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EFFECT OF ANNEALING ON THE SURFACE AND OPTICAL PROPERTIES OF ZnCdS NANOCRYSTALLINE THIN FILMS

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Zinc cadmium sulphide (ZnCdS) is a ternary II-VI semiconducting material. ZnCdS nanofilms can be developed by chemical bath deposition using non aqueous medium. It is important for the window material in solar cells, photoconductors, optical waveguide etc. The ZnCdS film is deposited on molybdenum substrate using $CdCl_2$, $ZnCl_2$ and thiourea in ethylene glycol. The prepared ZnCdS nanofilm was annealed at 400^0C. The influence of annealing on the solid state and optical properties of the films were studied by XRD, FESEM, EDS, AFM, UV-VIS, PL. The crystallite size of the as deposited and annealed ZnCdS films are estimated to be 36nm and 41nm using the Scherrer's formula. According to Tauc theory the bandgap of ZnCdS thin films were determined. Compositional analysis peaks indicates the presence of Zn, Cd and S. The surface roughness of both the films is observed to be 127 nm and 39 nm.

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1. Introduction

II-VI semiconducting materials are valuable due to their applications in various fields of science and technology. Ternary ZnCdS semiconducting material is one of them. ZnCdS semiconductor is used as a larger energy bandgap in heterojunction solar cells [1-3] and in photoconductive devices [4]. Binary CdS semiconductor has bandgap 2.4eV. Addition of Zn into CdS leads to variable energy bandgap 2.4eV – 3.7eV which is dependent on the Zn:Cd ratio. Therefore, the material much more attractive for the fabrication of solar cells. In solar cell systems, the replacement of CdS with the higher bandgap ZnCdS led to a decrease in window absorption losses, and has resulted in an increase in the short circuit current density in the solar cell [5-11].The ZnCdS compound is also useful as a window material for the fabrication of p-n junction without lattice mismatch in the devices based on materials like CdTe or $CuIn_xGa_{1-x}Se_2$ [12]. ZnCdS thin films have been prepared by various techniques such as spray pyrolysis [13-14], ion beam deposition [15], molecular beam epitaxial growth [16], vaccum evaporation, chemical bath deposition etc. Among these deposition techniques, CBD is simple, cheap and easy coating of large surface area deposition of material. Nanocrystalline ZnCdS thin film can be prepared by CBD techniques in non-aqueous medium. Non-aqueous bath offer greater flexibility in choosing deposition sources, higher working temperature ranges and also free from the ubiquitous hydrogen evolution reaction which is often a nuisance in producing stress and pinhole free deposits [17]. The ZnCdS as deposited nanoparticles is annealed at 400^0C.

In this paper, we have reported that the effect of annealing on the prepared ZnCdS thin films deposited on molybdenum substrate by CBD in non-aqueous medium. The as-deposited as well as annealed ZnCdS films were grown and characterize to study the crystal structure, surface

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morphology, compositional analysis of the film, surface roughness, optical bandgap and emission spectra of the films.

2. Experimental Procedure

The electrolyte was prepared by using AR grade 0.2M $CdCl_2$, 0.12M $ZnCl_2$ dissolved in 40ml of ethylene glycol. The electrolyte was two hours continuously stirring and temperature maintained at 160^0C. With the help of rigid support, molybdenum substrate having dimension 1.5cm×1cm×0.1cm was dipped into the electrolyte and 0.4M thiourea was introduced into the electrolyte. The electrolyte was again continuously stirring and deposited for 15 minutes on the molybdenum substrate. The prepared as-deposited ZnCdS film was annealed at 400^0C in air.

The crystallographic structure of ZnCdS as deposited and annealed films was analysed by Bruker AXS Diffractometer model D8 with CuK_α wavelength 1.54 A^0. The average grain size of as deposited and annealed ZnCdS films were obtained by using Debey- Scherrer's formula. Surface morphology and elemental analysis of the films were characterized by using Field Emission Scanning Electron Microscope model Quanta 200F, FEI Netherland. An absorption spectra was collected by UV-VIS spectrophotometer model Lambda-25Perkin-Elmer with the wavelength range300nm–900nm. Using Atomic Force Microscope analysis model Nano Surf EZ2, AFM Instrument, Switzerland was determined the surface roughness of the as deposited and annealed ZnCdS samples. PL studies of both the films were carried out with the help of spectrophotometer model-RF 5301PC,Shimadzu with wavelength range 300nm – 800nm.

