PHYSICAL PROPERTIES OF SUBLIMATED TERNARY COMPOUND CdZnS THIN FILMS

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Mechanically mixed Cadmium Sulphide (CdS) powder with Zinc (Zn) (99.9% purity) was used as a source material to sublimate a ternary compound of Cadmium Zinc Sulphide (CdZnS) by using Closed Space Sublimation (CSS) under high vacuum. Annealing was carried out under optimized temperature and time for better diffusion of Zn into CdS. X-ray diffraction (XRD) studies revealed that (002) was preferred orientation with hexagonal phase after annealing. Crystallite size of prepared films increased from 17 to 89 nm after annealing at higher temperatures. The surface morphology of the films was changed and the average composition of elements was confirmed by energy dispersive X-rays (EDX). The optical band gap energy increased from 2.42 eV and 2.45 eV after annealing. Electrically, the variation in mobility and increase in carrier concentration was due to the decrease of the grain boundary region. There was also variation in activation energy which confirmed the improvement in structure.

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1. Introduction

II-VI compound semiconductors are based on the elements of cadmium, zinc and mercury with the combination of sulphur, selenium and tellurium. These compound semiconductors have caused much attention for the researchers because of their use in solar cells and are known as suitable materials for photovoltaic device applications [1, 2] as they have high optical absorption co-efficients.

CdS is a member of II-VI group compound semiconductor possessing a wide band gap of 2.42 eV [3] and has been used extensively in photovoltaic as window material for the fabrication of solar cells [4-6]. This is usually n type material and also attractive for optical devices and other optoelectronic devices. This window layer absorbs the blue portion of solar spectrum causing a decrease in current density of solar cells. The replacement of CdS with an appropriate window material is necessary for the high performance of solar cells. When Zn is diffused in CdS, a ternary compound CdZnS is formed. Since CdZnS has a larger band gap than CdS therefore thin films of CdZnS can lead to a decrease in window absorption losses and has resulted in short circuit current in solar cells [7-9].

Much work has been done on physical properties of CdZnS prepared by different techniques i.e, chemical bath deposition, thermal evaporation, chemical vapour deposition and spray pyrolysis. There is very little information available about CdZnS system by closed space sublimation (CSS) technique. This system has a very simple process which produces adherent,

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uniform and stable films and economically viable than other techniques. In the present study, Cadmium Zinc Sulphide (CdZnS) thin films have been fabricated by employing CSS technique. CdZnS has been used instead of CdS by mechanical mixing of powders of CdS and Zn which is not much studied before by this single technique. Effects of annealing temperature on physical properties of CdZnS have been investigated.

2. Experimental

Cadmium sulphide (CdS) powder (99.9 % pure) was mixed with Zn powder to form a ternary compound of CdZnS. 25% Zn was mechanically mixed with CdS for CdZnS sample. Closed space sublimation (CSS) system unit was used for the preparation of films. The information about the CSS technique used in this work has been well documented before [7-17]. CdZnS powder was taken as a source material. A glass slide cleaned with isopropyl alcohol in ultrasonic bath for 30 min was used as a substrate. The amount of source material placed in graphite boat was 20 mg. The source and substrate were separated by a small distance of 5 mm and this was must to get fine quality films. The chamber was vacated up to 10^{-4} mbar by using rotary and diffusion pump. Halogen lamps of 1000 W and 500 W were used to heat directly the source and substrate respectively. K type thermocouples attached with the temperature controllers were used to measure the temperatures of graphite boat and substrate slab. A mica sheet was used as temperature gradient between the source and substrate. Vacuum gauges were used to measure the vacuum level. Source material was heated with Halogen lamp slowly up to 550 ^{o}C and substrate was heated up to 350 ^{o}C. When source temperature increases under vacuum, the deposition rate increases also [18]. The lamps were switched off when the deposition time of 3 min reached, and the chamber was cooled down to room temperature.

