

STRUCTURAL AND OPTICAL PROPERTIES OF CHEMICALLY DEPOSITED NANOCRYSTALLINE CdS FILMS

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This work investigates the structural and optical properties of nano crystalline CdS films prepared by chemical bath deposition (CBD) technique. The deposition of film is based upon precipitation followed by condensation on the substrates. The absorption spectrum is recorded in the wavelength range 400-700 nm, which shows absorption to be dominating mainly in visible region. Results of structural, photoconductive (PC) and excitation spectrum are presented and discussed. Apart from this, the results of X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-visible spectroscopy are also reported. XRD results exhibit prominent diffraction lines of CdS while SEM micrographs show layered type growth of particles. PC results show linear behaviour of dark current with applied voltage. PC rise shows fast increase in the beginning followed by saturation thereafter and the PC decay shows a fast decrease. PC excitation spectrum is found to peak at ~524 nm (2.36 eV).

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1. Introduction

Nowadays semiconductor nano crystals are being investigated in different aspects from physical properties of low dimensional systems to their potential applications [1]. Efficient luminescent nanocrystals form an interesting and important class of luminescent materials. These materials have exhibited excellent optical properties and better chemical stability as compared to organic emitters [2]. Cadmium sulphide (CdS) ($E_g = 2.42$ eV) thin films are of great interest in hetero junction solar cells and are characterized by many techniques [3]. It is suitable also for applications like visible radiation sensor [4] because of its high photoconductivity (PC) gain ($10^3 - 10^4$) and better spectral response. Polycrystalline CdS thin films are widely popular as window material [5] in several hetero junction solar cells such as CdS/CdTe, CdS/CuS [6] for their favourable optical properties. CdS is also important material due to its novel properties like photoconductivity, high refractive index and its high electron affinity [7, 8]. Earlier workers used sophisticated techniques like vacuum evaporation, sputtering, chemical vapour deposition, screen-printing, molecular beams epitaxy, multisource deposition and low pressure hydride-transport chemical vapour deposition etc [9-12]. In the present investigation, chemical bath deposition (CBD) technique has been used to prepare CdS nano crystalline films, which is considered to be an inexpensive, simple and capable of depositing optically smooth, uniform, and homogeneous layers. It is being used to grow CdS films since 1960s [13-15]. CBD technique also enhances the performance of CdS window layer. The films deposited by CBD are composed of closely packed nanocrystals (NCs) which make them attractive for basic and applied research of NCs [16].

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Recently there is a new interest in the CBD, which is motivated by its successful use in depositing buffer layers of CdS in thin-film photovoltaic cells based on CdTe and CuInSe₂ [17].

2 Experimental techniques

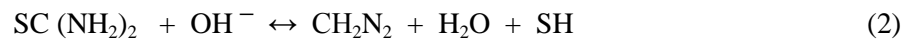
2.1 Sample Preparation

The films are grown through vertically dipping the commercially microscopic glass slides of dimension 75 mm x 24 mm x 2 mm in a chemical bath for 60 minutes. The substrates are cleaned thoroughly by ultrasonication using a standard procedure before immersing in chemical bath. The solution is prepared using 1 M solutions of highly pure and analytical reagent grade cadmium acetate [Cd (CH₃COO)₂], thiourea [SC(NH₂)₂], triethanolamine (HOCH₂CH₂)₃N (TEA) and 30 % aqueous ammonium hydroxide (NH₄OH) (mixture's pH ≈11). Thiourea and triethanolamine are two commonly used sulphiding agents [18]. Triethanolamine is used as a complexing agent and pH balancer also. The temperature of reaction mixture is maintained at the approximate temperature of 60° C. In the beginning, when precipitation starts, the solution is stirred for few minutes and no further stirring is done during the deposition. After that deposition is made in the static condition by placing glass substrates inclined vertically to the walls of the beaker until solution reaches desired temperature. The technique under this condition relies on the slow release of S⁻² ions to an alkaline solution in which the metal ion is buffered at a low concentration. Thereafter, the substrates are removed from the beaker and treated with distilled water to wash out the uneven overgrowth of grains at the surface and dried by keeping in open atmosphere under sun light until it dries completely. This helps in achieving adequate operating life of PL cell fabricated with such films. The dried film is quite adherent to the glass substrate surface and is irremovable. Bhushan and Chandra [19] reported that films prepared through CBD last for more than two years.