3. Results and discussion

3.1 Structural characterization

The as deposited ZnCdS films deposited on Mo substrate are physically stable and shows good adhesion. Figure 1(a) shows XRD pattern of as deposited ZnCdS thin film and the annealed ZnCdS thin film is carried out in the range of 20-90 degree. It is observed that the as deposited ZnCdS thin film indicates that the exhibited peaks located at $2\theta=26.72^0$ and 87.90^0 arise on the spectra and the peaks are identified as (002) and (302) diffraction planes of the crystalline hexagonal structure. Reflections due to molybdenum substrate, the subsequent peaks are attributed to the scattering from (110), (200) and (211) planes. When ZnCdS thin film was annealed at 400^0C, the characteristic peaks appeared at 28.48° and 87.96^0 as shown in figure 1(b).

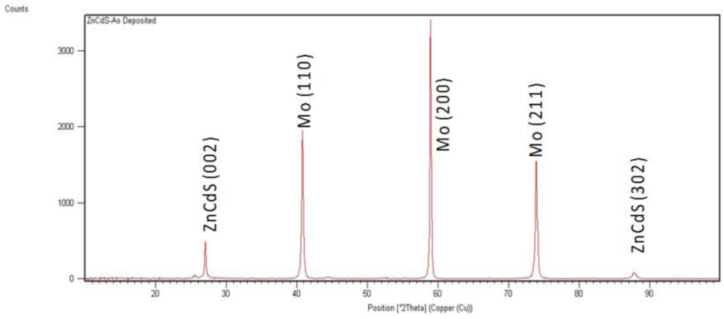

Fig. 1(a) XRD Spectra of As deposited ZnCdS Thin Film

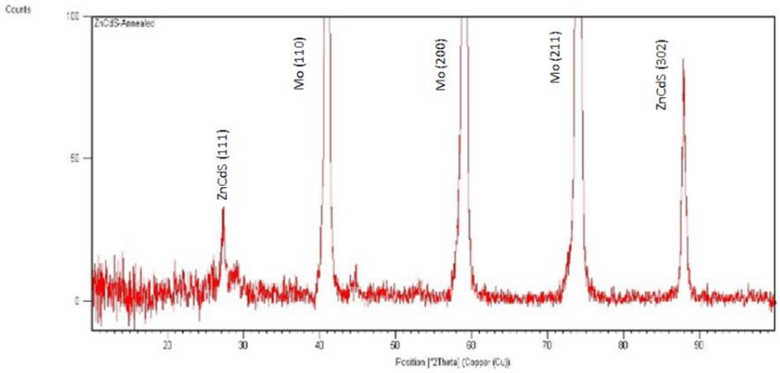

Fig. 1 (b) XRD Spectra of Annealed ZnCdS Thin Film

The Scherrer's relation was used to calculate crystallite size of the as deposited and annealed ZnCdS thin films [18].

$$D= 0.94\lambda /\beta \mathrm{Cos}\theta$$

Where, λ = Wavelength of incident X-ray (=1.54A°)
β = Full width at half maxima of (002) peak in radian
θ = Diffracted angle

The microstrain developed in the films are calculated from the equation below [19]

$$\text{Microstrain } (\varepsilon) = (\beta \cos\theta)/4$$

The calculated crystallite size of the as deposited and annealed ZnCdS thin films was 36 nm and 41 nm respectively. The increase in average grain size due to annealing clearly indicates the crystallinity improves. The increase in average grain size decrease the grain boundaries and thus reduce the recombination center at the grain boundaries. The calculated 2θ, d values, miller planes and average crystalline size, microstrain of the as deposited and annealed ZnCdS thin films are shown in table 1 and 2 respectively. The micro-strain is decreased in the case of annealed film also supports the recrystallization process in polycrystalline material. Due to annealing of film the dopant zinc segregate at the grain boundaries which further help to reduce the recombination at grain boundaries.

Table 1 shows the observed 2θ, d and miller planes of as deposited and annealed ZnCdS respectively.

