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EFFECT OF Zn CONCENTRATION ON THE STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF TERNARY ZnCdS NANOCRYSTALLINE THIN FILMS

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A technological challenge is to develop a ternary semiconductor ZnCdS thin film by controlling the concentration of Zn changes (X=0.2, 0.3, 0.4 and 0.5) in non aqueous medium that allows us to tune the band gap energy between 2.54 – 2.85 eV. In this paper, ZnCdS (X = 0.2, 0.3, 0.4 and 0.5) films were deposited on molybdenum substrate containing $ZnCl_2$, $CdCl_2$, thiourea in 40ml of ethyleneglycol. The optimal bath temperature was maintained at 160 ^{0}C. The structural, morphological, compositional analysis and optical properties of different concentration of deposited ZnCdS thin films were studied by XRD, FESEM, EDS, UV-VIS, PL and FTIR. X-ray diffraction study showed that all the films have wurtzite structure with (002) plane. Grain size has been calculated by using Scherrer formula and is to be 30nm to 23nm. With increase in Zn concentration the optical energy band gap of ZnCdS films varied from 2.54eV to 2.85eV and photoluminescence emission at around 350 nm and 550 nm.

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Keywords: Concentration, Optical, Structural, Thin films, ZnCdS etc.

1. Introduction

Nanocrystalline II-VI semiconductor materials have more interest due to their easy synthesis in the required size, possess large number of surface atoms. Now, a days, there is an attentation in chalcogenide based ZnCdS semiconducting materials widely used in heterojunction solar cells [1-3] and in photoconductive devices [4].Ternary ZnCdS materials are useful for the production of flat panel display, electroluminescent and field emission devices [5,6]. As the Zn content into CdS material, ZnCdS semiconductor is developed which have the properties lies in between ZnS and CdS [7], the optical band gap of ZnCdS also changes from 2.4eV – 3.7eV which is dependent on the Zn:Cd ratio [8]. By comparison to the binary semiconductor, the band gap of the ZnCdS film is tuned by changing percentage of the composition. Many techniques have been reported for the ZnCdS thin film deposition such as metal organic chemical vapour deposition [9], spray pyrolysis, sputtering, electrodeposition, vaccum evaporation, chemical vapour deposition, chemical bath deposition (CBD), etc [10-13]. Among these deposition techniques, CBD has the following advantages: i) Simple ii) Cheap iii) Uniform particle size distribution iv) Easy coating of large area deposition material. Nanocrystalline ZnCdS thin film can be prepared by CBD technique 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 [14].

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With this aim in the current work, we study ZnCdS thin films fabricated by CBD technique in non-aqueous medium with different Zn concentration (X= 0.2, 0.3, 0.4, 0.5) and the effect of Zn doping on the structural, morphological, and optical properties have been investigated. It is able to clearly understood that the effect of concentration of Zn on the growth mechanism of the ZnCdS film.

2. Experimental Procedure

The electrolyte was prepared by using AR grade 0.2M $CdCl_2$, 0.12M (X) $ZnCl_2$ dissolved in 40 ml of ethylene glycol. The temperature of the electrolyte was maintained at 160°C. The electrolyte was aged for two hours. The deposition was carried out under continuous stirring. The polished and thoroughly washed molybdenum substrate having dimension1.5cm×1cm×0.1cm was dipped inside the electrolyte with the help of rigid support. After loading the sample 0.4M thiourea was introduced in the electrolyte. The electrolyte was moderately stirred and deposited for 15 minutes. From this process different Zn-concentration [$X=ZnCl_2/CdCl_2 + ZnCl_2$] was varied in the range from 0.2 to 0.5. The as deposited films were uniform free from pin holes, pits, voids etc.

The crystallographic structure of the films was analyzed by Bruker AXS Diffractometer model D8 with CuK_α radiation (λ = 1.54Å), current =40mA, voltage =45KV, scanning angle (15^0-90^0) with scanning rate of 3^0 min^{-1}. Surface morphology and elemental analysis of the films were characterized by using FESEM model Quata 200F, FEI Netherland. The optical properties were measured by UV-VIS Spectrophotometer model Lamba-25 Perkin-Elmer with the wavelength range 300nm-900nm. PL studies were carried out by spectrophotometer model –RF5301 PC, Shimadzu with wavelength range 300nm - 800nm.

