.1. Preparation of In:CdS thin films by CBD technique

This film formation by CBD is described as a process of ion-by-ion condensation at the surface of the substrate [15]. In CBD even though the deposition is by the reduction of metal salts, the reaction does not go autocatalytically unlike electroplating. Here the substrates whether metallic or non-metallic are directly dipped into the reaction bath for deposition. The film formation on the substrate takes place when ionic product (IP) exceeds solubility product (SP) and the method has many advantages as reported earlier [15, 16].

TABLE I

Concentration and volume of chemicals used in the preparation of CBD In:CdS.

Chemical	Trail	Concentration [g]	Volume [ml]
CdCl <sub>2</sub>	1/2/3	0.0603	15
thiourea	1/2/3	0.3806	25
InCl <sub>3</sub>	1	0.0828	3
	2	0.2484	3
	3	0.4140	3

The deposition of CdS thin films is based on the reaction of Cd<sup>2+</sup> and S<sup>2-</sup> ions in deionised water solution.

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Chemical baths used for the deposition of CdS thin films consist of cadmium chloride, thiourea, triethanolamine, ammonia and indium trichloride. The pH of the solution can be adjusted by adding ammonia. Three different trials with different concentration of indium trichloride and same proportion of cadmium chloride and thiourea were used for the deposition of In:CdS thin films (Table I). The films are adherent and uniform only for the trial 1 and therefore trial 1 In:CdS thin films are used for the analysis after annealing at 100 °C for 1 h.

### 2.2. Preparation of In:CdS thin films by SILAR technique

In the present work CdS thin films have been synthesized by SILAR technique which is often termed as modified chemical bath deposition. Actually SILAR process involves immersion of substrates into separately placed cationic and anionic precursors for reaction at chosen temperatures. Between every immersion it is rinsed in distilled water or deionised water and the rinsing time is important for ionic layer formation. SILAR technique involves adsorption of a layer of complex ion on the substrate followed by reaction of the adsorbed ion layer [17]. So, the immersion programs which can alter the chemical distribution of the deposit layer by layer provides an opportunity to tailor CdS precursor deposits with homogeneous element distribution for easy phase synthesis in the subsequent processing [18].

TABLE II

Preparatory parameters of SILAR In:CdS thin films.

Preparatory parameter	Solution	Optimised value
pH	cationic precursor	5
	anionic precursor	9
temperature cycle	cationic/anionic precursor	80 °C
	cationic/anionic precursor	25

In:CdS thin films are deposited by two precursors, one cationic precursor and another is anionic precursor. The cationic precursor consists of cadmium acetate (0.025 M) and indium trichloride (0.1 M) whereas the anionic precursor consists of sodium sulphide (0.1 M). Well-cleaned substrates were immersed into the cationic precursor for 15 s and then rinsed with deionised water for 10 s to remove unattached ions. Then the substrates were immersed into anionic precursor solution for 15 s. Finally the substrates were rinsed in water for 15 s. The above cycle was repeated and the optimized dippings were 25 to get enough film thickness. After deposition the films were taken out and washed in deionised water to remove the unattached ions and dried naturally. The deposition process mainly depends on the parameters such as pH, temperature and time. The optimized deposition parameters were given in Table II.

### 2.3. Characterization

A Shimadzu XRD-6000 X-ray diffractometer with vertical goniometer fitted with vanadium filter and copper radiation ( $\lambda = 1.5406 \text{ \AA}$ ) was used for the structural analysis of thin films of different thicknesses. The surface morphology of In:CdS thin films was studied using a scanning electron microscope (JEOL JSM 6330F). A JASCO (V570: UV-VIS-NIR) double beam spectrophotometer was used for optical studies in the wavelength range 400–2500 nm. Energy dispersive X-ray (EDAX) analyser (LEICA.S440i) was used to confirm the composition of the constituents in In:CdS thin films.

## 3. Results and discussion

### 3.1. Structural analysis of In:CdS thin films

CBD and SILAR In:CdS thin films have been prepared with same percentage of In concentration (0.1 M/0.0828 g/3 ml). From the XRD profiles (Fig. 1) the lattice spacing “ $d$ ” has been determined and it has been found that it is in very good agreement with those of ASTM DATA (80-0006) (Table III). Predicted peaks (002) and (110) are reported as the characteristic peaks for In:CdS thin films by several workers [5–7] and the absence of other peaks proves the purity of the prepared thin films. From the diffraction profiles it has been found that the films are polycrystalline in nature with hexagonal structure having the preferential orientation along (002) plane.