		Observed Value			**Standard Value**		
Sl. No.	Compound	2 Theta (2θ)	"d" value	Miller Indices	2 Theta (2θ)	"d" value	Miller Indices
1.	ZnCdS (Asdeposited)	26.72	3.42	(002)	26.48	3.36	(002)
2.	ZnCdS (Annealed)	28.42	3.13	(111)	28.20	3.16	(111)

Table 2. Average crystalline size ,microstrain of asdeposited and annealed ZnCdS films

Sl. No	Compound	FWHM (degree)	Average Crystalline Size	Micro-strain (X 10^{-3})
1.	ZnCdS (Asdeposited)	0.2378	36 nm	1.008
2.	ZnCdS (Annealed)	0.2080	41 nm	0.882

3.2 Surface Morphology and Energy Dispersive Spectroscopy (EDS) Analysis

Figure 2 (a) and (b) shows the surface morphology of the as deposited and annealed ZnCdS film using FESEM. 15000 magnification is taken for the FESEM photograph. The microstructure of the as deposited film indicates that the surface was smooth and equal sized uniform spherical grains are distributed either in single state as well as in cluster forms. However, annealed at 400^0C, surface morphology of the film was changes. From figure we conclude that the distribution of grains on the film surface was more compact and have dense in cluster forms which indicates the improved crystalline quality of the ZnCdS film.

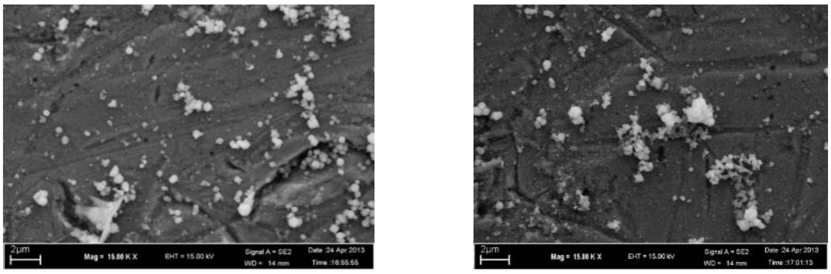

Fig.2(a) FESEM micrograph of as deposited ZnCdS thin film (b) FESEM micrograph of annealed ZnCdS thin film

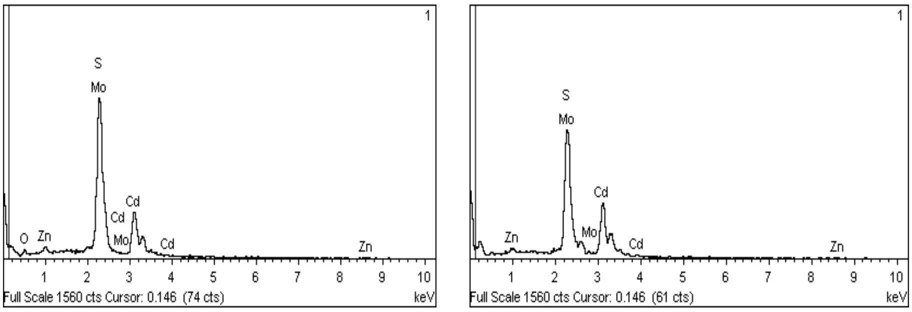

Fig.3(a) EDS spectrum As deposited ZnCdS thin film , (b) EDS spectrum Annealed ZnCdS thin film

Table 3 shows the atomic percentage and weight percentage of as deposited and annealed ZnCdS thin film

As deposited ZnCdS				Annealed ZnCdS		
Element	Wt %	Atomic %		Element	Wt %	Atomic %
S	16.58	38.89		O	5.71	23.68
Zn	3.01	3.46		S	9.92	20.52
Mo	33.31	26.12		Zn	2.95	2.99
Cd	47.10	31.53		Mo	46.91	32.44
Totals	100.00			Cd	34.51	20.37
				Totals	100.00	

Film composition of ZnCdS thin film was evaluated using EDS. ZnCdS thin film composition as a function of $CdCl_2$ and $ZnCl_2$ concentration in the chemical bath deposition solution. The ZnCdS film is deposited on the molybdenum substrate. The elemental Zn, Cd and S peaks arise in the spectra satisfied that the prepared ZnCdS films are composed of Zn, Cd and S on the molybdenum substrate. It is clearly shows that the sulphur peak overlap with the molybdenum substrate. Zn and Cd stoichiometry was calculated using EDS. The atomic percentage and weight percentage of Zn, Cd and S are given in table 3. It is observed that the as deposited ZnCdS film is sulphur rich but in case of annealed ZnCdS film, the ratio of atomic percentage of Cd and S are observed to be nearly equal to 1.0. There is a considerable loss of sulphur after annealing the ZnCdS thin film which is also very well matched with earlier reported result[20].