3. Results and Discussion

The as deposited ZnCdS film with varying concentration of Zn (X= 0.2M,0.3M,0.4M,0.5M) are deposited on Mo substrate. The films are physically stable and show good adhesion. The X-ray diffraction spectra of different concentration from Zn doped ZnCdS (X=0.2, 0.3, 0.4 and 0.5) as-deposited films are shown in figure 1.

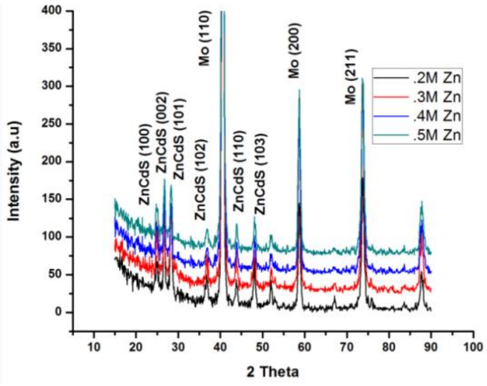


Fig1. XRD spectra of asdedpositedZnCdS film with different concentrations (X= 0.2M, 0.3M, 0.4M, 0.5M)

The XRD pattern indicates that all the as-deposited concentration change Zn doped ZnCdS films exhibits peaks attributed to (002) plane with reflection at 2θ =26.76° shows that the films have hexagonal structure and its intensity increases with the increase of Zn composition in the films. All the varying Zn content ZnCdS films have same caharacteristics and show the same preferential orientation. XRD spectra data gives the information that the concentration changes

ZnCdS (X=0.2, 0.3, 0.4 and 0.5) as-deposited films have cubic and hexagonal structure exhibits peaks corresponds to (100), (002), (101), (102), (110) and (103) planes with reflections at $2\theta = 24^0, 26^0, 28^0, 36^0, 43^0$ and 48^0 respectively. Reflections due to molybdenum substrate, the subsequent peaks attributed to the scattering from (110), (200) and (211) planes of ZnCdS. The average grain size (D) of varying Zn content ZnCdS films were calculated using the Scherrer formula $D = 0.94\lambda/\beta \cos\theta$ Where, β is the full width at half maxima (FWHM), λ is the wavelength of the X-ray ($1.542A^0$) and θ is the angle of diffraction[15].It is observed that the grain size value (D) decreases with increasing Zn content in the films which are shown in table 1.Micro-strain (Ɛ) developed in varying Zn content films were calculated by using the following relation [16].

$$\mathcal{E} = \beta\cos\theta/4$$

Table 1. Shows the value of 2θ (XRD), d spacing (XRD), FWHM (XRD), Grain size (nm), hkl plane and calculated micro-strain (Ɛ)

Varying Zn concentration $X = ZnCl_2/(CdCl_2 + ZnCl_2)$	2θ degree (XRD)	'd' Spacing (XRD)(Å)	FWHM (XRD) °/Radian	Grain Size (XRD) nm	Plane (hkl)	Micro-strain (10^{-3})
0.2	26.6428	3.34312	0.2789	30	002	0.678
0.3	26.6464	3.34268	0.2941	29	002	0.715
0.4	26.7067	3.33527	0.3038	28	002	0.738
0.5	26.6845	3.33799	0.3689	23	002	0.897

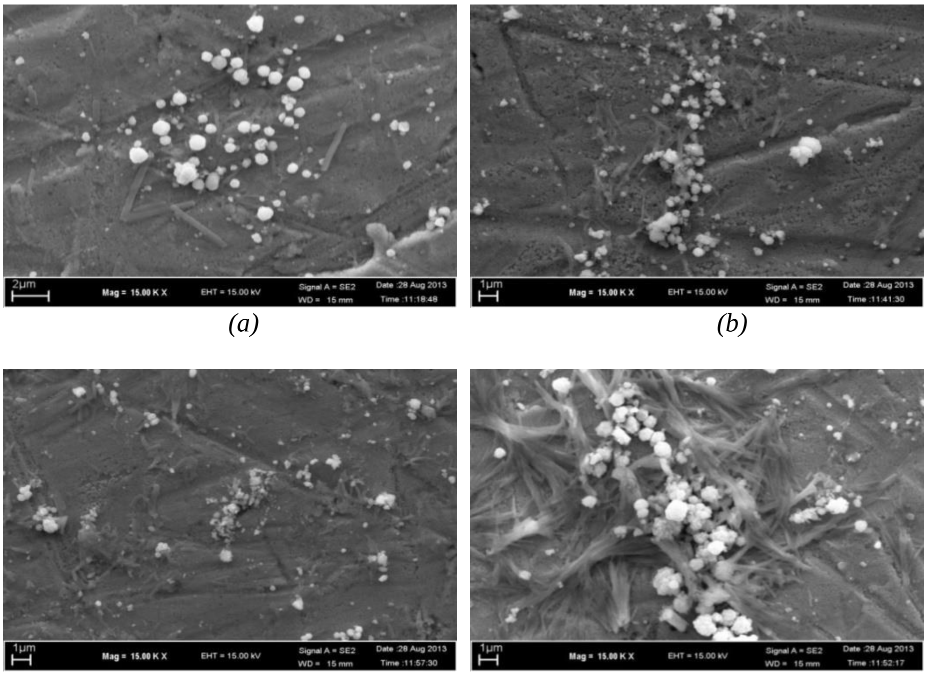
The relative percentage error for the observed and standard values for all the varying Zn concentration films were calculated by using the formula [17]-