The mechanism of deposition of CdS films is based on the slow release of Cd⁺⁺ and S⁻⁻ ions in aqueous basic bath and subsequent condensation of these ions on the substrates suitably mounted in the bath. The slow release of Cd⁺⁺ ions is achieved by dissociation of a complex species of cadmium Cd (TEA)⁺⁺. Deposition takes place by an ion-by-ion process, or by the absorption of CdS particles on the substrate [20, 21]. The availability of Cd⁺⁺ ions is governed by the following dissociation equilibrium –



The S⁻ ions are provided by the dissociation of thiourea [SC (NH₂)₂] in the ammonical medium.



Since the solubility of CdS is low, even the low concentration of Cd⁺⁺ and S⁻⁻ yield the solid phase.

2.2 Measurement Details

Optical absorption spectra are recorded with a Varian (UV-VIS) DMS-100 spectrophotometer in the 400-700 nm wavelength range. The various X-ray analyses were made at RSIC, Nagpur using a computerized Philips diffractometer with Cu/K-alpha radiations. Further, SEM studies were performed at BSIP, Lucknow using a LEO (430) scanning electron microscope. The PL emission spectra collected with RCA-6217 photomultiplier tube (PMT) are recorded using a Thermo - Jarrel Ash grating monochromator (Model-82415). The film thickness is measured using mass-difference method and is found to lay between 1 and 2 μm.

3. Results and discussion

3.1 Characterization Studies

X-Ray Diffraction (XRD)

The X-ray diffractograms of CdS film are presented in fig. 1 and corresponding data are listed in table 1. The assignment of diffraction lines is made by comparing with JCPDS file of CdS (cubic, JCPDS 10-454) and the evaluated and reported values of parameters like lattice interval, lattice constant and Miller indices (table 1). If there is no inhomogeneous strain, the crystallite size d is estimated from the peak width with the Debye - Scherrer's formula [22] –

$$d = 0.9 \lambda / \beta \cos \theta \quad (3)$$

where λ - wavelength of X-ray radiations, β - the full width at half maxima (FWHM) of the peak and θ is the angle of diffraction. The estimated average particle size in the CdS sample is found to be in the 100 nm range.

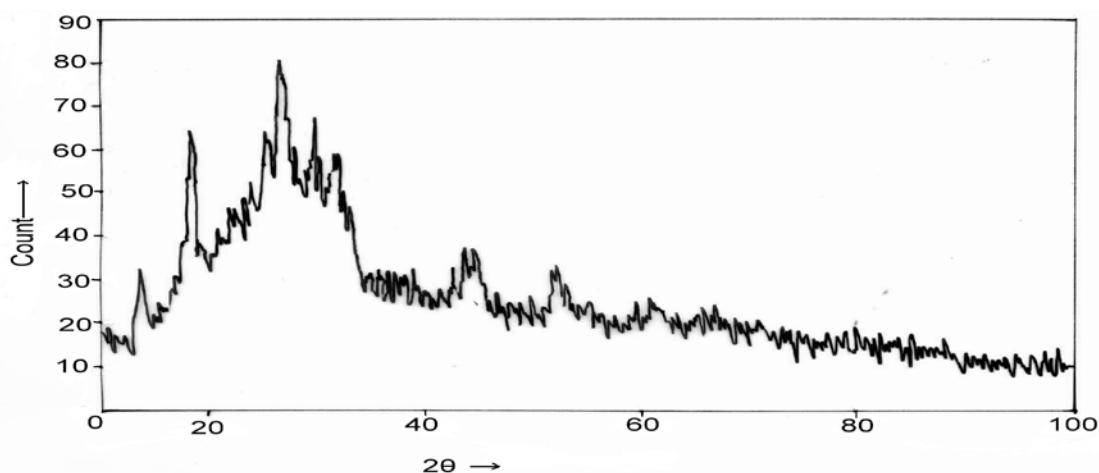


Fig. 1 X-ray diffractograms of CdS film

Table 1 XRD data for CdS film (Preparational temperature – 60°C, deposition time – 1 hour)

System	d (Å)	h k l	a (Å)	Intensity
CdS	3.5167	(100)h	$c/a=1.79$	10
	3.3422	(111)c	$a=4.4825$	26
	2.8246	(200)c	$a=5.659$	10
	1.7673	(112)h	$c/a=1.77$	7

Scanning Electron Microscopy (SEM)

The SEM micrographs of CdS films in unannealed and annealed cases are presented in fig. 2 and 3 respectively, each at magnification of 10 k. In the former case some cabbage like structure is seen, which improves in the later one. Earlier workers [23] found well developed cabbage structure, which they interpreted in terms of overlapping of different layers formed under continuous growth.

