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Deposition of Cadmium doped Zinc Selenide Thin Films and its Characteristics

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Abstract*: *Extensive research is being carried out by many researchers for the purpose of developing solar cells and photo-electrochemical cells with II-IV and II-IV-VI compounds. As an attempt to this, CdZnSe thin films with a varying concentration of Cadmium have been deposited on the glass micro slides by employing chemical bath deposition technique, which provides large area deposition for fabricating optoelectronic devices. The growth mechanism and chemical kinetics of these materials have been studied considering its elementary parameters such as basic constituents, molarities, pH of reaction mixture and deposition conditions like temperature time, rotations per minute etc. Composition of the films was estimated by EDAX studies. Thickness of as- deposited films have been measured by weight difference and interferometric method decreases with increasing Cadmium doping. UV-VISIBLE Optical studies show a high absorption coefficient with direct type of transitions. The energy band gap decreased from 2.81ev to 1.72ev as the doping concentration of Cadmium increases from 0 to 1.

Keywords: chemical bath deposition technique, chemical kinetics, elemental and morphological studies, optical properties

I. INTRODUCTION

Large number of semiconducting thin films has been deposited for optoelectronic device applications such as optical switches, transistors, modulators, laser diodes, solar cells etc. [1]-[3]. Zinc Selenide and Cadmium Selenide are widely used materials belonging to the category of II-IV semiconductors because of their major applications in converting solar energy into its electrical counterpart. Zinc Selenide is stable enough but have wide band gap which reduces its photoactivity, whereas Cadmium Selenide having lower band gap have high photosensitivity that is high absorption coefficient [4],[5]. By alloying these two semiconductors, a series of compounds of CdZnSe can be obtained to fulfill the need of photo-electrodes. The specificity of these semiconductors can be achieved through composition alteration [6], [7].

Mixed compound semiconductor electrodes are found to exhibit better photo-response than simple photo-electrodes [2]. Hence, we have selected doping of Cd into ZnSe to form $Cd_xZn_{1-x}Se$ ternary semiconductor films, where the parameter x is varied from 0 to 1 to change the elemental composition.

Various techniques have been used for the fabrication of thin films as per their requirements. This includes sol gel method, chemical bath deposition, brush painting [6], electron beam evaporation [8], solution growth technique [9], Electrosynthesis [10] etc. Among these techniques, we have selected chemical bath deposition (CBD) as large area thin films of semiconductor chalcogenides can be produces in a very low cost [4]. The advantages of CBD are minimum cost, low operating temperature, less incorporation of impurities, high reproducibility, environment friendly and require no sophisticated instruments [11],12]. In this technique, deposition of thin films takes place based on the chemical reaction between the ingredients and the deposition rate can be adjusted by controlling the preparative parameters viz. bath temperature, concentration of reactants, rate of stirring, pH of the solution, complexing and reducing agent etc. [13]. Uniform deposition of compound element instead of co-deposition can be achieved by this method. Also, the toxic effects of vapor phase Cd, Se can be avoided as we use liquid phase elements.

In view of this, we present the synthesis and growth mechanism of CdxZn1-xSe thin films by varying the compositional parameter x. The physical, elemental and morphological, optical properties of these thin films are studied.

II. MATERIALS AND METHODS

The chemicals used for preparation of $Cd_xZn_{1-x}Se$ thin films were AR grade Cadmium Sulphate ($CdSO_4$), Zinc Sulphate ($ZnSO_4$), Sodium Sulphite (Na_2SO_3), elemental selenium powder (99%), triethanolamine (TEA) [$N(CH_2CH_2OH)_3$] and liquid ammonia (NH_3). The commercially available non-conducting micro glass slides were used as a substrate for deposition of CdZnSe films. The micro glass slides were kept in chromic acid for 10-12 hours and washed by using detergent powder. They were rinsed in acetone and double distilled water. For synthesis of these thin films, Sodium seleno-sulphate (Na_2SeSO_3) solution was made by refluxing 10gm of selenium metal powder and 24gm of sodium sulphite in 360ml double distilled water for 9hr at 80^0C temperature.