Relative percentage error $=|Z_H - Z|\times 100/Z$
Where, Z_H is the observed'd' value
Z is the standard'd' value

Table 2. Comparison of standard and observed 'd' spacing values of varying ZnCdS thin films using JCPDS file No.41-1049.

Plane (hkl)	Standard 'd' values Å	Zn Concentration (X= 0.2, 0.3, 0.4 and 0.5)							
		X= 0.2		X= 0.3		X= 0.4		X= 0.5	
		Observed 'd' values Å	d% error	Observed 'd' values Å	d% error	Observed 'd' values Å	d% error	Observed 'd' values Å	d% error
(100)	3.586	3.577	0.25096	3.575	0.30673	3.569	0.46010	3.572	0.39039
(002)	3.359	3.343	0.50001	3.342	0.51489	3.335	0.73514	3.337	0.65478
(101)	3.163	3.154	0.306593	3.153	0.32871	3.150	0.42038	3.151	0.39825
(102)	2.451	2.446	0.23655	2.442	0.37521	2.441	0.43231	2.432	0.77898
(220)	2.058	2.065	0.37900	2.062	0.23809	2.063	0.28182	2.069	0.53449
(103)	1.899	1.892	0.40004	1.892	0.36845	1.889	0.52110	1.891	0.42636

The surface morphology using FESEM of as deposited Zn doped CdS films with varying concentration are shown in Fig. 2(a,b,c,d).The magnification was fixed 15000X in all the concentrations. The surface morphology of ZnCdS is found to be very similar as that of CdS.