In the next step, the annealing process was adopted. Different sets of samples were annealed at different temperatures i.e 350 ^{o}C, 400 ^{o}C and 450 ^{o}C for 1 h and 2 h. The crystallographic properties were investigated using XPERT PRO PAN analytical spectrometer with Cu-Kα line (λ= 1.5406 Å). The surface morphological features of the deposited films were taken by using analytical low vacuum SEM, JEOL JSM-6490 A. Optical measurements were carried out at room temperature. Absorption spectra of different samples were acquired on UV-VIS-NIR using Perkin Elmer spectrophotometer LAMDA 950. Electrical properties i.e, mobility and carrier concentrations of the films were measured using Hall measurement system (HMS) and the activation energy was determined by using Arrhenius plots.

3. Results

The crystal structure of CdZnS was studied by X-rays Diffraction (XRD) technique. It was done by X-rays diffractrometer and diffraction angle ranges between 20^{o}-80^{o}. The films exhibited hexagonal phase scattering from (002), (101), (103) and (114) planes respectively as shown in Fig. 1.

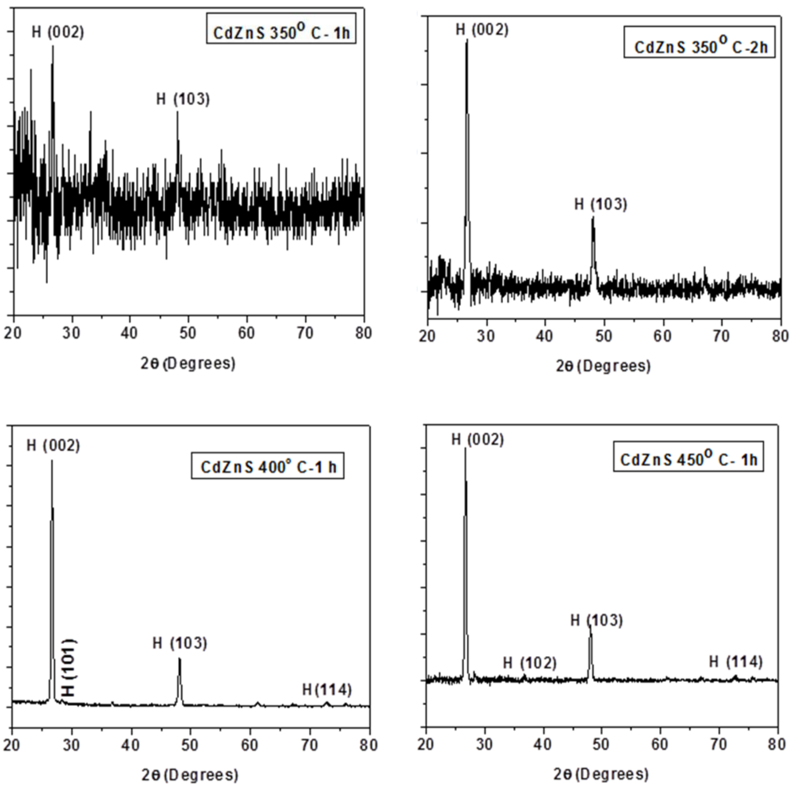


Fig. 1. XRD patterns of annealed CdZnS thin films.

The presence of sharp peaks showed polycrystalline nature of films. The peaks were matched with ICSD reference card 00-040-0834. The peak (002) was revealed as high intensive peak with preferred orientation at 26.6773^0. CZS thin films were hexagonal structured. Peaks with different intensities show different planes and crystallinity [19].

In CZS 350 ^{o}C-1h the structure was amorphous only two phases (002) and (103) were present. But when films annealed at high temperatures new phases had shown. The crystalline quality was studied with crystallite size determined by Scherrer formula [20].

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where λ = wavelength, β = full width at half maximum (FWHM) and θ = Bragg's angle.