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The equimolar solutions of $CdSO_4$, $ZnSO_4$ and Na_2SeSO_3 were taken in a stoichiometric proportion. The rate of chemical deposition depends on slow release of Zn^{2+}, Cd^{2+} and Se^{2-} ions in the bath solution and then condensation of these ions on glass slide

which are mounted with specially designed substrate holder in the solution [14]. Triethanolamine acts as a complexing substance and adequate quantity of Sodium hydroxide was used to adjust pH of the reaction mixture equal to 10.5. The composition of Cd^{2+} ions was varied by changing the x parameter from 0 to 1. The formation of thin films take place when the ionic product exceeds the solubility product and precipitation takes place by recombination of ions on the substrate by nucleation process.

Thin uniform CdZnSe films were obtained by optimizing the parameters. The temperature of reaction bath was kept at 60^0C, deposition time was 90min and substrate rotation speed was 70 ± 2 rpm. After the deposition, the micro glass slides were taken out of the beaker, cleaned several times with double distilled water, dried in natural air and kept in the desiccators.

The thickness measurement of as-deposited thin films was done by using weight difference method and interferometric method. Scanning electron microscopy measurements were conducted using JEOL JSM 7600F FEG-SEM operating at an accelerating voltage 0.1v to 30kv. The elemental composition measurements were carried out by an energy dispersive X-ray analysis (EDAX) coupled to the scanning electron microscope. The optical absorption spectra were obtained by using ELICO SL27 UV-Spectrophotometer at room temperature in the wavelength range of 300nm to 900nm.

III. RESULTS AND DISCUSSION

A. Chemical Kinetics

Fundamental chemical reactions were as follows:

1. Preparation of Sodium Seleno-sulphate:

Selenium metal powder is refluxed with Sodium Sulphite at 80^0C for 9hrs.

$$Na_2So_3 + Se \rightarrow Na_2SeSo_3$$

2. Formation of Zn^{2+} and Cd^{2+} ions:

Zinc sulphate and Cadmium Sulphate dissolve in water to release Zn^{2+} and Cd^{2+} ions

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$$
$$CdSO_4 \rightarrow Cd^{2+} + SO_4^{2-}$$

The addition of TEA in this solution results in a milky colored mixture, which is an indication of complexed ions.

$$Zn^{2+} + TEA \rightarrow [Zn\ (TEA)]^{2+}$$
$$Cd^{2+} + TEA \rightarrow [Cd\ (TEA)]^{2+}$$

To avoid fast precipitation of zinc sulphate and Cadmium sulphate in an alkaline solution Zn and Cd ions are complexed with NH_3 until the solution mixture becomes clear.

$$[Zn\ (TEA)]^{2+} + 4NH_3 \rightarrow Zn\ (NH_3)_4^{2+} + TEA$$
$$[Cd\ (TEA)]^{2+} + 4NH_3 \rightarrow Cd\ (NH_3)_4^{2+} + TEA$$

3. Formation of Se^{2-} ions:

Hydrolysis of Sodium seleno-sulphate takes place in the alkaline medium to release Se^{2-} ions.

$$Na_2SeSo_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$$
$$HSe^- + OH^- \rightarrow H_2O + Se^{2-}$$

4. Formation of CdZnSe thin films:

Finally, the deposition of CdZnSe thin films on the glass substrate takes place as per the following reaction,

$$Cd\ (NH_3)_4^{2+} + Zn\ (NH_3)_4^{2+} + Se^{2-} \rightarrow CdZnSe + 4NH_3$$

The as deposited films were uniform and well adhered to the glass slides. The thin films appeared pale white in color for x=0 but the color changed to deep orange red as Cd content has been increased up to x = 1.

B. Physical Properties

The as-deposited films thickness was measured by weight difference and interferometric technique were in agreement with each other (Table I). Thickness of these as-deposited films went on decreasing as the doping of Cd increases (Fig.1).

