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Characterization of chemically deposited (Zn-Cd)S: Cu nano-crystalline films

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II-VI semiconductor nano particles are presently of great interest for their practical applications in many areas like photonics and optoelectronics. Modification in these properties result due to confinement of charge carriers within the nano particles. Reproducible and good quality (Zn-Cd)S: Cu are deposited on microscopic glass substrates by chemical bath deposition (CBD) technique. Characterization of these films mixed with KI/LiF/$CdCl_2$ is done to fabricate high efficiency electroluminescent (EL) & photoluminescent (PL) devices. The crystal structure and grain size of the particles are studied using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The UV-visible absorption spectra and photoluminescence (PL) spectra of various samples mixed with KI/LiF/$CdCl_2$ are reported and discussed.

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Keywords: Zinc sulfide (ZnS), nano crystalline, chemical deposition, SEM, XRD, thin film

1. Introduction

In last decade nano-scale materials have revolutionized the research all over the world because of their potential impact in many fields such as photonics, electronics, sensing and catalysis [1]. These materials possess large number of applications in the areas of organic solar cells, carbon nanotubes, solid state batteries, fuel cells, super plastic ceramics, multifunctional materials, molecular electronics, single electron devices, biosensors and lasers [2] etc. Such materials take advantage of size-induced changes in structural, optical and electronic properties to create enhanced luminescent materials, whose properties differ from the corresponding bulk phase [3]. II-VI semiconductor nano crystals (quantum dots) whose radii are smaller than bulk exiton constitute a section of materials intermediate between molecular and bulk forms of matter. Quantum confinement of the electron-hole pair leads to an increase in the effective band gap with decreasing crystallite size [4]. A similar relationship has been deduced for nano structures prepared from the direct band gap semiconductors e.g. ZnS, CdS, & PbS etc. Nano structured zinc sulfide (ZnS) & cadmium sulfide (CdS) thin films are promising materials for its use in various devices. Characterization of these materials has been largely based upon the surface analysis techniques [5]. For example XRD technique has been widely used for determination of crystallinity, crystal structures, lattice constants etc. of different materials. Sutrave et al [6], Sebastian [7] and Bouroushian et al [8] used this technique for the characterization of (Zn-Cd)S films. On the other hand SEM studies present a very important and convenient method of making topographical studies. Both these studies are helpful in calculating particle size in these films. The optical absorption spectrum is a measure of absorbance as a function of wavelength of incident light. Particularly in thin films such studies are very important as it is possible to determine the optical constants conveniently [9]. Many sophisticated techniques like molecular beam epitaxy [10], plasma chemical sputtering [11], MOCVD [12] and MOVPE [13] have been used to produce thin films with adequate properties such as high crystalline, low resistive and high transmittance. However, chemical deposition technique appears as an interesting technique for preparing ZnS/CdS thin films [14, 15]. Indeed this technique for preparation of thin films is very attractive because of being inexpensive, simple and capable of deposition of optically smooth, uniform and homogeneous layers. In recent years Bhushan and co-workers used chemical deposition technique and reported high photoconductivity (PC) gain in (Cd-Pb)S & (Cd-Zn)S films doped with rare earths [16-21, 26], moderate photovoltaic efficiency [22, 23], efficient PL and EL in (Zn-Cd)S films using NaF/LiF/KI/$CdCl_2$ as flux and Cu as impurity [24, 25]. In the present study we have prepared (Zn-Cd)S: Cu nanocrystalline films by CBD technique, which are characterized using SEM, XRD, UV-visible and PL spectroscopy.

2. Experimental Techniques

2.1 Film Preparation

Nanocrystalline (Zn-Cd)S: Cu films are prepared in aqueous medium by CBD technique using triethanolamine as capping agent. The films were prepared on cleaned substrates of glass plates with high transmission coefficient. The substrates were first washed with acetone & distilled water and by using ultrasonic cleaner. Such cleaned glass slides were dipped into a mixture of appropriate amounts of 1 M solutions of zinc acetate / cadmium acetate, thiourea and 30 % aqueous ammonia (All analytical reagent grade-99.9 % pure; mixture showed pH~11). In addition appropriate amounts of 0.01 M solutions of copper acetate and KI/LiF/$CdCl_2$