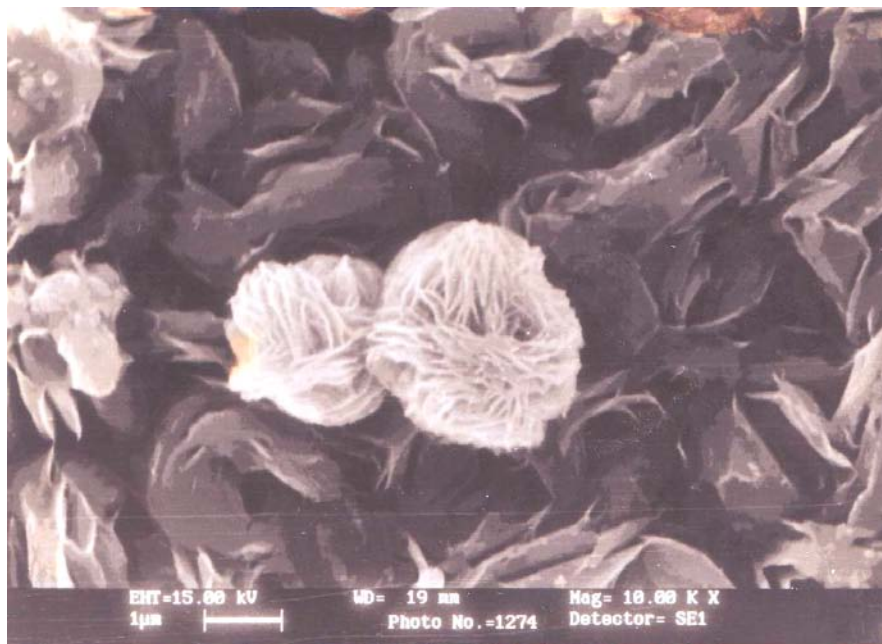


Fig.2 SEM of unannealed CdS film (magnification = 10 k)



Fig. 3 SEM of annealed CdS film (magnification = 10 k)

Absorption Spectra

The study of optical absorption is important in understanding the behavior of semiconductor nanocrystals. A fundamental property of semiconductors is band-gap energy separation between the filled valence band and the empty conduction band. Optical excitations of electrons across the band-gap are strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band-gap energy.

The absorption spectrum of CdS film in the wavelength range 400-700 nm is presented in fig.3 and the corresponding Tauc's plot [24] is shown in fig. 4. From figure 3, it is noticed that the

absorption mainly takes place between 400 and 500 nm wavelengths. The energy band-gap value calculated from Tauc's plot is found to be 2.44 eV.

