Effect of Thickness on the Structural, Optical and Electrical Properties of MW-CBD CdZnS Thin Films

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Abstract — **Thin films of CdZnS have found extensive applications in various optical, electrical and optoelectronic devices. In the present work CdZnS (Cadmium Zinc Sulphide) thin films have been deposited by a simple, inexpensive and rapid synthesis route, microwave-assisted chemical bath deposition (MW-CBD).The bath solution is composed of Cadmium Sulphate, Zinc Sulphate, thiourea, ammonium Sulphate and ammonia. The concentration of $ZnSO_4$ is maintained at Y= [$ZnSO_4$]/ {[$CdSO_4$] + [$ZnSO_4$]} for Y=0.3. The deposition has been carried out for five different radiation time from 60s to 180s, in steps of 30s. X-ray diffraction (XRD) indicates the hexagonal structure (002) peak at 2θ =26.59° for the as-deposited CdZnS thin films. The grain size, dislocation density and strain in the deposited films have been determined. SEM image gives the morphology, size and shape of particles in the deposited CdZnS thin films. EDX results show that the composition of the film is maintained irrespective of radiation time. Optical transmission measurements reveal that the films show good transparency over 80% in the wavelength region of 500-1100nm. The band gap of CdZnS thin films is found to be around 2.6 eV. Sheet resistance of the samples calculated by using Van der Pauw technique is in the order of 10^6Ω/Sq. Resistivity of the films is in the order of 10^1 to 10^2 Ω-Cm.**

Keywords — **CdZnS, microwave, resistivity**

I. INTRODUCTION

CdZnS thin films have become the subject of considerable interest due to their use in solar cells [1]. CdZnS have attracted technological interest because the energy gap can be tuned and the lattice parameters can be varied [2]. The techniques which have been adopted for the preparation of CdZnS films are vacuum evaporation [3], chemical solution spray [4], Chemical bath deposition [5] etc. In recent years the replacement of CdS with its ternary alloy CdZnS has been attempted for improvement of the (Cd, Zn) S/Cu (In, Ga) Se_2 solar cell performance [6]. In the present work CdZnS thin films have been prepared by microwave assisted chemical bath deposition, since the transfer of microwave energy is rapid and direct. This rapid energy transfer creates non – equilibrium conditions resulting in high instantaneous temperatures (T_i). These high T_i activate a higher percentage of molecules above the required activation energy. With energy transmitted directly to the reactants, the more energized molecules will form products more rapidly. In this way uniformly deposited CdZnS thin film is obtained in few seconds compared to some minutes or hours by the conventional chemical bath deposition technique [7, 8]. For the deposition of thin films, there exist very few studies based on microwave [7]. To the best of our knowledge this is the first study on the preparation of ternary semiconductor compound CdZnS (thin films) by microwave assisted CBD.

II. METHODOLOGY

The chemicals used in this work consist of aqueous solutions of $5.8x10^{-3}$mol/l $3CdSO_4.5H_2O$, 0.037mol/l NH_3SO_4, 0.065mol/l H_2NCSNH_2, $1.738x10^{-3}$mol/l $ZnSO_4.7H_2O$ and 1.5 mol/l NH_3. The value of Y = 0.3 and. We define Y = [$ZnSO_4$]/ ([$ZnSO_4$] + [$CdSO_4$]). Thin films of CdZnS were deposited on well cleaned glass substrates. Microwave assisted bath temperature of the solution was kept in the temperature range between 90°C to 95°C. Deposition time varied from 60s to 180s. The effect of deposition time and hence the thickness is also studied for all the five different concentrations.

In this case, the advantages of microwave such as rapid reaction, small particle size and narrow particle size distribution are taken into account [9]. At the same time to have a controlled deposition of thin film, a cyclic microwave radiation is applied to the bath solution, where the microwave is on for the first 30 seconds; by this time the temperature reaches around 70 degrees and the color of the solution changes to yellow (formation of the product). After this the microwave is switched OFF and ON, for every 5 seconds (so that the temperature is maintained below 95 degrees) until the desired time. By this way we tried to control the deposition process to achieve small particle sizes–with narrow Size distribution.

