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STRUCTURAL AND OPTICAL PROPERTIES OF NANOSTRUCTURED CdS THIN FILMS DEPOSITED AT DIFFERENT PREPARATIVE CONDITIONS

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A modified Chemical bath deposition technique have been reported for the controlled synthesis of polycrystalline and monocrystalline CdS thin films on glass substrates. The method involves the preparation of aqueous solutions containing cadmium acetate and thiourea as source material for cadmium and sulfur components. The influence of different preparative parameters such as bath pH and pre-deposition heat treatment of the reactants on the structural and optical properties of the films were investigated by X-ray diffraction (XRD) technique, scanning electron microscopy (SEM), UV-visible and photoluminescence spectroscopy. All films deposited with pre-deposition heat treatment were polycrystalline in nature while the films deposited without pre-deposition heat treatment were monocrystalline in nature. From the shift in optical band gap, particle sizes were calculated using effective mass approximation (EMA) and were found to be in good agreement with those determined from XRD broadening. The SEM analysis shows that the CdS films were also nanocrystalline in nature.

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1. Introduction

Among the wide band gap II-VI semiconductors cadmium sulphide(CdS) with its direct band gap of 2.42eV at room temperature is a promising material and is applied in wide variety of fields such as solar cells [1-3], thin film FET transistors [4], Light emitting diodes [5] and photonic devices [6]. Polycrystalline CdS thin films are widely used as window material [7] in several heterojunction solar cells such as CdS/CdTe, CdS/CuS, CdS/Cu(In)Se [8-11] for their favourable optical properties. CdS thin films have been deposited by several techniques including chemical bath deposition(CBD)[12], thermal evaporation [13], spray pyrolysis [14], laser ablation[15], close space sublimation [16],molecular beam epitaxy(MBE)[17]and electrochemical deposition technique [18]. However, among all, CBD is a very simple and low cost technique and is suitable for large area deposition. CBD is a process to achieve high quality films by controlled chemical reaction which allows fabrication of solar cells with suitable efficiencies. The chemical mechanism of CdS CBD usually involves the thermal decomposition of thiourea ($CS(NH_2)$) in an alkaline solution containing cadmium salt.

There are a number of reports [19-31] on the different structural, optical, electrical, photoelectric and physical properties of CdS thin films deposited by different methods including CBD and only a few of them [19-23] considered the effect of pH on the structural and optical properties. It is well known that the deposition conditions (bath compositions, reagents

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concentrations, temperature and pH etc.) have a significant effect on the quality of the films. X. Li *et.al.* [19] studied the structural and optical properties of CdS thin film grown in the pH range from 9.1 to 10.4 and showed that too high concentration of NH_3 is not suitable for deposition of good quality CdS thin film. J.Barman et.al. [22] studied the interrelation between particle size and crystal structure in PVA capped CdS thin films by varying the pH from 1.6 to 2.2. V.B.Snap et.al.[23] reported the time dependent growth of CdS films by regulating the pH from 8.2 to 10. In the present work, the CBD technique was modified with a change in reaction temperature and pre- deposition heat treatment of the reactants for the deposition of monocrystalline and polycrystalline CdS thin film. The effects of pH, and pre-deposition heat treatment of the reactants on the structural and optical properties of CdS thin films were investigated.

2. Experimental

2.1 Chemicals

All reagents were of analytical grade, obtained from Merk Ltd. of India and used as received without further purification. Deionized water was used throughout the experiments.

2.2 Synthesis of CdS thin films

CdS thin films were deposited on glass substrates by CBD technique using cadmium acetate [$(CH_3COO)_2$ $Cd.2H_2O$] as Cd^{++} ion source and thiourea [$CS(NH_2)_2$] as S^{-2} ion source with cadmium to sulfur (Cd:S) molar ratio 3:5. The technique used here is a modification of the method used by Ubale et.al. [32] for deposition of ZnS thin film. The change is brought in the reaction temperature and pre-deposition heat treatment of the reaction solution. In a typical reaction equal volume of 0.6M cadmium acetate and 1M thiourea solutions were taken in a beaker, stirred for 15-20 minutes and then the reaction mixture is heated at 60^0C for 8 hours. As the reaction was started the reaction system gradually changed from transparent to light yellow and after completion of the reaction this turns bright yellow. The pH of the final solutions was found to be 5.6. The solution was left overnight for stabilization.