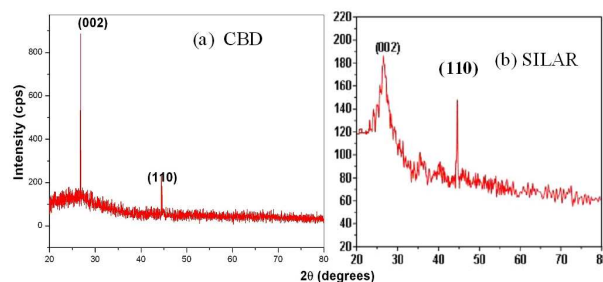


Fig. 1. XRD profiles of In:CdS thin films.

The individual crystalline sizes ( $D_c$ ) in the films have been estimated [15] and are in good agreement with the reported values [1, 2, 7]. Using the size of the crystallites the dislocation density, the number of crystallites per unit surface area and strain have been determined [15] and are presented in Table IV. The intensities of the peaks (110) is significantly higher in CBD In:CdS than in SILAR In:CdS. This may be due to lower atomic percentage of In in CBD In:CdS thin films than SILAR thin films confirmed from compositional analysis (Table V) and earlier reports [19]. Irrespective of the preparation technique the crystalline size increases and the defects, dislocation density and strain decrease with film thickness which may be due to the improvement in crystallinity.

XRD data of CBD and SILAR In:CdS thin films.

TABLE III

Preparation technique	Film thickness [nm]	<i>hkl</i> plane	$2\theta$ (degrees)		<i>d</i> spacing [Å]	
			observed	ASTM	observed	ASTM
CBD	530	(002)	27.0	26.66	3.29	3.34
		(110)	44.8	43.91	2.02	2.06
SILAR	140	(002)	26.5	26.66	3.36	3.34
		(110)	44.71	43.91	2.02	2.06

Structural parameters of In:CdS thin films.

TABLE IV

Method	Film thickness [nm]	Lattice constant				Crystalline size [Å]	Dislocation density [ $10^{14}$ /lines/m <sup>2</sup> ]	Number of crystallite per unit area [ $10^{15}$ m <sup>-2</sup> ]	Strain [ $10^{-4}$ ]
		<i>a</i> [Å]		<i>c</i> [Å]					
		observed	JCDPS	observed	JCDPS				
CBD	530	4.04	4.121	6.60	6.682	631	2.51	2.12	5.78
SILAR	140	4.04	4.121	6.72	6.682	187	28.53	2.14	20.20

### 3.2. Compositional analysis

EDAX spectra of CBD and SILAR In:CdS thin films are presented in Fig. 2 and the atomic percentage of different constituents are given in Table V. From Table V it can be concluded that the films prepared from CBD method has less In concentration [3.35%] and that from SILAR has more In concentration [18.82%]. This implies that In ions enter Cd sites more easily in SILAR In:CdS thin films than in CBD thin films.

### 3.3. Morphological analysis

Figure 3 shows the scanning electron micrographs of CBD and SILAR In:CdS thin films. The SEM micrographs of CBD In:CdS thin film indicate that films are dense, smooth and homogeneous without visible pores. The film surface is seemed to be continuous with overgrowth of particles [7] and the micrographs clearly indicate that the grain size is higher for smaller In concentration (CBD In:CdS) [5] and it was also proved in the XRD analysis (Table IV) and also earlier reports [19]. Higher intense peaks of XRD profile of CBD In:CdS thin film may be one of the other reasons for larger grains observed in SEM.

### 3.4. Optical analysis

The optical transmittance spectra of CBD and SILAR In:CdS thin films is presented in Fig. 4. Transmittance of the films decreases with thickness irrespective of preparation technique. The transmittance of the films is comparatively less in lightly In doped CBD thin films and the typical behaviour was observed by earlier workers (Kim et al. [19]). The absorption and extinction coefficient of In:CdS thin films are calculated and are given in Table VI.

Elemental composition of In:CdS thin films.

TABLE V

Preparation method	Thickness [nm]	In [at. %]	Cd [at. %]	S [at. %]
CBD	530	3.35	48.52	48.13
SILAR	140	18.82	35.31	45.87

Transmittance spectra of In:CdS thin films of CBD and SILAR methods.

TABLE VI

Method	Thickness of the film [nm]	$\alpha$ [ $10^6$ m <sup>-1</sup> ] ( $\lambda = 1000$ Å)	$k$ ( $\lambda = 1000$ Å)	$E_g$ [eV]
CBD	530	2.41	0.19	2.00
SILAR	140	0.94	0.07	2.23

Plot of  $(\alpha h\nu)^2$  versus  $(h\nu)$  (Fig. 5) of In:CdS thin films were plotted and the straight line portion is extrapolated to cut the  $x$ -axis which gives the band gap. The estimated band gaps are in the range of 2–2.3 eV, respectively (Table VI), and it was observed that the band gap decreases with increase in film thickness and increases with In concentration [19]. The increase in  $E_g$  of SILAR In:CdS thin films may be due to replacement of larger number of substitutional or interstitial cadmium ions by indium ions.

