

PHOTOLUMINESCENCE ANALYSIS OF CHEMICAL BATH DEPOSITED CADMIUM SULPHIDE THIN FILMS

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Using chemical bath deposition (CBD) technique, CdS thin films of different thicknesses were prepared on glass substrates. From x-ray diffraction analysis the structure of the films has been identified as hexagonal. Using energy dispersive x-ray analysis the films prepared has been found as Cd_{0.9}S_{1.04}. Room temperature photoluminescence analysis in the 400-650 nm emission wavelength ranges for the excitation energies 3.27 and 4.89eV show the 'well known' green emission band of CdS. From the photoluminescence spectra analysis the existence of Stoke's shift, good polycrystalline quality of the deposited films, influence of excitation energy, back ground emission and the defects in the films have been studied and are presented in this paper in detail.

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1. Introduction

Cadmium sulphide is a suitable window layer for solar cells [1-3] and also finds applications as optical filters and multilayer light emitting diodes [2], photo detectors [3], thin film field effect transistors [3-5], gas sensors [6], and transparent conducting semiconductor for optoelectronic devices [7]. Among various methods the reliable, simple and cost effective route to synthesis CdS thin films is chemical bath deposition techniques. In a previous work we reported the preparation, structural, and optical properties of CdS thin films [8]. In this paper we present the results of our studies on photoluminescence measurements carried out on CdS thin films in 400- 650 nm emission wavelength range.

2. Experimental details

The deposition of CdS thin films is based on the reaction of Cd²⁺ and S²⁻ ions in deionised water solution. It is found that the solution having pH value of 10 gives uniform and compact films. The deposition parameters such as temperature and deposition time have been optimized [8]. The well-cleaned glass substrates are introduced in the chemical bath and films of various thicknesses can be prepared by repeated deposition. Films prepared by a simple deposition were used for the photoluminescence analysis. The thicknesses of the deposited film have been determined by gravimetric technique. All the films were annealed in air at 50°C for 30 minutes and

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then used for the analysis. A Shimadzu XRD-6000 X-ray diffractometer with vertical goniometer fitted with vanadium filter and copper radiation ($\lambda = 1.5406 \text{ \AA}$) was used for the structural analysis of the films of different thicknesses. Energy dispersive X-ray analyzer (LEICA.S440i) confirmed the composition of the constituents in CdS thin films. Photoluminescence spectra were obtained at room temperature using the instrument Perkin –Elmer-L555 Spectrofluorometer using pulsed Xenon as a excitation source.

3. Results and discussion

3.1 XRD analysis

An X-ray Diffractogram of CdS thin film of thickness 9600 \AA is shown in Fig 1. The predicted peaks (002), (101), (102), (110) and (202) are reported as the characteristic peaks for CdS thin films by several workers [2,6]. The diffraction profile reveals that the deposited film is polycrystalline in nature with hexagonal structure (α - CdS, Greekite form) which is the stable phase of CdS.

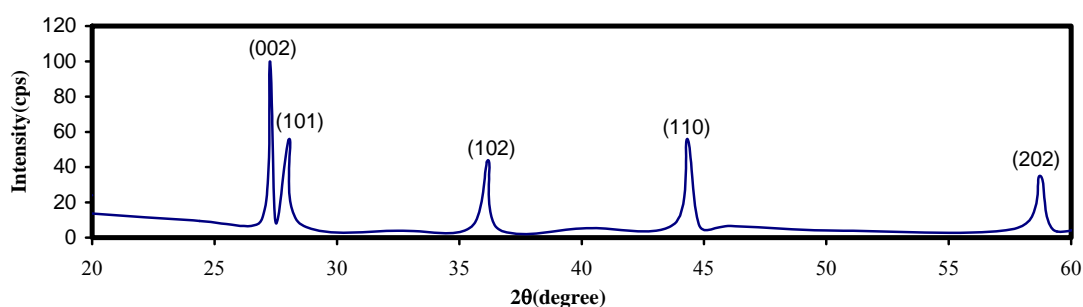


Fig. 1. X-ray Diffractogram of CdS thin film of thickness 9600 \AA .

3.2 . EDAX analysis

Fig.2 shows the Edax result of CdS thin films of thickness 1490 \AA . EDAX analysis confirms the composition of the constituents in the deposited films as $\text{Cd}_{0.96}\text{S}_{1.04}$. The presence of Si and O peaks are due to glass substrates.