For the deposition of CdS thin films, ultrasonically cleaned glass substrates were introduced vertically into the chemical bath with the help of substrate holder. An alkaline solution of ammonia was used to adjust the pH of the solution. The temperature of the bath was maintained at 60^0C for an initial period of 1hour and then left itself to cool to the room temperature. The time of depositions was 18 hours. A set of films (Z1 to Z6) were obtained by adjusting the pH of the solutions at values 5.6-9.5 with a pH meter while Cd:S ratio was fixed at 3:5 throughout the experiments. After deposition, the substrates were removed from the chemical bath and thoroughly washed in doubly distilled water.

2.3 Characterization

The crystallographic structures of the films were analyzed with a Rigaku Ultima -IV X-ray diffractometer using Cu –Kα radiations operated at 40kV and 40mA. For optical studies, optical absorbance spectra in the vicinity of absorption edge were recorded using Perkin–Elmer spectrophotometer and photoluminescence spectra with a JOBIN-YVON Fluoromax-4 spectrophotometer. Surface morphology and particle size was examined by LEO 1430VP Scanning Electron Microscope.

3. Results and discussion

3.1. Structural characteristics of the films:

XRD patterns of the CdS films deposited by CBD at different pH values are shown in Fig1. XRD analysis reveals that films deposited at lower concentrations of NH_3 (pH=5.6, 7.6) were of amorphous structure while those of deposited at higher NH_3 concentrations (pH=8.1 to 9.5) were polycrystalline in nature. The XRD patterns of the CdS films (Z3 to Z6) deposited at pH 8.1 to 9.5 are indicative of hexagonal structure with a preferential orientation along (200) directions. The peaks were detected at 2θ = 26.6, 29.2, 44.08 and 51.88 which can be ascribed due to (002), (200), (110) and (201) reflection planes of the hexagonal CdS structure, respectively [28]. A comparison between observed and standard d-values for the CdS thin films are shown in table.1 and it is also observed that there is a good agreement between the d-values.

In Fig.2, (a) and (b) represent the XRD patterns of the CdS films deposited with and without pre-deposition heat treatment of the reactants. It is observed that the pre-deposition heat treatment of the reactants has an important influence in the structural property of the films. The XRD spectra show that films prepared with pre-deposition heat treatment are polycrystalline in nature while those prepared without pre-deposition heat treatment are monocrystalline in nature. Thus our method has a good control over the crystalline structure of the CdS thin film.

It is also observed that as pH increases (from 8.1 to 9.5), the X-ray peaks become more prominent, new peaks are observed and preferred orientation changes from [200] to [002] directions. The change of preferential reflection plane with the variation of pH was also reported by C.Yan et.al [20].

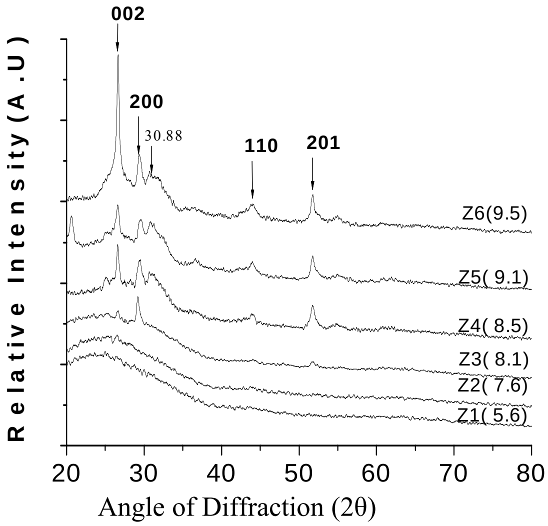

Fig 1. XRD spectra of CdS thin films deposited at pH 8.1 to 9.5.

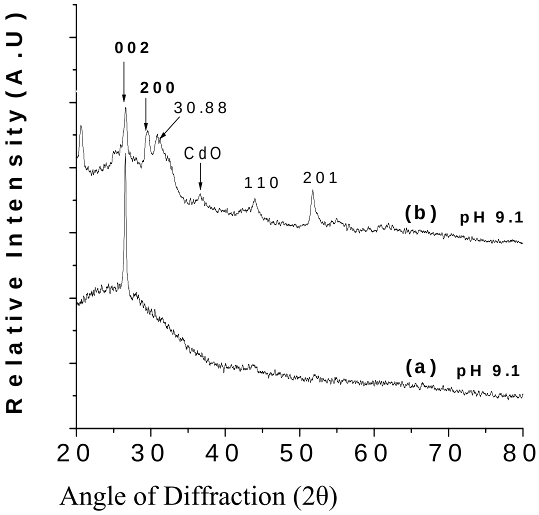

Fig 2. XRD spectra of CdS thin films (a) without and (b) with pre-deposition heat treatment.