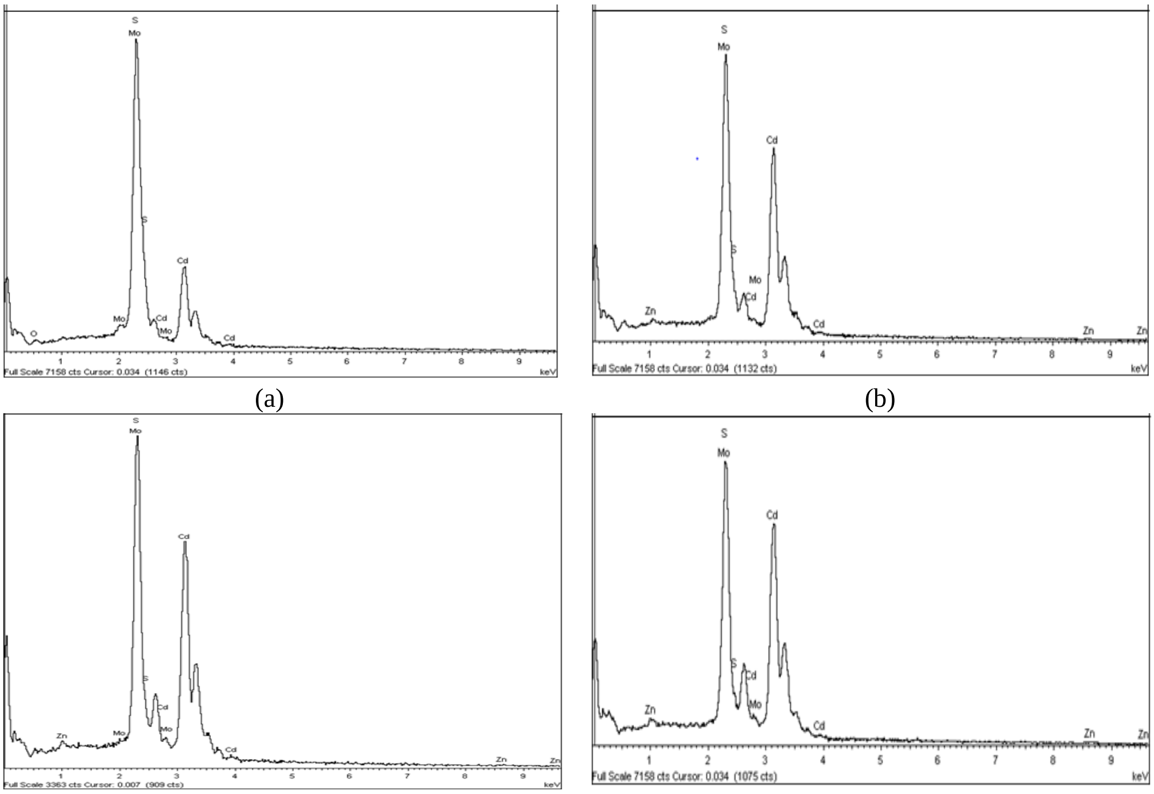
(a) *(b)*

(c) *(d)*

Fig. 2(a) FESEM image of 0.2M Zn doped CdSfilm ; (b) FESEM image of 0.3M Zn doped CdS film; (c) FESEM image of 0.4M Zn doped CdS film; (d) FESEM image of 0.5M Zn doped CdS

The micrograph reveals compact surface with grains interconnected to each other. The grains of the film surface were less densed when doped Zn concentration was 0.2 M. whereas after doping with Zn concentration 0.3M and 0.4M, grains are heavily densed. The grains are unevenly distributed over the surface. This may be probably due to formation of colloidal particle in the solution. The ZnCdS film surface is smooth, equal sized uniform spherical shaped grains. ZnCdS film coated with 0.3 concentration Zn indicates the surface are covered with grains of equal size throughout the entire surface in cluster forms. With further increase in 0.4 concentration of Zn doping into CdS film have big spherical shaped grains area in cluster form and no cloudy surface is observed. Increase in 0.5 concentration Zn doped CdS films have spherical grains are attached in fibres like structure appears throughout the entire surface of the film.

The composition from varying concentration of Zn doped CdS thin films by EDS are shown in Figure 3(a,b,c,d). Different concentration of Zn doped ZnCdS thin films were deposited on the molybdenum substrate. The peak of molybdenum is due to the substrate. It clearly shows that the sulphur peak overlaps with the molybdenum substrate. At 0.2 content Zn doped ZnCdS EDS spectra indicates that the film have no traces of Zn was found and the spectra of cadmium, sulphur in addition to oxygen elements are observed. The presence of oxygen was due to surface contamination. Again increasing 0.3 concentration of ZnCdS film it is observed that the presence of Zn is appeared because Zn is used as a dopant. Further increasing 0.4 concentration of ZnCdS, small traces of Zn are observed. But it is more than the earlier concentration. In 0.5 concentration have the percentage of Zn increases as the ratio increase.



(a) (b)

(c) (d)