The reaction procedure for the formation of CdZnS may be described by the following steps

$$SC(NH_2)_2+OH^- \leftrightarrow SH^-+CH_2N_2+H_2O \quad (1)$$

$$H^-+OH^- \leftrightarrow S^{2-}+H_2O \quad (2)$$

The deposition process is based on the precipitation of cadmium and zinc sulphide in the reaction bath. To avoid the formation of cadmium and zinc hydroxides, a complexing agent such as ammonia is used, which form cadmium and zinc complex ions with coordination number of 4 [10].

$$NH_3+H_2O \rightarrow NH^{4+}+OH^- \quad (3)$$

$$Cd^{2+}+4NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+} \quad pK_{C1}=6.92 \quad (4)$$

$$Zn^{2+}+4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+} \quad pK_{C2}=9.06 \qquad (5)$$

The dissociation equilibrium of those complexes are given by [11]

$$X\,[Cd\,(NH_3)_4^{2+}] + (1-x)\,[Zn\,(NH_3)_4^{2+})] + S^{2-} + NH_3 \rightarrow Cd_xZn_{1-x}S \qquad (6)$$

Thicknesses of the deposited films were measured by profilometer. The structure of the films were analyzed using a Grazing Incidence X-ray diffractometer (Siemens D5000, using Cu-Kα radiation with λ = 1.5406 Å). Measurements were made for 2θ values over 20-70° in steps of 0.03° with a count time of 5 s and a grazing angle equal to 1.5º. Surface morphology and particle size of the deposited films were analyzed by JEOL JSM-7401F Field Emission Scanning Electron Microscope (FESEM). Composition of the deposited CdZnS thin films was analyzed by JEOL 840 SEM-energy dispersive X-ray analysis (EDS).

Transmittance spectra of CdZnS thin films were measured using the, UV – VIS spectrometer (Schimadzu Japan) in the wavelength range 300-1100 nm. The substrate absorption is corrected by introducing an uncoated cleaned glass in the reference beam. The absorption coefficient α is calculated using the relation

$$\alpha = \frac{2.303 \log\left(\frac{1}{T}\right)}{t}, \qquad (7)$$

where T is the transmittance and t is the film thickness.
The extinction coefficient and the refractive index can be evaluated from the relations [12]

$$\alpha = \frac{4\pi k t}{\lambda}, \qquad (8)$$

$$T = \frac{n_2}{n_0} \frac{(1+\delta_1)^2 + (1+\delta_2)^2}{1 + (\delta_1^2 \delta_2^2) + 2\delta_1\delta_2 \cos 2\Gamma}, \qquad (9)$$

Where

$$\delta_1 = \frac{n_0^2 + n_1^2}{(n_0 + n_1)^2}, \delta_2 = \frac{n_1^2 - n_2^2}{(n_1 + n_2)^2}, \text{ and } \Gamma = \frac{2\pi n_1 t}{\lambda},$$

Where λ is the wavelength of the incident radiation, n_0, n_1, n_2 are the refractive indices of air, film and glass, respectively. Substituting the experimental values for T, t, n_0 and n_2, the above equation can be solved for n_1 and k using the method of iteration until the desired convergence is achieved.

For measurement of electrical resistivity, Van der Pauw [13] technique was used. CdZnS samples were cut in square shape 1cmx1cm and sufficiently small contacts were made at four corners of the sample with silver conducting paint. A current of 50 nA was applied through the contacts 1 and 3, and the voltage V_{24} was measured across contacts 2 and 4. The resistance $R_{13,\,24}$ was calculated by using the relation $R_{13,24} = V_{24}/I_{13}$.Similarly, a current of 50nA was applied through contacts 2 and 4, while the voltage V_{13} was measured across points 1 and 3. The resistance $R_{24,13}$ was calculated from the relation $R_{24,13} = V_{13} / I_{24}$.

III. RESULTS

Structural

Thickness of the deposited films is found to increase with the increase in radiation time, as shown in table 1. II-VI chalcogenide semiconductors show the structural duality, and can be formed as either spharlite (cubic, zinc blend type) or Wurtzite (hexagonal type). From the diffraction patterns of the MW-CBD CdZnS thin films in Figure 1, it is clearly seen that the intensity of diffraction peaks increases with the extended microwave irradiation time, which indicates higher cystallinity. The film deposited for 60 s radiation time is amorphous, whereas for 90s and 120s a weak diffraction peak (002) can be detected. As the microwave irradiation time increases to 180s three diffraction peaks (002), (110) and (201) can be observed and the intensity of (002) peak is stronger with the increase in time of radiation. This diffraction peak corresponds to the CdZnS hexagonal crystalline phase (JCPDS card no: 40-0835). Ran Zhai et al [14] have reported a similar trend for microwave assisted chemical bath deposited CdS thin films. Lattice parameter 'c' has been calculated using the equation (10) given below. The micro structural parameters grain size (D), dislocation density(δ) and strain (ε) of the deposited CdZnS thin films have been determined by the relations (11-13) given below and the values are tabulated. Grain size is found to increase where as dislocation density and strain are observed to decrease with the increase in film thickness.