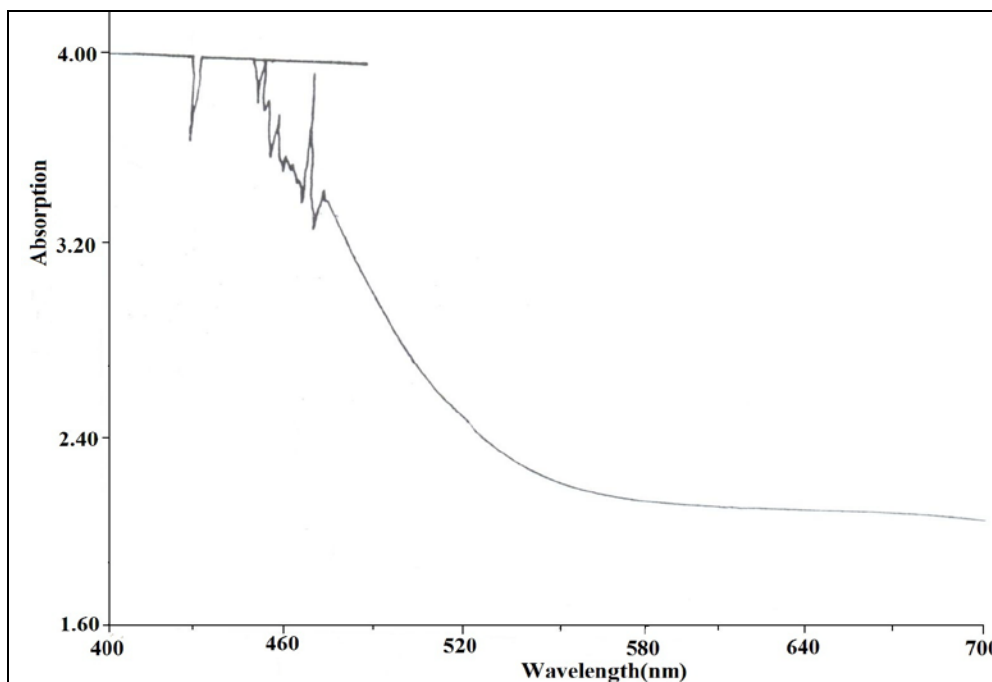


Fig. 4 Absorption spectra of CdS film

3.2 Optical Properties

PC Studies

Fig. 6 represents the behavior of dark current with the applied voltage for CdS film. From the figure it is noticed that with increasing voltage, the dark current of nano ampere order increases almost linearly. Fig. 7 represents rise and decay curve of CdS film. The rise consists of a fast increase in the beginning followed by saturation due to the net effect of the generation and recombination phenomena. Similarly the decay shows a fast decrease due to recombination and a slow variation arising due to trapping and enhanced mobility. It is generally believed that PC in CdS types materials is of N type due to trapping of photo generated holes at the negatively charged grain boundaries in poly crystalline thin film [25]. The infection barrier height (band bending) is lowered in this process, which in hence that electron mobility. The values of I_{pc} , I_{dc} and I_{pc}/I_{dc} for CdS film are found to be 0.4 mA, 5.2 nA and 0.12×10^5 respectively. With increasing dipping time the photo current I_{pc} increases but due to simultaneous increases in I_{dc} , the highest value of the ratio I_{pc}/I_{dc} comes out to be maximum for 1 hour of dipping. It was also found that with increasing temperature I_{pc}/I_{dc} increases but due to certain limitations of value both the highest temperature available conveniently was 60 °C, used in the present case. The PC excitation spectrum of CdS film is presented in fig. 8. The maximum photo current was recorded at ~524 nm corresponding to its band-gap of 2.36 eV.