Plots of  $(h\nu)$  versus  $(\alpha h\nu)^{1/2}$ ,  $(\alpha h\nu)^{1/3}$ , and  $(\alpha h\nu)^{3/2}$  (not shown) reveal that In:CdS films did not have line above  $h\nu > E_g$ . Since extrapolation of it did not touch the zero absorption axis, it confirms the fact that In:CdS phase do not have indirect allowed direct forbidden and indirect forbidden transitions.

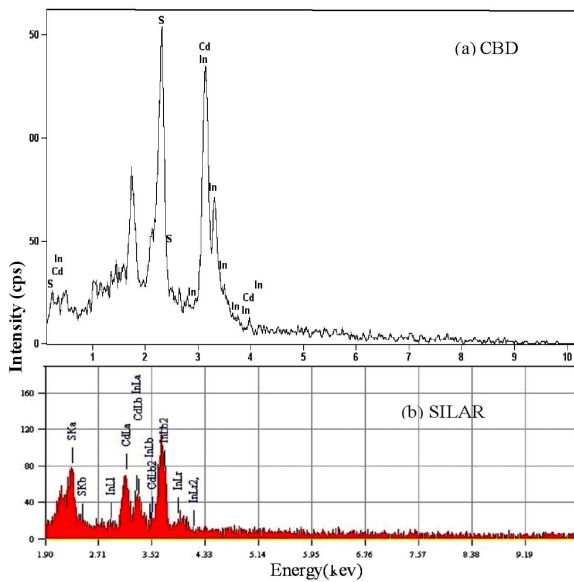


Fig. 2. EDAX spectra of In:CdS thin films.

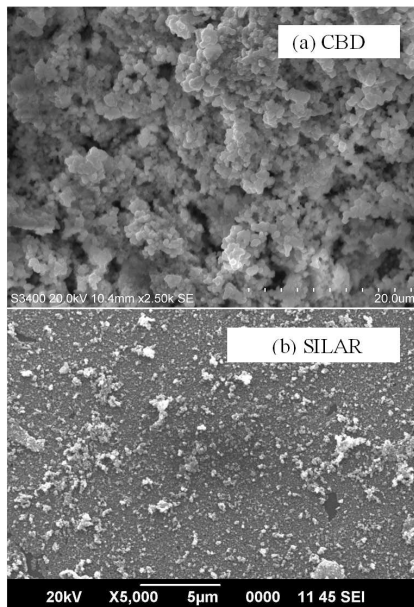


Fig. 3. SEM micrographs of In:CdS thin films.

#### 4. Conclusion

In:CdS thin films have been prepared by simple CBD and SILAR techniques. The investigations revealed that the higher intense peaks with larger grains, reduced defects and lesser dense morphology are observed in lightly In doped CBD thin films. It has also been found that the transmittance as well as the band gap energy of In:CdS thin films are higher in comparatively heavily In doped SILAR In:CdS thin films. Therefore the method of preparation technology is helpful to prepare In:CdS thin films with different properties.

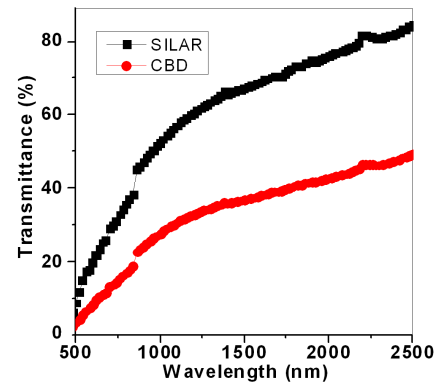


Fig. 4. Transmittance spectra of In:CdS thin films.

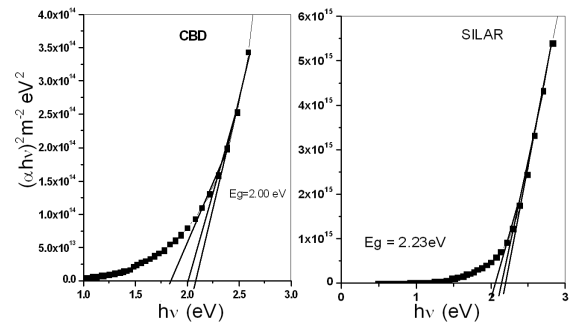


Fig. 5. Plot of  $(\alpha hv)^2$  vs.  $(hv)$  of In:CdS thin films.

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