$$1/d^2 = 4/3[(h^2+hk+k^2)/a^2] + [1/c^2] \qquad (10)$$

$$D = (0.94\lambda)/(\beta\cos\theta) \qquad (11)$$

$$\beta = [\lambda/(D\cos\theta)] - \varepsilon\tan\theta \qquad (12)$$

$$\delta = 1/D^2 \qquad (13)$$

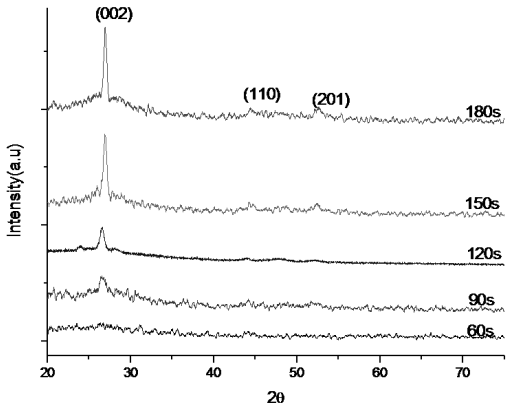


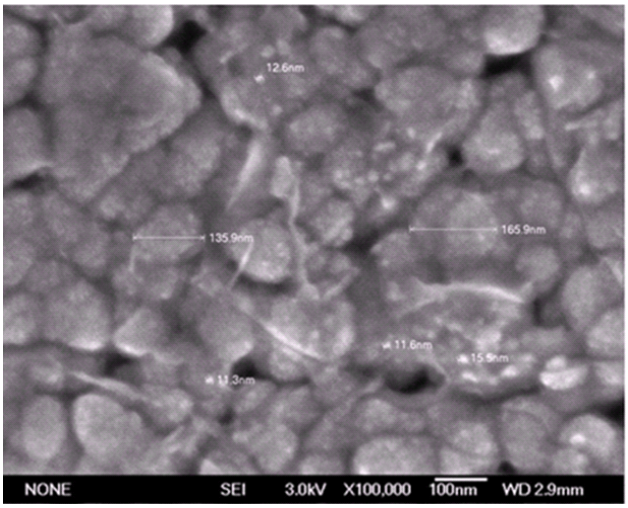
Figure 1. XRD pattern of MW-CBD CdZnS thin films.

Table 1.Microstructural and optical parameters of MW-CBD CdZnS thin films.

t(nm)	c Å	(D)	$\delta x10^{15}$ lines/m^2	$\varepsilon x10^{-3}$	Eg (eV)	n at 800nm	k
58.23	-	-	-	-	2.5	2.15	0.20
90.9	6.628	10.94	8.355	3.678	2.54	2.18	0.21
94.2	6.637	14.21	4.945	2.864	2.59	2.37	0.68
107.4	6.628	19.32	2.678	2.678	2.67	2.38	0.56
110.2	6.652	20.80	2.309	1.973	2.67	2.41	0.53

Morphology and Composition

From the FESEM analysis in figure 2, uniform sized 150-200nm clusters which are made up of closely packed nano particles of size 10 to 20nm is observed. With the increase in radiation time from 60s to 180s; the cluster size becomes more regular, leading to the formation of more compact film. Many approaches have been used to control the growth process such as microwave irradiation [14], magnetic field [15], ultrasonic vibration [16] etc. Among this microwave irradiation has shown very rapid growth due to its unique reaction effects such as rapid heating and the consequent effective increase in reaction rates. A preferential adsorption of negative and positive ions induced by electromagnetic interaction will result in nucleation and heterogeneous growth on the surface .Thermal effects by long irradiation duration can also accelerate the cluster-by-cluster homogenous precipitation.