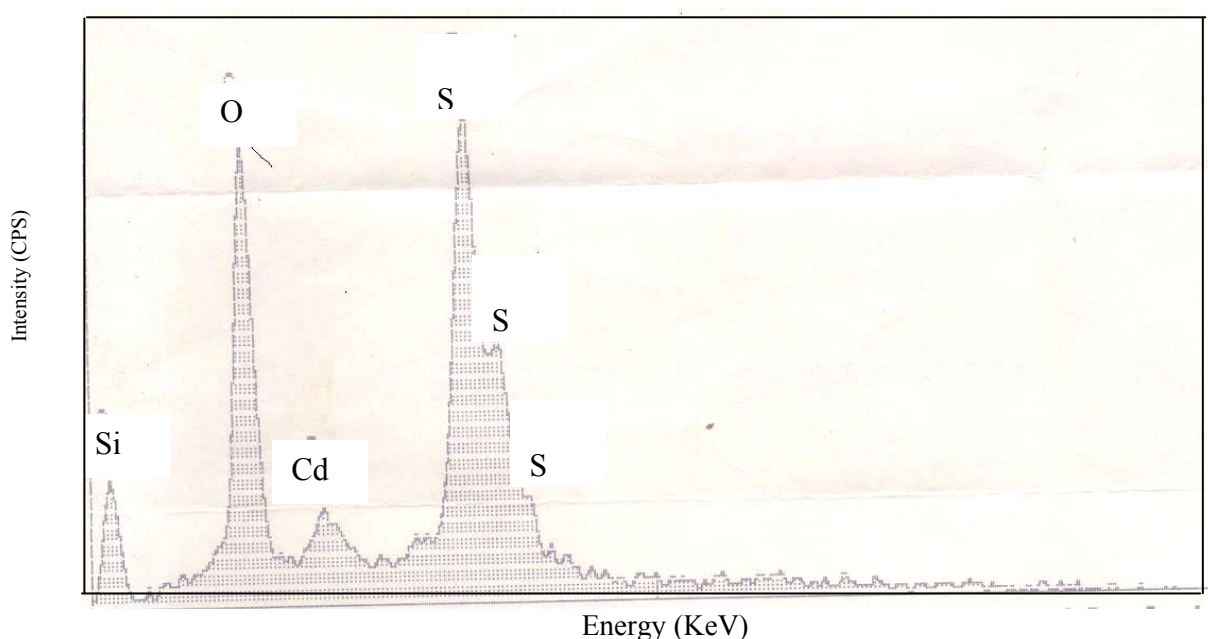


Fig. 2. EDAX result of CdS thin film of thickness 1490 \AA .

3.3. Photoluminescence analysis

Fig .3 shows the absorption spectra of CdS thin films whereas Fig .4 & Fig.5 show the room temperature photoluminescence (PL) emission spectra for the excitation energies 3.27 eV and 4.89 eV respectively. The principle of PL measurements is to create carriers by optical excitation with photon energy above the band gap of the films (2.4eV). Electrons and holes relax to their respective ground states in the conduction and valence band. They can then recombine radiatively as most free carrier or excitations. When light energy input is applied to the film there is an electronic transition between two energy levels, E_1 & E_2 ($E_2 > E_1$), with the emission of wavelength λ , where

$$hc/\lambda = E_2 - E_1 \quad (1)$$

Invariably E_1 and E_2 are part of two groups of energy levels so that instead of a single emission wavelength a band of wavelength is observed [13].

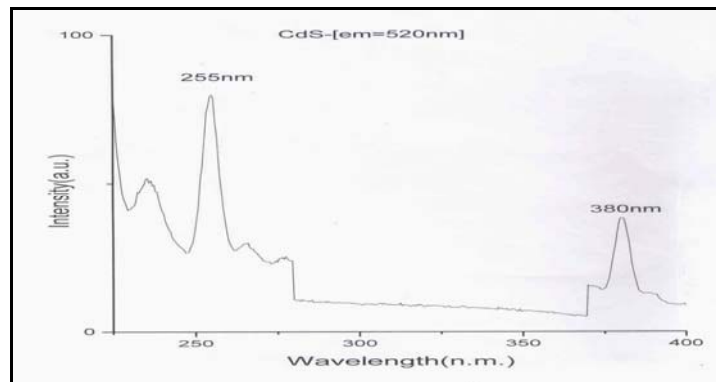


Fig. 3. Absorption spectra of CdS thin film (emission intensity = 520 nm).

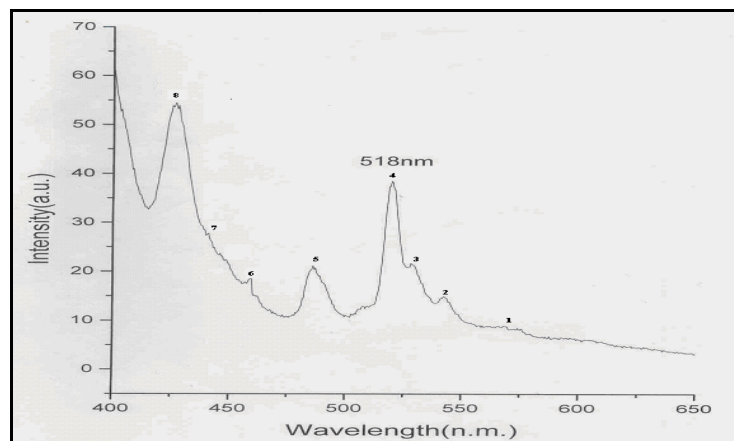


Fig. 4. Photoluminescence spectra of CdS thin film (excitation energy = 3.27 eV).