The dislocation density and Strain of thin film ($\mathcal{E}$) were calculated using $\frac{1}{D^2}$ [21] and $\frac{\beta\cos\theta}{4}$ respectively. Crystallite size of CZS thin films was about 17 nm which increased to 89 nm after annealing; results are reported [22]. The dislocation density and strain decreased as clear from table 1 which showed the improvement in crystalline structure of the films.

Table 1. Structural parameters of CdZnS thin films.

Samples	Crystallite Size D (nm)	Dislocation Density ($x10^{-4}$ nm^{-2}) ± 0.01	Strain ($x10^{-4}$) ± 0.01
CZS 350^o C-1h	17	40	20
CZS 350^o C-2h	26	10	10
CZS 400^o C-1h	48	4	7
CZS 450^o C-1h	89	1	4

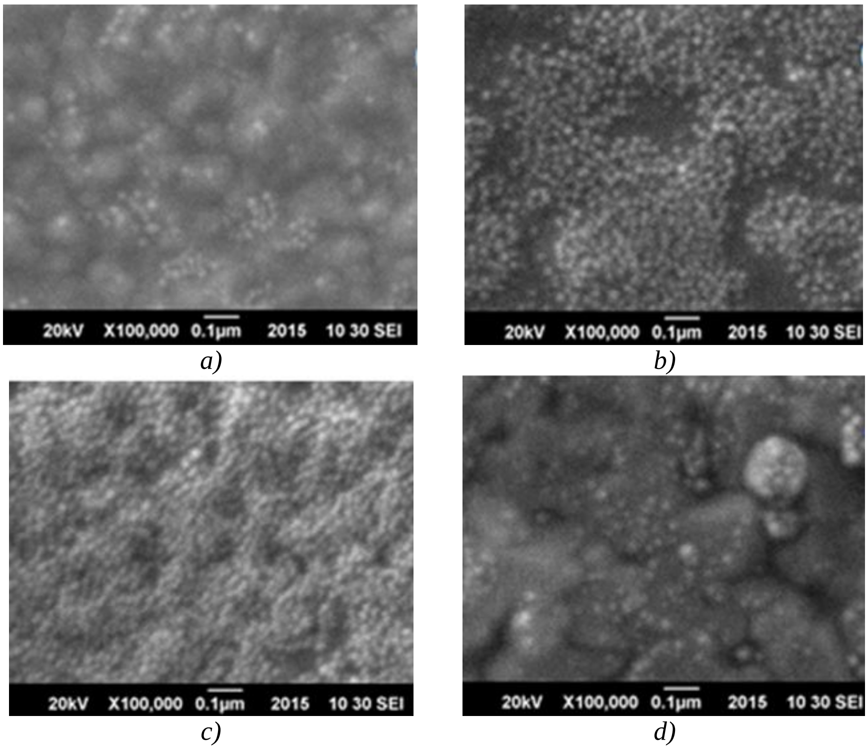


Fig. 2. SEM micrographs of (a) CdZnS 350^{o}C-1h (b) CdZnS 350^{o}C-2h; (c) CdZnS 400^{o}C-1h (d) CdZnS 450^{o}C-1h.

The SEM is a technique used to study the surface of the material. Fig 2 gives us the information about morphology of CdZnS films with different temperatures. SEM images confirmed that small grains were in cluster form. Small grains merged into large grains after annealing at high temperatures. The merging of small grains into large grains is called Coalescence. The roughness of thin films was reduced to some extent after annealing and smoothness in the films was present. It was good for window layer material.

It was clear from EDX study in Table 2 that Zn diffused in the surface of the material in sample 350 ^{o}C-1 h. In sample 450 ^{o}C-1 h, the movement of Zn atoms increased when more energy was provided. An excess amount of Zn was re-evaporated at higher annealed temperature.

Table 2. EDX of CZS.