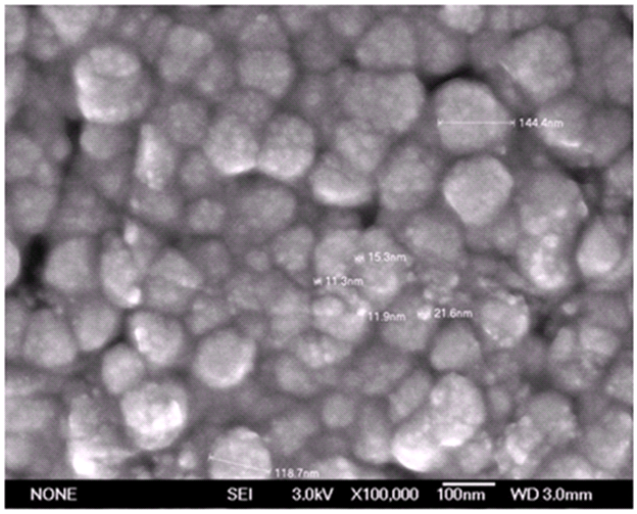


Figure2.FESEM images of CdZnS thin films deposited for 60s and 180s microwave irradiation time.

Composition of the deposited CdZnS thin films are determined by Energy Dispersive X-ray analysis and the results are given in table 2.It is observed that all the deposited films are sulfur deficit.

Table 2 .Composition of the deposited CdZnS thin films.

Radiation time(s)	Cd At%	Zn at%	S at%	Zn/Cd	Cd/S
60	55.03	7.95	37.01	0.144	1.48
90	54.26	7.67	38.06	0.141	1.43
120	55.51	7.47	37.03	0.134	1.49
150	55.93	5.65	38.41	0.101	1.46
180	55.35	6.64	40.01	0.120	1.38

Optical

The transmittance spectra of MW-CBD CdZnS thin films are shown in figure 3. The films show good transparency of 80% and more in the wavelength region of 500-1100nm. This value is comparable to the values for CdZnS films reported elsewhere [17]. Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CdZnS thin films is shown in figure 3.Straight –line nature of the plot reveals that the transition is direct allowed. Similar plot was made for all the films. The determined band gap values (E_g) is given in table 1. The calculated values of refractive index (n) and extinction coefficient (k) at 800nm is given in table 1.It is clearly seen that the refractive index increases with the increase in thickness. Similar trend has been reported by S.Velumani et al [12] for CdSe thin films.

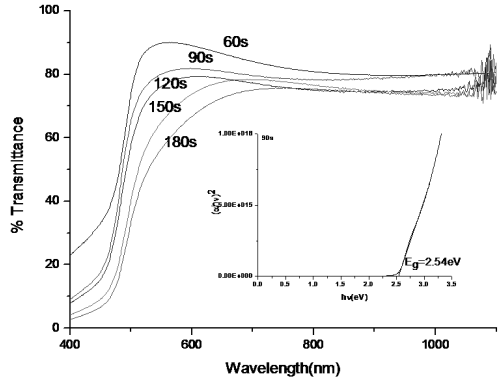


Figure 3.Transmittance spectra and $(\alpha h\nu)^2$ Vs hν plot of MW-CBD CdZnS thin films.

Electrical

Current-voltage (I-V) characteristics of the films were examined and sheet resistance, resistivity and conductivity of the samples were calculated by using the following relations

$$R_s = \pi/\ln(2)*(R_{13,24} + R_{24,13})/2\times f \quad (14)$$

where f is the correction factor and is equal to 1 when $R_{13,24} = R_{24,13}$.

$$\text{Resistivity } \rho = R_s*t \quad (15)$$

t is the thickness of the thin film samples.

$$\text{Conductivity } \sigma = 1/\rho \quad (16)$$

Figure 4 shows the I-V plots. Current from -50nA to 50nA was applied to all the samples. The measurement results were investigated and the regions where ohmic conduction mechanism is dominant are determined.