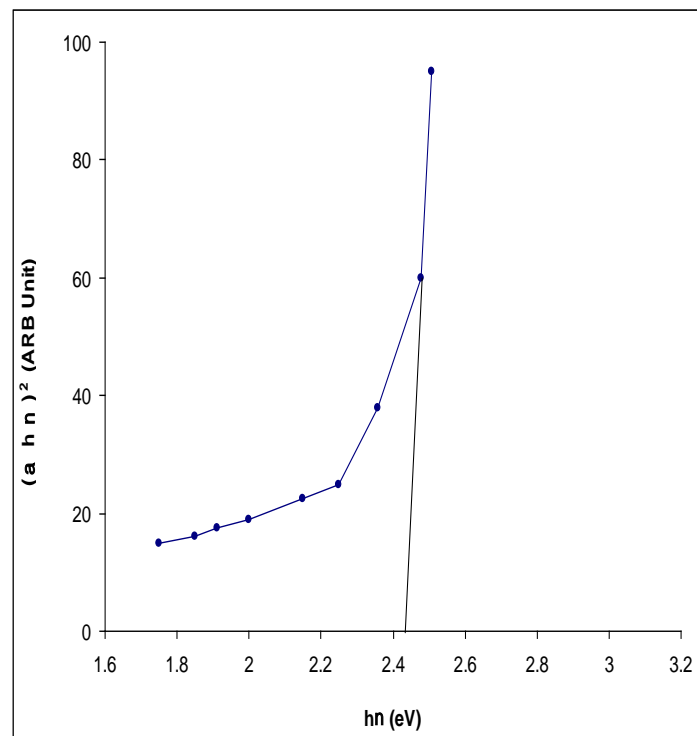


Fig. 5 Tauc's plot for CdS film

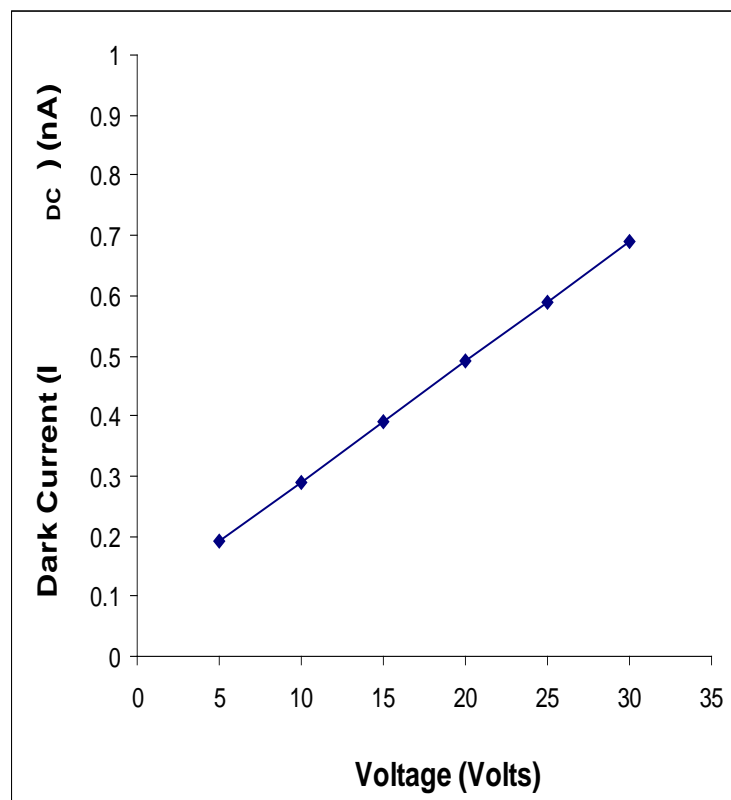


Fig. 6 Variation of dark current with voltage for CdS films

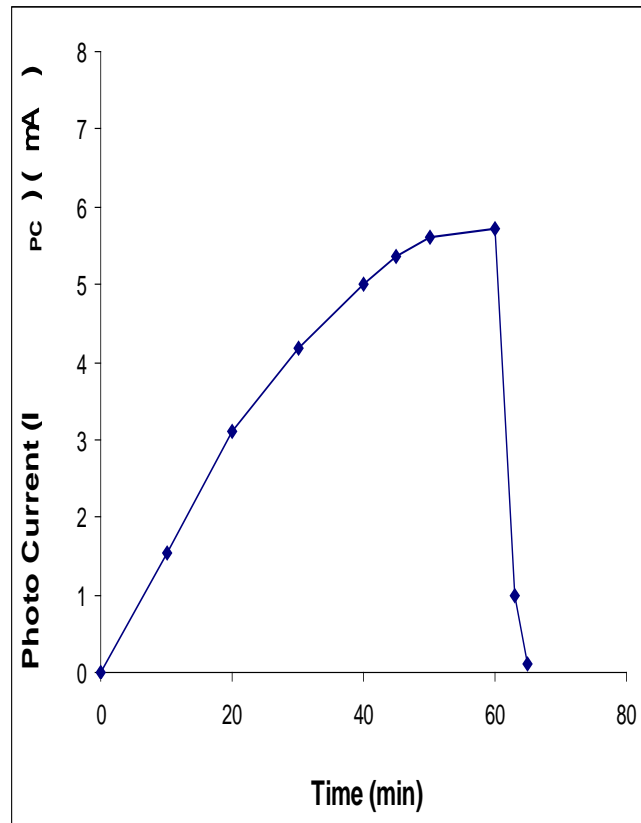


Fig. 7 Rise and decay curve for CdS film

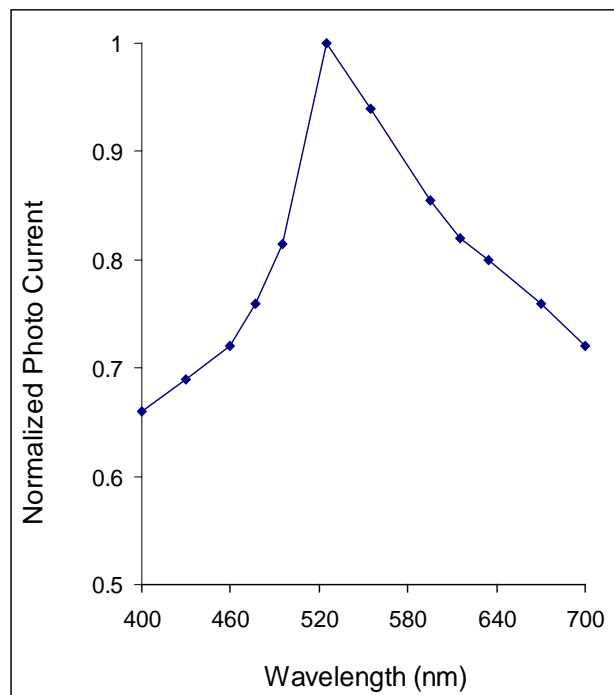


Fig. 8 Excitation spectrum of CdS film.

4. Conclusions

- CdS films are prepared through CBD technique, which is a simple and suitable method for obtaining smooth, uniform, high reflecting and strong adherent thin films.
- Sufficiently intense PC excitation spectrum is observed in CdS film prepared on glass substrate at 60°C.
- The peak in PC excitation curve is centered at 524 nm wavelength.
- Absorption spectra exhibit direct band-gap nature of material.
- SEM studies show layered growth of film particle while XRD patterns exhibit diffraction lines corresponding to CdS.
- The photo current to dark current ratio I_{pc}/I_{dc} is observed to be $\sim 0.12 \times 10^5$.

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