Table.1. Comparison of standard and observed 'd' values

Sample	Reflection Planes(hkl)	Standard d- values	Observed d-values for			
			Film Z-3	Film Z-4	Film Z-5	Film Z-6
CdS	002	3.357 [28]	3.3409	3.3533	3.348	3.3385
	200	2.907 [28]	3.0058	3.0134	3.0294	3.0375
	110	2.068 [28]	2.0527	2.0580	2.0607	2.0571
	201	1.731 [28]	1.7641	1.7641	1.7641	1.7641

The additional peak at 2θ = 30.88 for the films (Z4 to Z6) deposited at pH 8.5 to 9.5 indicates the incorporation of cubic phases [33] in the structure. Thus there is a transition from mixed phase (cubic and hexagonal) to hexagonal as pH is decreased from 9.5 to 8.1. A similar phase transition from cubic to hexagonal was also reported by Udaya S. et.al.[21]. Again, broadening of the peaks indicates the increase in full width half maxima (FWHM) and decrease in particle size. The reduction of the grain size is an indication of change in crystal structure from hexagonal to cubic. The crystallite sizes of the films can be determined using Debye- Scherer formula [34]

$$D_{hkl} = K\lambda / \beta \cos \theta \qquad (1)$$

where K is a constant and taken to be 0.94, β is the full width half maxima (FWHM) of the XRD peak at 2θ, recorded with an incident wavelength λ (= 1.54Å). The crystallite sizes are found to be within the range 4.1- 4.6nm and are tabulated in table.2. It is also observed that crystallite size decreases with the increase of pH values (Table.2).

3.2 Optical studies

The optical absorption spectra of the CdS thin films deposited at pH 8.1 to 9.5 are shown in fig. 3(a) and 3(b). The spectra shows that the absorbance edges are blue shifted with respect to the bulk CdS, indicating quantum confinement effect in nanoparticles.