Table-I: Thickness Measurements of thin films

Cd Content in $Cd_xZn_{1-x}Se$ Thin films	Thickness (nm)	
	Weight Difference Method	Interferometric Method
0.0	566	570
0.2	531	542
0.4	500	501
0.6	439	450
0.8	389	384
1.0	373	367

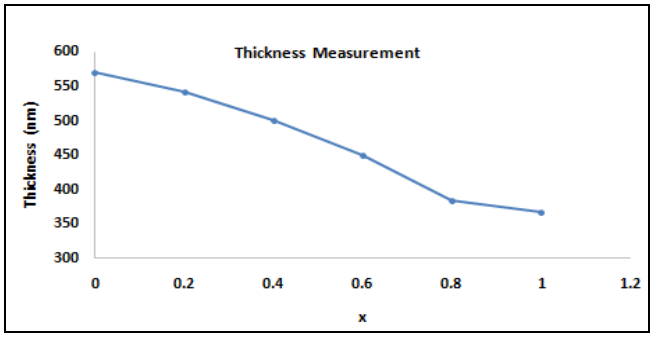

Fig. 1

C. Elemental and Morphological Studies

Morphological properties of these chemically deposited thin films were studied using SEM technique to understand the variation in the crystal growth as composition of Cadmium ions increased. The SEM micrographs exhibit the polycrystalline nature of these films (Fig.2). The thin films consist of approximately spherical grains having nearly identical diameters and are homogeneously arranged without interfusion [15] Fig2(a) micrograph of $Cd_{0.4}Zn_{0.6}Se$ shows agglomeration of crystallites at some places while agglomeration reduces and grain size increases for higher x values (Fig.2b and Fig.2c). The homogeneity increases and no interfusion found for $Cd_{0.8}Zn_{0.2}Se$ films. This type of surface morphology has large surface area, which is useful for absorption of maximum solar radiation. [1]

The elemental analysis was carried out by energy dispersive X-ray (EDAX) studies.

Fig.3 shows a representative EDAX analysis of CdZnSe thin films which confirms the presence of desired Cd, Zn and Se ratio. Table 2 indicates the comparison between precursor composition and EDAX composition. The elemental composition observed in the as deposited films was nearly equal to that of basic ingredients taken in the bath [6].

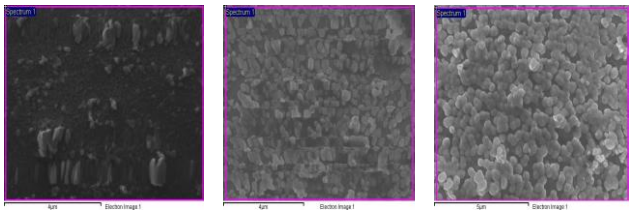

Fig. 2 (a) $Cd_{0.4}Zn_{0.6}Se$ (b) $Cd_{0.6}Zn_{0.64}Se$ (C) $Cd_{0.8}Zn_{0.2}Se$

Table- II: Elemental composition of Thin films

Preparatory Composition	EDAX composition
$Cd_{0.0}Zn_{1.0}Se$	$Cd_{0.0}Zn_{0.83}Se$
$Cd_{0.2}Zn_{0.8}Se$	$Cd_{0.15}Zn_{0.76}Se$
$Cd_{0.4}Zn_{0.6}Se$	$Cd_{0.34}Zn_{0.36}Se$
$Cd_{0.6}Zn_{0.4}Se$	$Cd_{0.5}Zn_{0.17}Se$
$Cd_{0.8}Zn_{0.2}Se$	$Cd_{0.64}Zn_{0.12}Se$
$Cd_{1.0}Zn_{0.0}Se$	$Cd_{0.8}Zn_{0.00}Se$