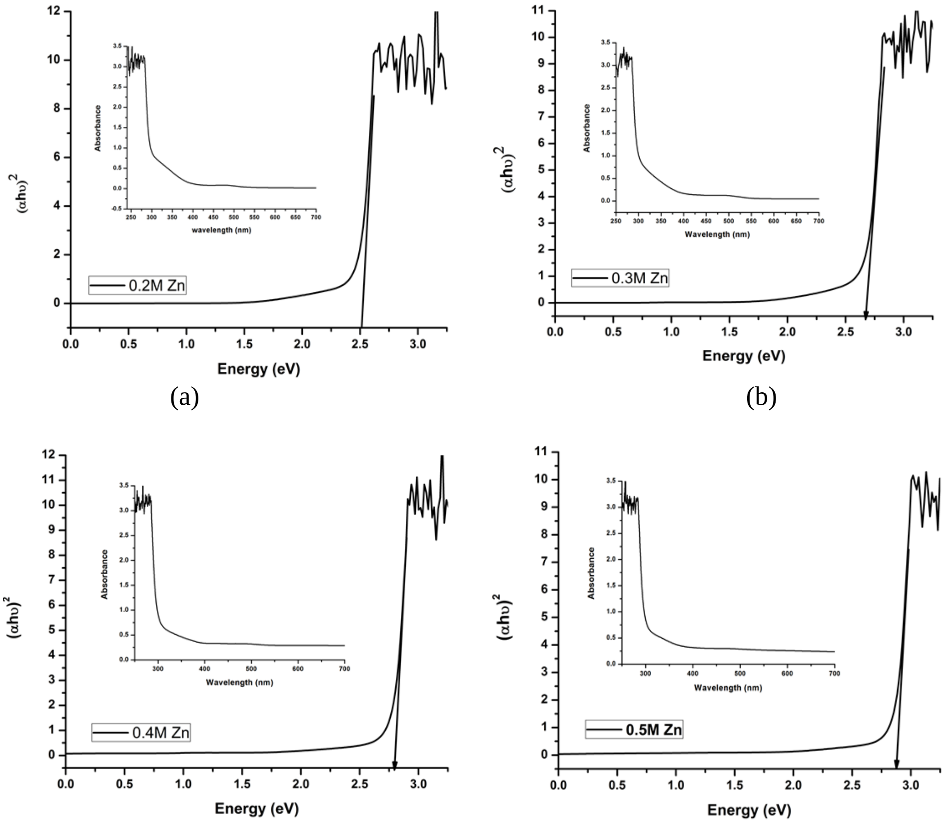
Fig. . 3(a) EDS spectra of 0.2M Zn doped CdS film;(b) EDS spectra of 0.3 Zn doped CdS film; (c) EDS spectra of 0.4 Zn doped CdS film; (d) EDS spectra of 0.5 Zn doped CdS film

From the table it is observed that as the concentration increases the ratio of Zn also increases and the ratio of atomic percentage of Cd and S are nearly equal to 1 in all the cases of varying concentration of Zn doped ZnCdS thin films. According to Zhou et al [18], the elemental ratio of ZnCdS thin films have the ratio of Zn is very much less than the Cd ratio.

Table 3. Shows the atomic percentage and weight percentage of CdS and different concentration(X =0.2, 0.3, 0.4 and 0.5) of Zn doped ZnCdS thin films

Elements	Weight Percentage (CdS)	Atomic Percentage (CdS)	Weight Percentage (ZnCdS)				Atomic Percentage (ZnCdS)			
			X =0.2	X =0.3	X =0.4	X=0.5	X =0.2	X =0.3	X =0.4	X =0.5
Cd	39.23	29.11	36.43	50.79	60.09	66.64	23.66	28.96	40.73	44.24
S	10.43	27.13	9.94	13.92	16.99	18.77	22.64	27.93	40.42	43.79
Zn	-	-	-	1.06	1.77	1.92	-	1.02	2.05	2.16

Fig. 4 shows the energy band gap was determined from the absorbance data by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ where the interception of linear portion on the energy axis gives the energy band gap of the material. The optical absorbance spectra have been studies from wavelength of 250nm - 700nm.



(a) (b) (c) (d)

Fig. 4(a-d)- Plot of $(\alpha h\nu)^2$ *versus (Energy) for the ZnCdS thin film with different concentrations*
(X= 0.2M, 0.3M, 0.4M, 0.5M)

Absorption spectra indicates that long wavelength region have transmission of radiations is maximum due to at this region have minimum absorption. The absorption spectra confirm that the Zn concentration increases, absorption edges shift towards the short wavelength. At 0.4 concentration ZnCdS film, covers larger area of shorter wavelength as compared to other Zn concentration changes due to the structural changes in the thin film which increase the grain size**.** The relationship between absorbance coefficient (α) and photon energy (hν) is expressed to calculate the energy band gap of different Zn concentration by the following relation [19].

$$\alpha h\nu = A (h\nu - E_g)^{1/2}$$

The band gap (E_g) obtained for each Zn concentration is different. The variation of band gap of different Zn concentration is to be linear because the band gap of ZnS is greater than CdS [20]. When the Zn concentration changes from (X= 0.2 to 0.5), the energy band gap of the films varied in the range from 2.54eV, 2.65eV, 2.77eV and 2.85eV [21]. For higher Zn concentration (X=0.5), the band gap is 2.85eV and for lower Zn concentration (X=0.2) it is to be 2.54eV. Due to Zn concentration increases band gap also increases indicates that the formation of solid solution. Higher energy band gap developed in the films due to higher Zn concentration indicates the presence of secondary phase in small quantity. Increase of band gap is due to the Zn^{2+} ions replaced Cd^{2+} ions in the CdS lattice.