Samples	% of S	% of Zn	% of Cd
CZS 350^o C-1h	46.75	3.7	49.54
CZS 350^o C-2h	46.82	2.59	50.59
CZS 400^o C-1h	47.58	2.27	50.15
CZS 450^o C-1h	46.12	1.33	52.54

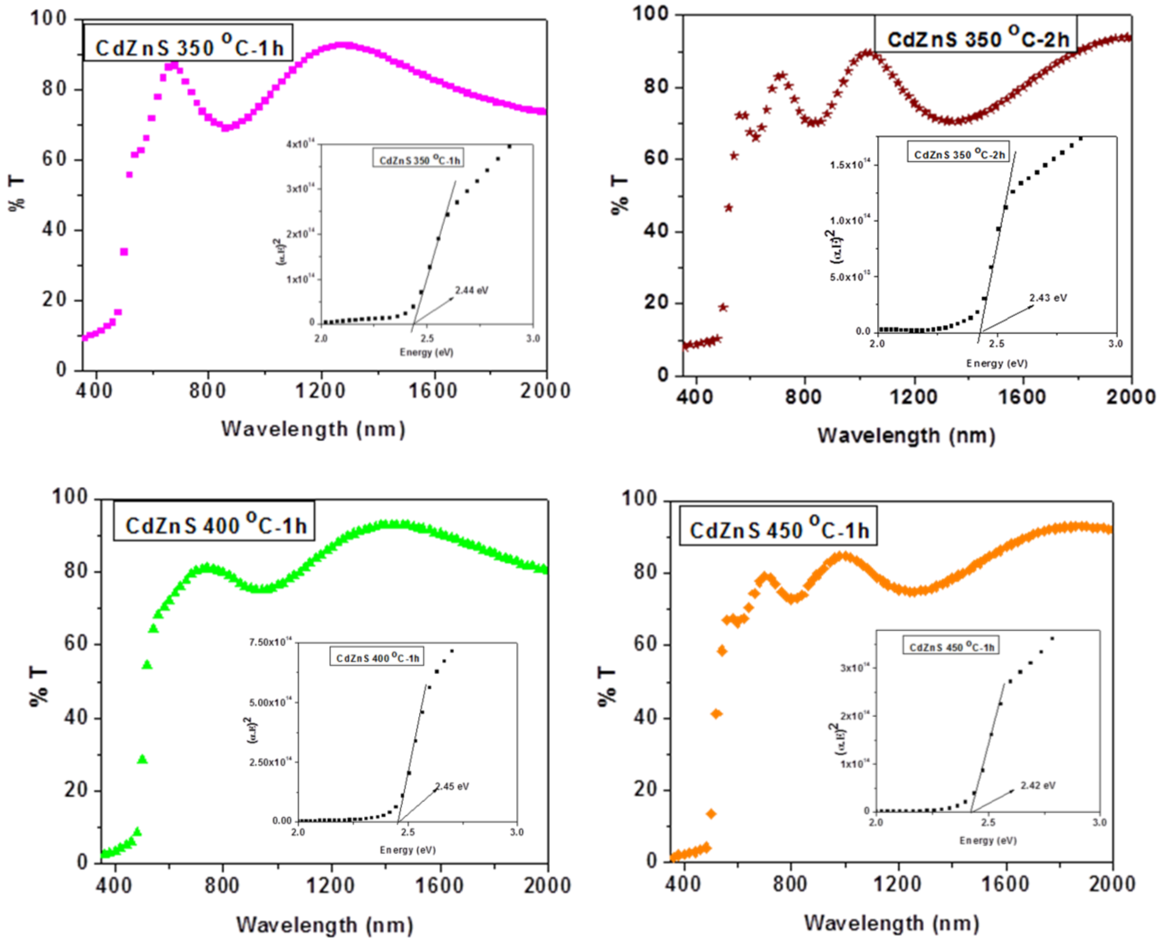


Fig. 3. Transmittance vs. Wavelength of different temperature annealed CdZnS thin film samples.