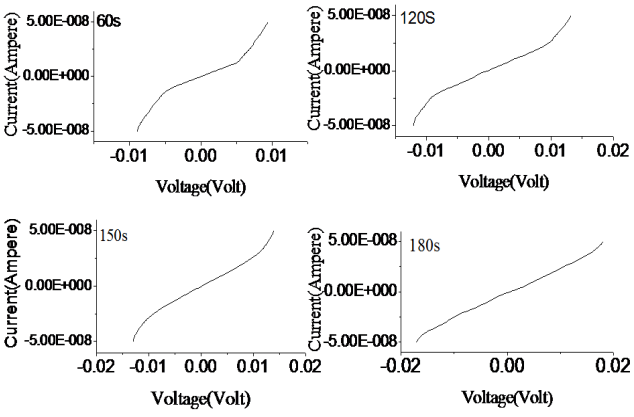


Figure 4. I-V plot of MW-CBD CdZnS thin films.

In the ohmic region, number of free carriers is higher than the injected ones from metal contact [18]. After the investigations and calculations, the resistivity values of the films were determined. Resistivity of the CdZnS thin film decreases with the increase in thickness, due to the improvement in crystallinity and grain size as is evident from the XRD results. Ran Zhai et al [14] have observed an improvement in crystallinity with the increase in deposition time for microwave assisted chemical bath deposited CdS thin films. Electrical conductivity of all the deposited films was determined to be n-type, which is in agreement with the reported results, for CdZnS thin films deposited by other techniques [4-5].

Table 3.Electrical parameters of MW-CBD CdZnS thin films.

Thickness(nm)	Resistivity (Ω-cm)	Conductivity (mho /cm)
58.23	20.93	0.047
94.2	14.31	0.069
107.4	13.27	0.075
110.2	7.44	0.134

IV. DISCUSSION

XRD analysis shows the preferred orientation along (002) diffraction peak in the deposited films. The plane (002) gives lattice matching to the chalcogenide semiconductor such as $CuInGaSe_2$, CuInSSe [5].FESEM analysis reveals the cluster-by–cluster homogenous precipitation of CdZnS. The possible deposition mechanism could be explained as follows. Metal sulphide with lower solubility product $\sim 10^{-28}$ (CdS) precipitates as a separate Phase, which absorbs both sulphide ions and Zn ions (Zn ions onto the absorbed S or onto lattice S).Eventually a shell ZnS probably containing CdS is formed as shown in figure 5. Depending on the time of microwave irradiation this core shell structure diffuses into a single phase solid CdZnS.

From EDX-composition analysis it is observed that the stoichimetric deficiency of S, which is responsible for n-type conductivity, is incorporated in CdZnS films [19]. Transmittance of the deposited films is found to decrease slightly with the increase in deposition time as a consequence of the increase in thickness of films [8]. The films with shorter deposition time have a higher transmittance at shorter wavelengths, which is desirable for enhancing the short- circuit current [20]. The films with longer deposition time could avoid damages caused by subsequent deposition of TCO layer. Therefore, optimization of buffer layer thickness is essential for improving the overall cell performance. At the same time it can be seen that the electrical resistivity of films decreases with the increase in film thickness .Similar behaviour has been observed in CdZnS thin films doped with indium [21]. As a consequence, a film thickness of 90 to 100nm (radiation time 120 to 150s) is preferred.

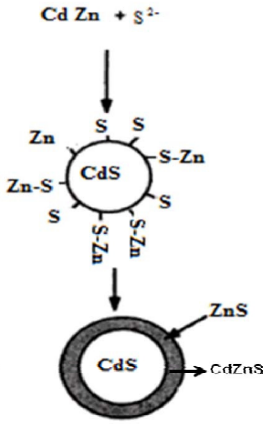


Figure 5.Deposition mechanism of CdZnS thin films

V. CONCLUSION

MW-CBD can be used to produce CdZnS thin films , in few minutes rather than hours in conventional CBD.Small particle size and uniform particle distribution is achieved by MW-CBD.XRD results indicate the presence of hexagonal structure. Thickness of the film increased with the increase in radiation time. Nanoparticles of 10-20nm is observed in the FESEM analysis. Optical studies show the transmittance of more than 80% for MW-CBD CdZnS thin films. Decrease in transmittance is observed with the increase in thickness of the film. Band gap of the deposited films is found to be around 2.6eV.Refractive index of the films increases with the increase in microwave irradiation time. Resistivity of the deposited films decreases with the increase in thickness. From the above results, we can select the radiation time of 120s to 150s to deposit a suitable window layer for the fabrication of solar cells. This is an intermediate step towards the reduced use of Cd in the n-type material for CIS based PV.

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