were also mixed in the original mixture. Main object of such mixing has been to facilitate the substitution of Cu in their presence because ionic radii of Zn^{+2}, Cd^{+2} and Cu^{+2} are 0.74 A^o, 0.97 A^o and 0.72 A^o respectively. Therefore, Cu can easily be substituted in lattice either in substitutional or interstitial position [24]. The solutions of the compounds used were prepared in double distilled water and films were prepared at a constant temperature of 70^o C in a water bath. Films were prepared on around 60 % area of the glass slide. The deposition of films is based on precipitation followed by condensation. In the beginning when precipitation started, stirring was done. After that, depositions were made in the static condition and after deposition; films were washed with distilled water and then dried by keeping in open atmosphere under sun light until its moisture content reduces completely. This helps in achieving adequate operating life of electroluminescent (EL) cell made with such films. Bhushan and Chandra [26] observed that such prepared films last for more than two years. The thickness of the film was measured by mass difference method and was found to be between 1-2 μm. The sample $(Zn_{0.7}$-$Cd_{0.3})S$: Cu was selected on the basis of satisfactory high EL brightness and proper band gap value. Here subscripts to Zn and Cd represent the percentage composition in the solution not the final compositions. Also the dipping time was taken as 75 minutes because of high EL intensity, uniformity and thickness of deposited films.

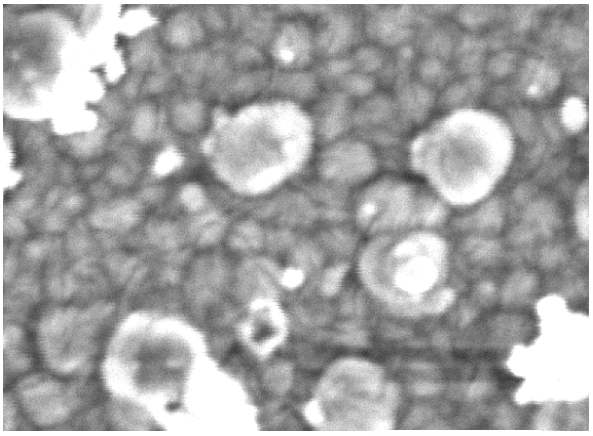
2.2 Measuring Instruments

Optical absorption spectra were studied with a Varian (UV-VIS) DMS-100 spectrophotometer in the wavelength range 350-600 nm. XRD and SEM studies were performed at University of Delhi using a computerized Shimadzu diffractometer (model-98XRD) and JEOL-JSM-6400 scanning electron microscope respectively. PL excitations were made by 365 nm Hg radiation obtained by using a high-pressure Hg source and a suitable Carl Zeiss interference filter.

3. Results and discussion

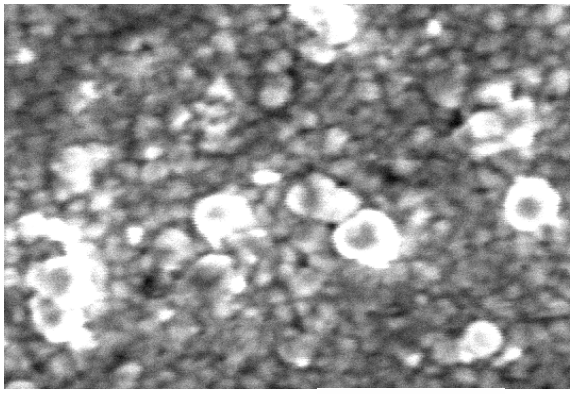
3.1 SEM Studies

The SEM micrographs of $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, KI; $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, LiF and $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, $CdCl_2$ films at a magnification of 5000 are shown in fig. 1 (a), (b), & (c) respectively. Spherically shaped grains are observed in different samples. The observed differences between the microstructures of (a), (b) & (c) can presumably be attributed to addition of KI, LiF, & $CdCl_2$. It is seen that in the $(Zn_{0.7}$-$Cd_{0.3})S$ sample mixed with $CdCl_2$ average particle size is smaller as compared to other two samples. Earlier workers [19, 21] found that $CdCl_2$ gave higher values of PC gain compared to that of KI and LiF. Karanjai and Dasgupta [27] found that CdS grains showed a greater tendency to coalesce with the increasing concentration of $CdCl_2$. Also $CdCl_2$ is known to promote recrystallization of CdS grains. This may be the reason for higher EL emission in presence of flux $CdCl_2$ because of increasing number of grains in its presence. As far known to us KI & LiF were not reported by earlier workers. From present studies it is clear that the grains in presence of KI and LiF are found to be bigger in size, which shows still better coalescences in these later materials. The average particle sizes, determined by Heyn's intercept method [28] are listed in Table 1.