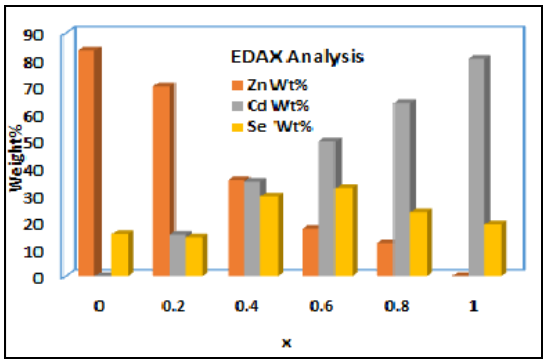

Fig. 3

D. Optical Properties

The fundamental absorption, which takes place from valence band to conduction band is used for the measurement of the optical bandgap of CdZnSe thin films. Fig.4 shows the optical absorption spectra of $Cd_xZn_{1-x}Se$ thin films. Absorption coefficient (Fig.5) shows that there is a shift in absorption edge towards the higher wavelength side for increasing Cd-content. The relation between the absorption coefficient (α) and the incident photon energy (hν) is expressed as:

$$\alpha h\nu = A\,(h\nu - E_g)^n$$

where Eg is optical bandgap, A is a constant, n is a factor that determines the nature of transition.[16] Fig. 6 shows a graph of $(\alpha h\nu)^2$ against (hν) for various x-parameters. The direct allowed transition was confirmed from the graphs which shows a linearity at the absorption edge. The straight-line part is extrapolated to give the x- axis intercept which shows the value of optical energy bandgap of thin films. The bandgap energy varies from 2.81ev to 1.72ev as x-parameter changes from 0 to 1 (Fig.7) and as depicted in Table - III. As the concentration of Cd is increased the inter-crystalline spaces decreases which reduces the energy bandgap of the films. This results into an increased crystalline nature of the films. This is also confirmed from micrographs.

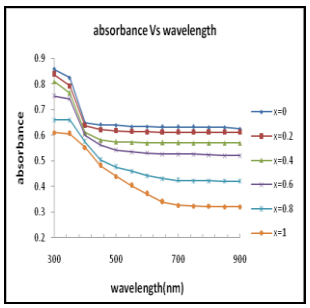

Fig. 4

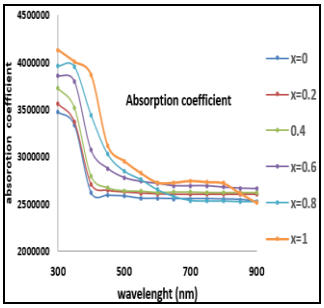

Fig. 5

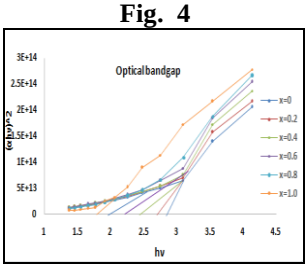

Fig. 6

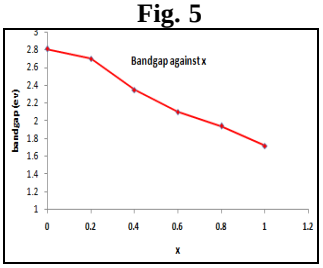

Fig. 7

Table- IIII: Energy bandgap for varying Cd concentration

X Parameter	0	0.2	0.4	0.6	0.8	1.0
Bandgap eV	2.81	2.70	2.35	2.10	1.94	1.72

IV. CONCLUSION

The well adhered Cadmium Zinc Selenide polycrystalline thin films of different Cadmium doping content have been deposited on glass substrate by Chemical Bath Deposition technique. Thickness of the films decreased from 568 nm to 370 nm as Cd- doping increases. These films were composed of spherically shaped grains. EDAX studies confirmed the formation of $Cd_xZn_{1-x}Se$ alloy and consists of Cd, Zn and Se. The optical bandgap calculated from optical absorption spectroscopy was found decreased from 2.81 eV to 1.72 eV as x varied from 0 to 1 with direct transitions. Thus, we conclude that doping of Cd in ZnSe gives significant decrease in optical bandgap of $Cd_xZn_{1-x}Se$ films.

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