3.3 Surface Roughness of ZnCdS thin films

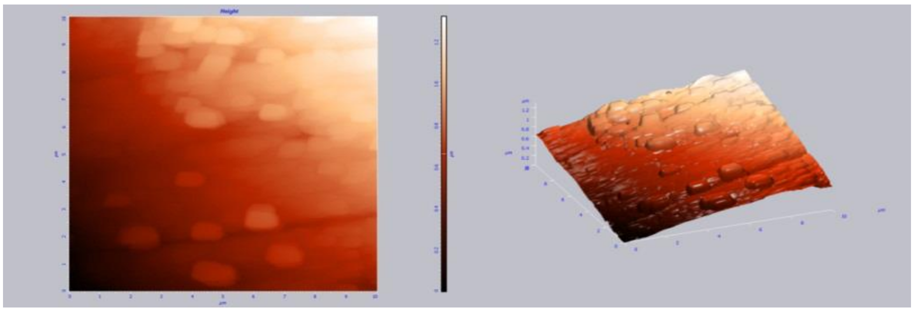

Fig.4 (a) AFM image 2D as deposited ZnCdS film (b) AFM image 3D as deposited ZnCdS film

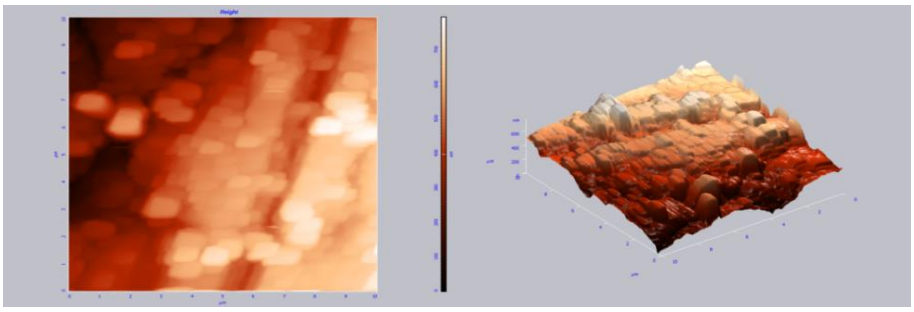

Fig.5 (b) AFM image of 2D annealed ZnCdS film (b)AFM image of 3D annealed ZnCdS film

From figure 4. (a), (b) and 5. (a), (b) shows AFM photographs of as deposited ZnCdS and annealed ZnCdS films in two dimension and three dimension. The variation of the surface roughness was observed at different temperatures. The root mean square (RMS) roughness, grain size and surface morphology of the films are studied. The as deposited ZnCdS films are observed to have small grains, uniform grain size and number of voids which indicates that the characteristics of the film is less crystalline [21]. The RMS roughness is estimated to be 127nm. The RMS roughness represents the standard deviation between the height of topographic feature and the mean feature height. But annealed at 400^{0}C, the films are smooth, crystallinity increases and roughness decreases to 39nm.

3.3 Optical Study

UV-visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum-sized particles. We know that ZnCdS is considered as direct band gap semiconductors. According to Tauc theory, the absorption coefficient (α) on the photon energy (hν) take the following relation [22]

$$(\alpha h\nu)^{1/m} = A\ ((h\nu - E_g)$$

Where, E_g is the optical band gap

A is a constant
m=1/2 for direct type of transition.

Fig. 6(a) and (b) shows optical absorption spectra of ZnCdS thin film in as deposited and annealed case which is plot of $(\alpha h\nu)^2$ vs hν and the band gap, Eg of ZnCdS is obtained by extrapolation of the curve for $(\alpha h\nu)^2 = 0$. The energy band gap is found to be 2.45 eV in as deposited case and 2.52 eV in annealed case [21].