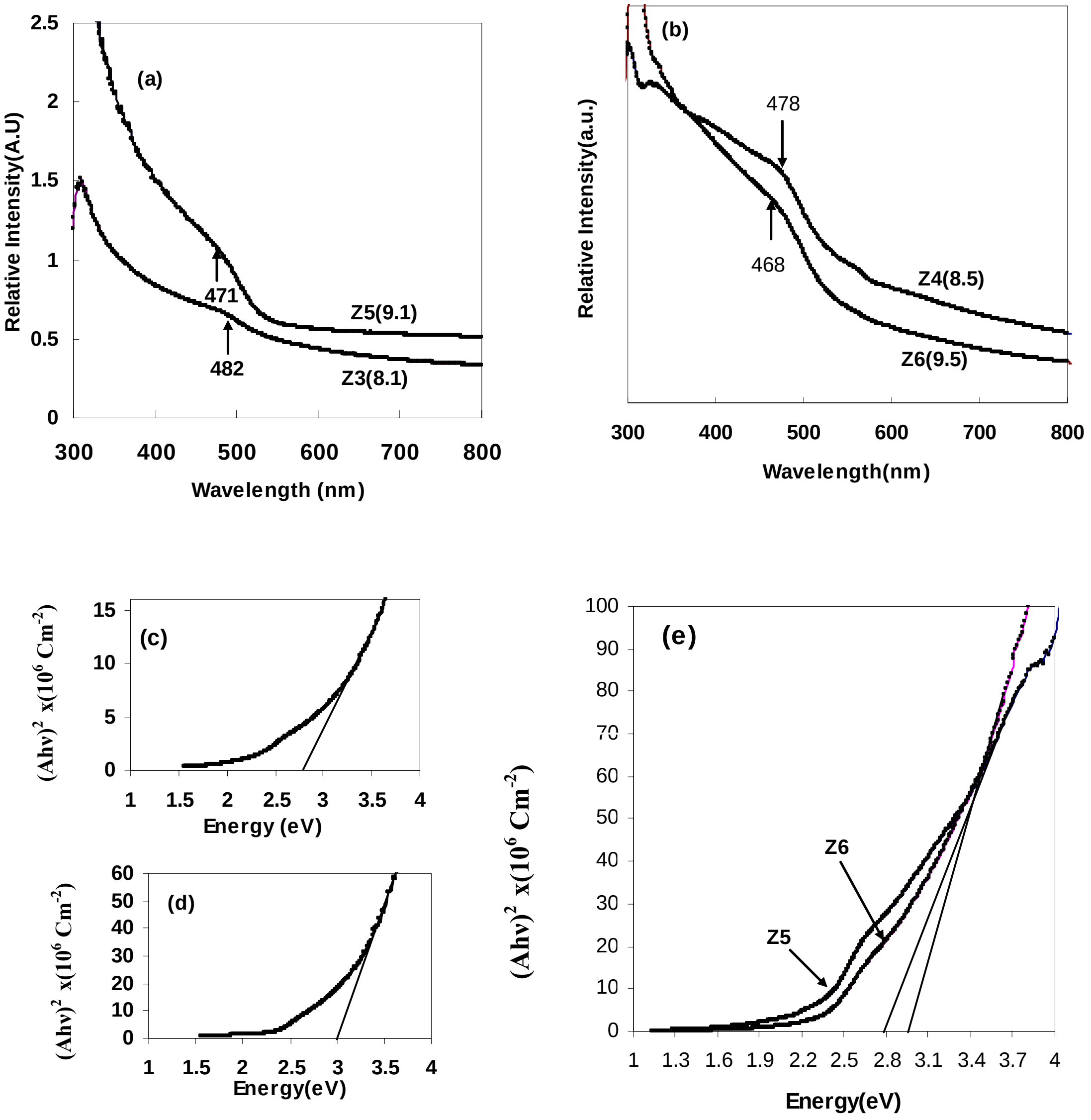

Fig. 3(a) and (b) UV-visible absorption spectrum of CdS thin films (Z3 toZ6) deposited at pH 8.1 to 9.5; (c) , (d) and (e) represents the band gap calculation of films Z3 , Z4,Z5 and Z6.

The optical band gaps of the films were obtained by using the following equation [35] for a semiconductor

$$A = K (h\nu - E_g)^{m/2}/h\nu \qquad (2)$$

where 'A' is the absorbance, 'K' is a constant and 'm' is equal to 1 for direct transition and 2 for indirect transition . Fig.3(c), 3(d) and 3(e) shows the plot of $(Ah\nu)^2$ versus photon energy *hv* for the CdS films. Linearity of the plots indicates that the material is of direct band gap nature. The extrapolation of the straight line to $(Ah\nu)^2=0$ axis gives the energy band gap of the film material. From the band gap information the size of the CdS nano particles were calculated using the effective mass approximation (EMA) method and following the equation [35].

$$E_{gn} - E_{gb} = [(h^2 \pi^2 / 2R^2) 1/m^*] \qquad (3)$$

In the above equation m^* is the effective mass of the specimen, E_{gb} is the bulk band gap and E_{gn} is the band gap of the sample. From the calculation it is found that the particle size decreases with the increase of pH. The observations are shown in Table.2.

Table. 2. Variation of size with pH from different method

Sample	pH	Band gap from UV-VIS (eV)	Shift in Band Gap (eV)	Grain size from EMA (nm)	Grain size from XRD (nm)
Film Z3	8.1	2.78	0.36	4.54	5.1
Film Z4	8.5	2.8	0.38	4.42	5.54
Film Z5	9.1	3	0.58	3.58	4.54
Film Z6	9.5	2.92	0.5	3.85	6.3

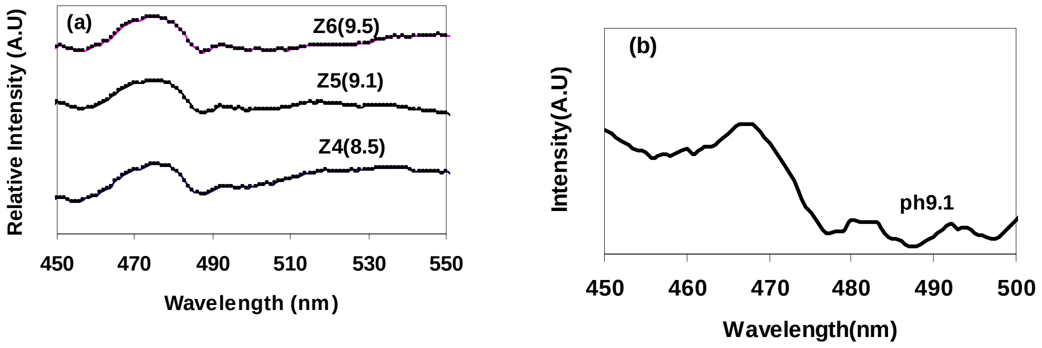

Fig.4 Photoluminescence (PL) spectra of CdS thin films deposited with (a) Pre-deposition heat treatment and (b) without heat treatment.