Fig. 3 shows Transmission (%T) vs wavelength of CdZnS thin films with different annealing temperatures. The transmission of samples was made in range of (UV-VIS-NIR) 300 nm to 2000 nm. These spectra indicated the annealing effects of temperature on optical parameters like optical thickness, refractive index, band gap energy and absorption co-efficient etc[23]. A sudden fall due to the absorption edge was observed in peak position below 500 nm wavelength. The variations of transmission affected the optical properties because of the trapping of light. CZS films were transparent in the visible region but these were more transparent in IR region.

A graph was plotted between $(\alpha\ E)^2$ and Energy ($h\upsilon$). Tauc's relation was used to calculate energy band gap of the samples.

$$(\alpha h\upsilon) = A\ (h\upsilon - E_g)^{m}$$

Optical transmission can be written by using the Swanpoel formula [24].

$$T = \frac{AX}{B - CXCos\emptyset + DX^2}$$

$A = 16n^2S$, $B = (n+1)^3\ (n+S^2)$, $C = 2(n^2 - 1)\ (n^2 - S^2)$, $D = (n-1)^3\ (n-S^2)$, $\emptyset = \frac{4\pi . nd}{\lambda}$, $X = e^{-\alpha . d}$

The refractive index n is calculated by

$$n = \frac{\left[N + (N^2 - 4S^2)^{\frac{1}{2}}\right]}{2}$$

where
$$N = 1 + s^2 + 4s\left(\frac{T_M - T_m}{T_M T_m}\right)$$

Thickness d is determined by the relation

$$d = \frac{1}{4n}\left[\frac{\lambda_m \lambda_M}{\lambda_M - \lambda_m}\right]$$

Table 3. Optical parameters of CdZnS thin films.

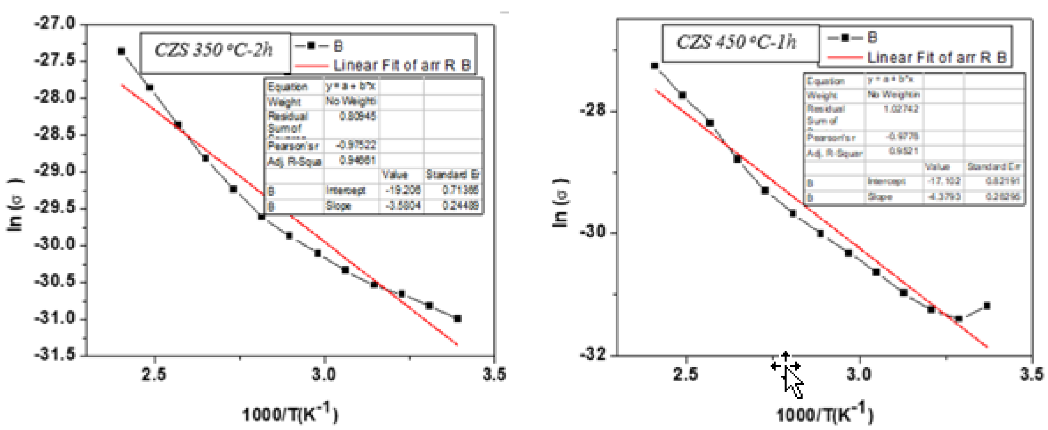
Samples	Band Gap E_g ±0.01 (eV)	Refractive Index n ± 0.01	Optical Thickness d (nm)
CZS 350 ^{o}C-1h	2.44	2.32	310
CZS 350 ^{o}C-2h	2.43	2.19	515
CZS 400 ^{o}C-1h	2.45	2.13	282
CZS 450 ^{o}C-1h	2.42	2.02	505

Table 3 shows the variation in refractive index and band gap due to increase of temperature. The variation was also observed in optical thickness. The energy band gap of CdZnS thin films was increased from 2.42 to 2.45 eV. These results are in agreement as reported by W. Mahmood and N. A. Shah [13].