Magnification = 5000

a



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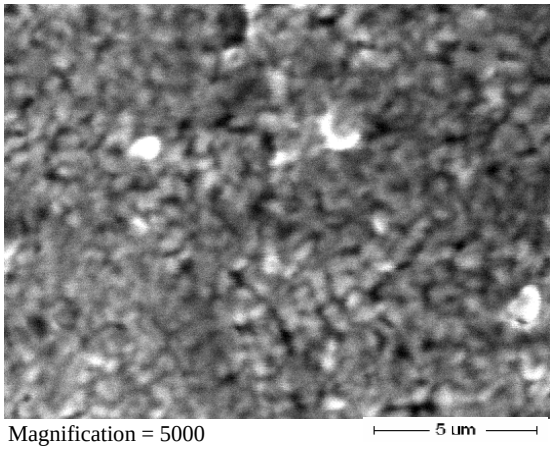
b



Magnification = 5000

Fig.1 SEM micrographs of different (Zn-Cd)S: Cu films[a- $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, KI;b- $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, LiF; c- $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, $CdCl_2$]

Table.1 XRD data of different (Zn-Cd)S films (Preparation time = 75 min.; Preparation temperature = 70 ^{o} C; film thickness ~ 1-2 μm)

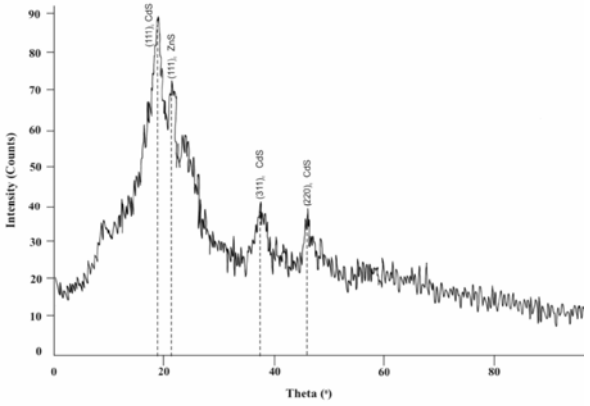
d-values		Relative intensities			h k l	Lattice constant (A^o)	
Obs.	Rep.	Obs.	Rep.			Obs.	Rep.
$(Zn_{0.7}$-$Cd_{0.3})S$:Cu, KI							
3.351	3.360	100	100	82	$(111)_c$ - CdS	5.8032	5.818
3.037	3.123	100	48.8	80	$(111)_c$ - ZnS	5.4091	5.406
2.081	2.058	46	60		$(220)_c$ - CdS	5.882	5.818
1.776	1.761				$(311)_c$ - CdS	5.890	5.849
$(Zn_{0.7}$-$Cd_{0.3})S$: Cu, LiF							
3.3600	3.360	97	100	71	$(111)_c$ - CdS	5.8196	5.818
2.0518	2.058	80	39	60	$(220)_c$ - CdS	5.8033	5.818
1.7616	1.761	37	51		$(311)_c$ - CdS	5.5000	5.849
1.8267	1.912				$(220)_c$ - ZnS	5.1600	5.406
$(Zn_{0.7}$-$Cd_{0.3})S$: Cu, $CdCl_2$							
3.5311	3.583	67	75	100	$(100)_h$ - CdS	4.077	4.135
3.3685	3.360	100			$(111)_c$ - CdS	5.834	5.818
1.9016	1.911	48	74	50	$(110)_h$ - α ZnS	3.803	3.820
1.7997	1.761	60			(311)c - CdS	5.969	5.849