Fig.4 shows the photoluminescence (PL) spectra of the CdS films deposited on glass substrates. The films deposited with pre-deposition heat treatment showed a PL maximum at around 476 nm whereas a film deposited without heat treatment showed PL maxima at 468nm. This indicates the formation of CdS nanoparticles in the as deposited CdS film.

3.3 SEM analysis

Fig.5 (a) and 5(b) shows the SEM micrograph of the CdS films (Z3 & Z4) deposited at pH 8.1 and 9.1. SEM observation of the films indicates larger value of particle size as compared to XRD and EMA approximation calculations. The bigger size of nanoparticles observed from SEM may be due to agglomeration of particles as they are not capped before deposition. Further XRD and EMA calculations give the value of average particle size including amorphous phases. The SEM micrograph of the film Z3 shows hexagonal morphology where as an irregular pattern is seen in case of film Z4. This may be due to incorporation of cubic and CdO phases in the structure.

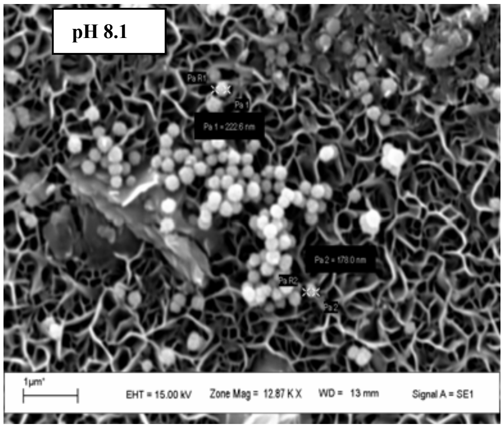

Fig 5(a) SEM images of film Z3

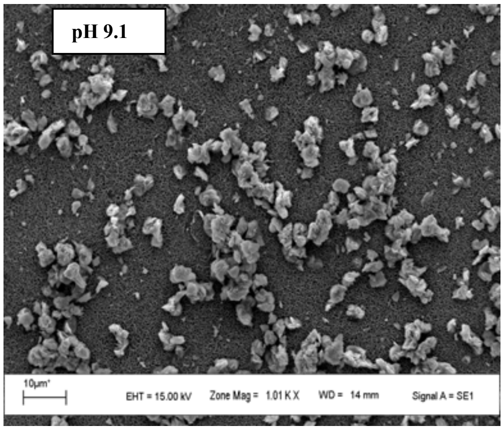

Fig 5(b) SEM images of film Z4

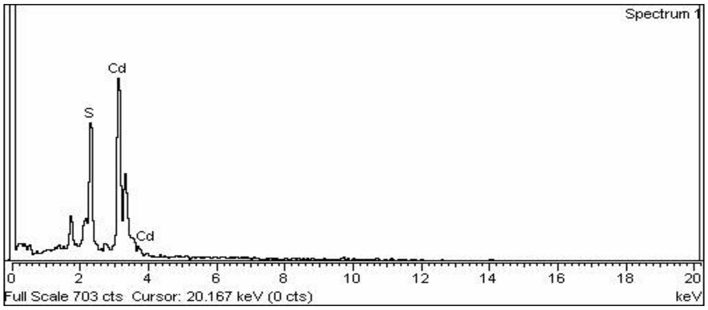

Fig 5(c) EDS spectra of CdS thin film (Z4)

3.4 Energy Dispersive X-ray Spectroscopy (EDS):

Fig 5(c) shows the composition of the CdS nanocrystalline thin film (Z4) with the help of Energy Dispersive X-ray Spectroscopy (EDS). Fig 5(c) shows the clear peaks of Cadmium (Cd) and Sulphur (S), but some additional peaks are also present which could be due to impurity in the reagents. The film appears to be sulphur deficient.

4. Conclusion

CdS thin films were prepared by modified CBD technique. Depending on the pre-deposition heat treatment of the reactants, the films were found to be of polycrysatalline and monocrystalline nature. Blue shifting of the absorption edge showed that the prepared films are composed of nanocrystals of CdS. Maximum band gap of 3.0 eV were calculated from the shift in absorption edge as a consequence of quantum confinement effect. The crystal structure of the films depends upon the bath pH value and moderate alkaline pH is suitable for deposition of CdS thin film with hexagonal structure. The typical CdS film (Z3) exhibits a hexagonal structure with a strong orientation along (200) direction and no mixed phase were observed. It is observed that high value of pH can result in the mixed phase although the crystallinity is improved. The particle size obtained from XRD and EMA method are nearly same but slightly different from SEM studies.

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