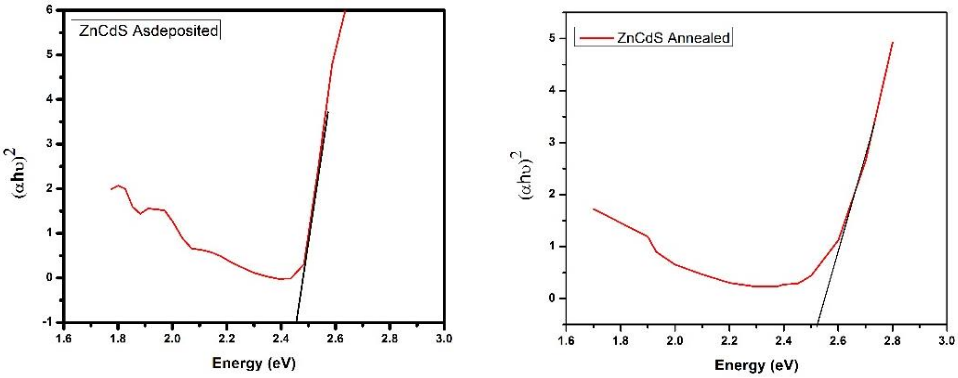

Fig.6 (a) Band gap of as deposited ZnCdS film (a) Band gap of annealed ZnCdS film

The band gap shift depends on the intrinsic defects in the ZnCdS films, change in zinc concentration, large density of dislocations etc due to annealing. In both the cases the measurement of band gap indicates the semiconductor behavior.

3.4 Photoluminescence Spectra Study

Further we carried out photoluminescence study to know the optical behavior of as deposited ZnCdS film and annealed ZnCdS film. Figure7 (a) and (b) Shows the photoluminescence spectra of ZnCdS as deposited and annealed thin film. As evident from figure the as deposited ZnCdS film shows a sharp emission intensity at 380 nm along with broad emission at 490 nm. From the respective photoluminescence spectra of annealed ZnCdS film it was observed that the peak at 380 nm is not well splited into two new peaks at 419 and 435 nm.

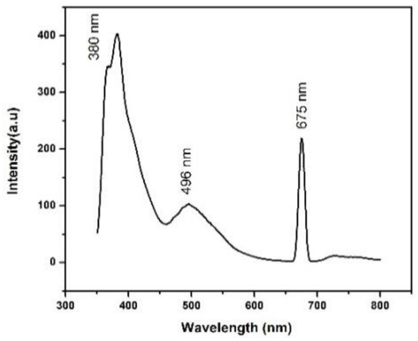

Fig. 7 (a) PL of as deposited ZnCdS film

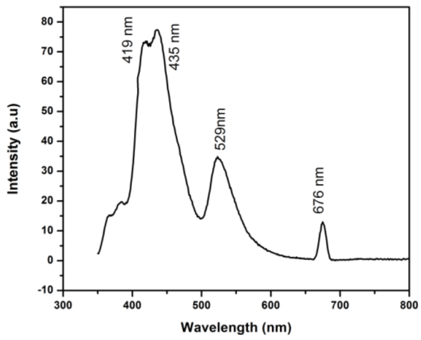

Fig. 7 (b) PL of annealed ZnCdS film

The yet another broad peak of asdeposited ZnCdS film at 496 nm was red shifted to at 529 nm for annealed ZnCdS film. Thus the change rebuild that after annealing the film, energy increases and annealed ZnCdS films are over stabilized incomparision to as deposited film. The broaden in emission peaks was due to the particle size distribution of ZnCdS nanocrystalline thin films [23-25].

4. Conclusions

Nanocrystalline ZnCdS thin film is deposited by using $CdCl_2$, $ZnCl_2$ and thiourea over molybdenum substrate by chemical bath deposition using non aqueous medium. The as deposited and annealed films were characteristised by XRD, FESEM,EDS, AFM, UV-VIS and PL. The XRD results shows that ZnCdS thin films are hexagonal structure with (002) plane which is related to nucleation of the reaction deposition. EDS analysis showed that sulphur is rich in as deposited film but the ratio of atomic percentage of Cd:S are observed to be nearly equal to 1.0.

Using Tauc theory, energy band gaps of the ZnCdS samples vary from 2.45 and 2.52 eV. When the temperature increases the value of surface roughness decreases from 127.745nm to 39.78nm. PL spectra exhibited an increase in peak position for annealing at 400^0C. The ZnCdS film presented have good characteristics to be used as for window layer solar cell materials, sensor applications, photovoltaic, etc.

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