3.2 XRD Studies

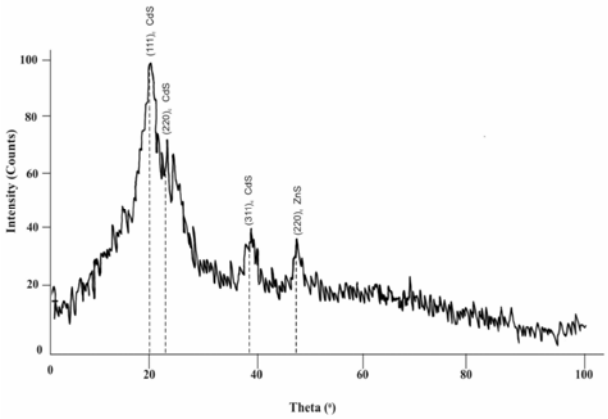
The XRD patterns of different $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, KI; $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, LiF and $(Zn_{0.7}$-$Cd_{0.3})S$: Cu, $CdCl_2$ films are shown in fig. 2 (a), (b) & (c) respectively. These patterns are some noisy, which may possibly be due to low crystallinity. In these diffractograms both cubic & hexagonal phases are observed. The assignment of the peaks has been done from the comparison of ASTM data and the evaluated lattice constants values with those of reported values. It is observed that the diffraction patterns show crystalline nature with prominent diffraction lines of ZnS as **$(220)_c$, $(110)_h$, $(111)_c$** and of CdS as **$(111)_c$, $(220)_c$, $(311)_c$, $(100)_h$.** Presence of different peaks along with difference in intensities are also observed, which indicate growth conditions to be affected by the presence of different fluxes. The evaluated and reported values of the lattice constants agree with each other. It was reported earlier that addition of ZnS affects the crystallinity i.e. the intensities of peaks in X-ray diffractograms reduce due to increase in concentration of ZnS [17]. The average particle size (D) was estimated from the full width at half-maximum (FWHM) of the diffraction peaks, using Sherrer's formula [29]-

$$D = K\lambda / (\beta_{1/2} \cos\theta) \quad (1)$$

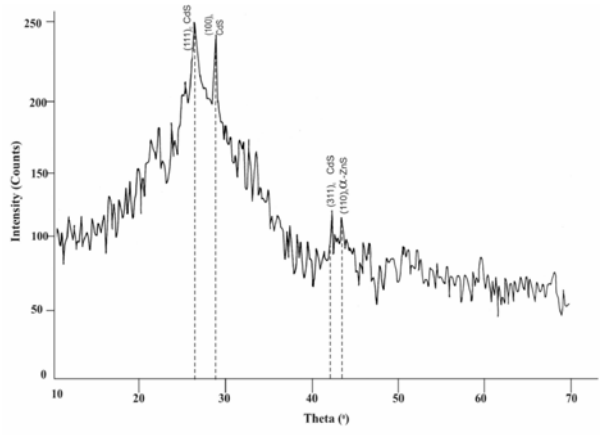
where 'λ' is the wavelength of X-rays, 'θ' the Bragg's angle (in radian), K a constant, which depends on the grain shape (0.89 for circular grains) & $\beta_{1/2}$ the full width at half maxima (FWHM). It is found that the average particle size of the different samples lie in the range 2.86 A^o - 6.15 A^o. These values are quite close to those obtained from SEM studies. The corresponding XRD data and particle sizes are summarized in table 1.



a



b



c

Fig.2 X-ray diffractograms of different ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu films [a- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, KI; b- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, LiF; c- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, $CdCl_2$]

3.3 Absorption Spectra

Results of optical absorption spectra for ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu films mixed with KI/LiF/$CdCl_2$ are shown in fig.3. The absorption coefficient (α) and the band gap E_g are related by the following relation in direct band gap materials [30]-

$$\alpha = \frac{C(h\nu - E_g)^{\frac{1}{2}}}{h\nu} \quad (2)$$

where 'E_g' is the optical band gap and 'C' is a constant. Thus, as shown in fig.4, the band gap of materials can be determined from the Tauc's plots. Thus, the materials of present study are of direct band-gap nature. It was also found that with increase in Zn content, the band-gap is also found to increase [25]. A further slight change in band-gap change occurs due to addition of impurities, which may be due to change in lattice constants [31]. These values are summarized in table 2.