Fig. 5 shows the photoluminescence spectra of different Zn concentration ZnCdS nanocrystalline thin films grown on molybdenum substrate. Photoluminescence is a process in which an electron excited by a monochromatic beam of energy undergoes radiative recombination at band edge luminesce or at red shifted luminesce within the forbidden energy gap [22]**.**Due to excitation at higher energy level emission peak observed at 335 nm attributed to transition. Peaks at 365nm 368 nm and 380 nm are observed due to recombination of excitations or trapped hole pair.

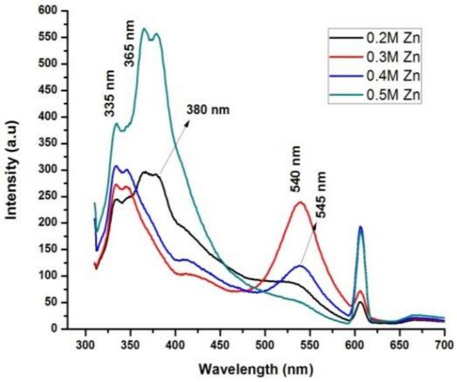


Fig. 5. Photoluminescence spectra of ZnCdS film with different concentrations (X= 0.2M, 0.3M, 0.4M, 0.5M)

From figure it is observed that broad green emission peak in visible region at 535nm, 540nm, 545nm, 536nm, at x =0.2M, 0.3M, 0.4M, 0.5M concentration in chemical bath [23]. Increasing Zn concentration into the ZnCdS films, broad peak of PL at 545 nm is attributed to deep-trap emission [24]. Increasing Zn concentration gives poor crystalline structure and morphological disorder. The corresponding peak positions of all spectra and energy band gap are given in table 4.

Table 4. shows the PL emission peak position and band gap of (X =0.2, 0.3, 0.4 and 0.5 concentrations)

S.No.	Zinc Concentration range	Peak Position (nm)	Bandgap (E_g) eV
1.	X =0.2	535	2.54
2.	X=0.3	540	2.65
3.	X=0.4	545	2.77
4.	X=0.5	536	2.85

Fig. 6 shows the FTIR Spectra of different concentration of Zn doped ZnCdS thin films. FTIR spectroscopy is used for determine the bonding of compound and was carried out in the wave number range from 400 to 4000 cm^{-1}.

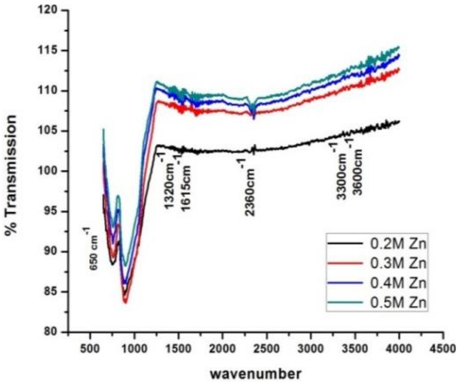


Fig. 6. FTIR spectra of ZnCdS film with different concentrations (X= 0.2M, 0.3M, 0.4M, 0.5M)

It is observed that the peak appeared at 3300 cm^{-1} - 3600 cm^{-1} is assigned to the presence of –OH stretching. This is due to atmospheric pressure [25]. The peak appeared at 2800 cm^{-1} – 2900 cm^{-1} is attributed to C-H stretching vibration [26] indicates the presence of species in the surface of nanocrystal. The presence of CH group is attributed to 2360cm^{-1}.The peak at 1615 cm^{-1} indicates the vibrational mode of OH bending [27]. The peak at 1320 cm^{-1} assigned to the C-O stretching vibration due to ethyleneglycol. The peak located at 650 cm^{-1} indicates the Cd-S stretching vibration.

4. Conclusions

ZnCdS nanocrystalline thin film with different Zn concentrations (X= 0.2M,0.3M,0.4M,0.5M)can be synthesized using nonaqueous medium by Chemical Bath Deposition technique.The films were physically stable and shows good adhesion. Hexagonal wurzite phase (002) of ZnCdS film is observed with average grain size 36nm.

The as deposited films are smooth, uniform, free from pin holes, pits etc. With increase in Zn concentration, the energy band gap increases. The wider band gap of the deposited films makes them suitable for optoelectronic devices, for instance window layer in solar cells. The visible peak at 540 nm, 545 nm indicate the deposition of ZnCdS nanocrystalline thin film. The presence of CdS film were observed at 650 cm^{-1}.

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