The increase in electrical conductivity can be attributed to grain size effect, order and increase in the carrier concentration. The grain size increases when samples are annealed at higher temperature. The carrier type was electron in CdZnS films. It is observed that carrier concentration increases with the increase in temperature which means the crystallinity improved [25]. The nonlinear increase of electrical conductivity of films followed by an Arrhenius' equation,

$$\sigma = \sigma_o\, e^{\frac{-Ea}{KT}}$$

σ is a temperature dependent quantity, σ_o pre-exponential factor, K_B Boltzmann Constant, T temperature in kelvin and Ea is activation energy of electrical conduction. Fig. 4 shows the graph between *ln* (σ) and 1000 / T giving slope of figure as activation energy.



a) b)

Fig. 4. Variation of ln (*σ*) *versus 1000 / T of (a) CZS 350 ^{o}C-2h (b) CZS 450 ^{o}C-1h.*

Table 5. Activation energy of CZS at different annealing temperatures.

Samples	Activation Energy ± 0.001 (eV)	Standard Error
CZS 350 ^{o}C-1h	- 3.95	0.719
CZS 350 ^{o}C-2h	- 3.58	0.245
CZS 400 ^{o}C-1h	- 4.63	0.501
CZS 450 ^{o}C-1h	- 4.38	0.283

Table 5 shows the value of activation energy determined from the slope of the graphs for different samples. Variation in activation energy occured when the samples annealed at high temperature for more time. The variation in activation energy confirmed the improvement in structure. The results show same behavior as reported by A. Hasnat and J. Podder [26].

4. Discussions

Amorphous structure was found in low annealing temperature of CZS thin films. CZS annealed at 350 ^{o}C with one hour showed only two phases of (002) and (103). The annealing temperature increased upto 400 ^{o}C for one hour and the new phases of (102) and (114) appeared. The crystallite size, Dislocation density and Strain varied accordingly. For the plane of 002) the size of crystallite was 17 nm it was further increased upto 89 nm for higher annealing temperature. The dislocation density decreased from 40 to 1 (x10^{-4} nm^{-2}) and strain is also reduced from 20 to 4 (x10^{-4}).

SEM micrographs showed the smaller grains were in clusters and annealing temperature influences the small grains and coalescence occurred and grains became larger in size. Annealing also showed a significant role on surface roughness which was reduced after subsequent annealing. It was clear from EDX study that Zn was diffused in the surface of the material in sample 350 ^{o}C-1 h. In sample 450 ^{o}C-1 h, the movement of Zn atoms increased as more energy was provided. When annealing temperature increased an excess amount of Zn was re-evaporated. The energy band gap of CdZnS thin films was increased from 2.42 to 2.45 eV. Carrier concentration increased from 1.28 x 10^{15} cm^{-3} to 1.65 x 10^{16} cm^{-3} showing that crystallinity improved. The variation in activation energy was due to the increase in energy band gap after annealing. It is good for window layer material.

5. Conclusions

Synthesized CZS thin film samples were examined by structural analysis, surface morphology, optical and electrical properties. In XRD pattern, the structure was hexagonal and CZS films were polycrystalline having preferred orientation with planes (002). Increasing of Crystallite size from 17 nm to 89 nm indicated that crystallinity improved. EDX study showed that maximum amount of Zn was 3.7 % in CZS 350 ^{o}C-1h.

The band gap energy varied between 2.42 eV and 2.45 eV and this variation confirmed the direct band gap. Carrier concentration increased from 1.28 x 10^{15} cm^{-3} to 1.65 x 10^{16} cm^{-3}. An increase in conductivity attributed to the fact that defects removed and Carrier concentration increased. It was also observed that activation energy was 3.58 eV. This indicated that CZS film annealed at different temperatures is suitable as a window layer for solar cells. The results supported the deposition of thin films by a single technique CSS.

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