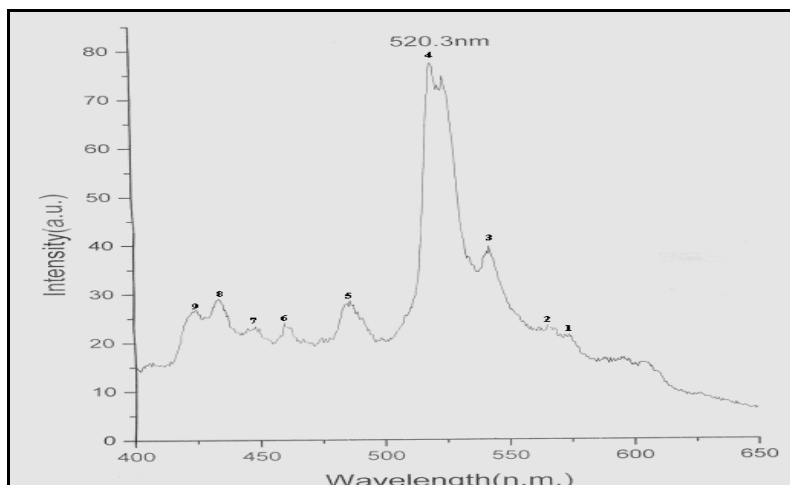


Fig. 5. Photoluminescence spectra of CdS thin film (excitation energy = 4.89 eV).

3.4 Stokes shift

It has been found that the absorption peaks occur at wavelength 254 and 380 nm (Fig.3) and emission peak is found at approximately 520 nm (Fig 4 & 5). The emission peak occurs at a higher wavelength than that of the absorption peaks. In fact the peak emission wavelength is invariably shifted towards red end of the spectrum compared to the peak of the absorption spectrum. This phenomenon is known as the Stokes shift, which finds commercial application in the fluorescent lamps [9].

3.5. Influence of excitation power

It can be clearly seen that for low excitation intensity (3.27eV) (Fig 4) the relative intensities of the low energy peaks (1,2,3) in the spectrum are larger while the relative intensities of high energy peaks (5,6,7,8) increase with excitation intensity or pump power (4.89eV) (Fig. 5). Energy peaks 2 & 3 result from transitions between excited states. This should require complete filling of the electron and hole ground states and partially filling of the excited states, which is unlikely at the low excitation intensity. The lowest excitation energy peak 1 corresponds to ground state transitions. PL spectra (Fig. 4) consist of 8 bands (the excitation energy is 3.7eV) whereas the spectrum (Fig.5) has 9 bands (the pump power has been increased to 4.89 eV). Moreover the relative intensity of the peak 4 Green Emission (GE) band of CdS is larger, when the excitation is large. With the increase in intensity of GE band, it is expected that many atoms move to hexagonal positions.

3.6. Evidence for good polycrystalline quality of the film

The bands 5 to 9 (Fig. 4 & 5) localized in the energy region 2.56 to 2.92 eV are attributed to bound excitation [10]. The band 4 which is localized approximately at 2.4 eV of green emission (GE) band is due to electronic transitions from the conduction band to an acceptor level due to interstitial sulfur [11]. The origin of GE band may be due to the recombination of free electrons with trapped holes and recombination of trapped electrons with free holes as well as recombination of electrons from a donor level with trapped holes [12, 13]. The band 1 to 3 in the energy range 2.19 to 2.28 eV is due to radioactive transitions from donor levels arising from Cd atoms in interstitial sites to the valence band [10]. The PL spectra of CdS thin films showed not only the well known defect band but also the evidence for bound excitation recombination. These results show a good polycrystalline quality of our films. The similar results have reported earlier for magnetron sputtered CdS thin films [14].

3.7. Background emission and defects in the films

The absence of back ground emissions such as red emission (RE) band yellow emission (YE) band confirms the absence of interstitial cadmium (I_{cd}) and there by $I_{cd} - V_{cd}$ (cadmium vacancy) defect. Absence of $I_{cd}-V_{cd}$ defect should not force the optical band gap (E_g) to decrease which is the desirable quality of CdS films. The disappearance of YE band confirms the improvement of crystalline quality decreasing the density of native defects in the lattice and on increasing the grain size and hence diminishing the total grain boundary surface [15].

The appearance of blue emission (BE) band may be due to interstitial sulphur atoms. The presence of excess sulphur atoms has also been confirmed from EDAX analysis result ($Cd_{0.96} S_{1.04}$). Interstitial sulphur atoms will create I_s-V_s defect population. The emitted blue radiation may have an appreciable amount of the radiant energy in the ultraviolet. The ultraviolet radiation may be converted into useful radiation; there by the luminous efficiency can be increased [15].

4. Conclusions

XRD analysis show that chemical bath deposited films are polycrystalline in nature with hexagonal structure. EDAX analysis confirms the composition of constituent in the films. Photoluminescence analysis of the films show the existence of stokes's shift in our films. The influence of excitation power has been discussed in this paper. PL analysis also enabled us to show the evidence for good crystalline quality of our films.

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