Table. 2 Values of band gap energies (E_g) for different (Zn-Cd)S:Cu films (Preparation time = 75 min.; Preparation temperature = 70 ^{o} C; film thickness ~1-2 μm)

Systems	E_g from absorption spectra (eV)
($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, KI	2.550
($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, LiF	2.575
($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, $CdCl_2$	2.650

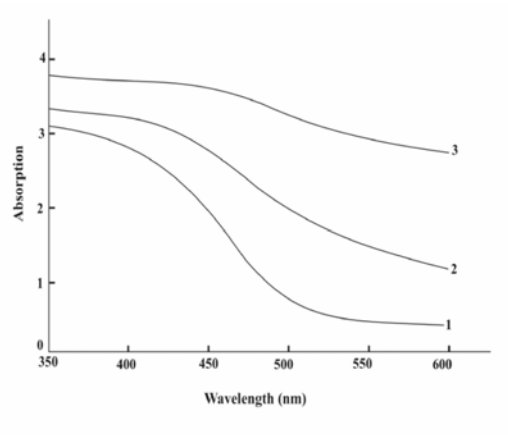


Fig.3 Optical absorption spectra of different ($Zn_{0.7}$-$Cd_{0.3}$)S:Cu films [1- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, KI; 2- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, LiF; 3 - ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, $CdCl_2$]

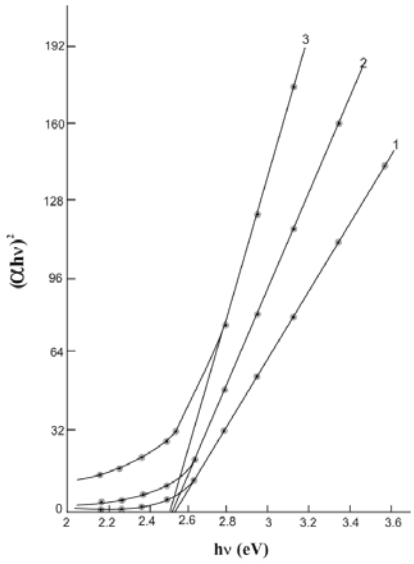


Fig.4 Tauc's plots of different ($Zn_{0.7}$-$Cd_{0.3}$)S:Cu, films [1- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, KI; 2- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, LiF; 3 - ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, $CdCl_2$]

3.4 Photoluminescence spectra

Fig. 5 represents the PL spectra of different (Zn-Cd)S: Cu, KI/LiF/$CdCl_2$ films. It is found that (Zn-Cd)S: Cu film shows a peak at 488 nm, which changes to 515 nm, 507 nm and 495 nm in presence of KI, LiF and $CdCl_2$ respectively (Cu acetate = 0.5 ml). Thus, PL spectra lie in blue-green region. These peaks may be associated to acceptor levels formed by Cd vacancies. At volumes higher than 0.5 ml of copper acetate, the PL emission almost seizes that may be because of concentration quenching. This has already been reported in our earlier paper [24].

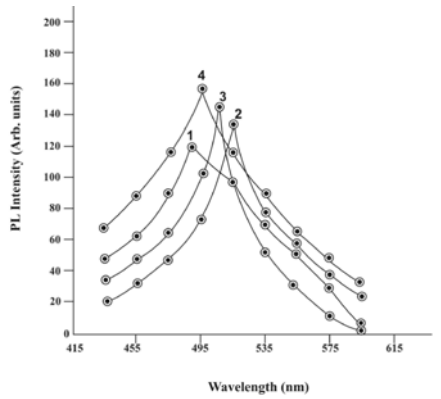


Fig.5 PL emission spectra of different ($Zn_{0.7}$-$Cd_{0.3}$)S films: 1- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu ; 2- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, KI; 3- ($Zn_{0.7}$-$Cd_{0.3}$)S: Cu, LiF; 4 - ($Zn_{0.7}$- $Cd_{0.3}$)S: Cu, $CdCl_2$]

4. Conclusions

The chemical bath deposition technique is a simple and suitable method for obtaining smooth uniform and strong adherent (Zn-Cd)S films. Nanocrystalline (Zn-Cd)S: Cu films are prepared by CBD method. The crystal structure and particle size are determined using SEM & XRD techniques. UV-visible spectra showed a blue shift indicating quantum confinement of charged particles. The PL spectra recorded for different excitation energies show shift of peaks towards higher energy side of the spectrum along with difference in peak intensities with different fluxes, which has been explained as due to selectively excited PL. The present work will be useful in the development of low cost EL devices.

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