Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2017, 9(5):92-97
(http://www.derpharmachemica.com/archive.html)

Influence of Ammonia Concentration on Optical, Structural and Electrical Properties of CdS Thin Films Grown by CBD Method

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ABSTRACT

CdS thin films were deposited on a glass substrate using chemical bath deposition method. The properties of deposited CdS thin film were characterized using the XRD, UV-Vis-NIR spectroscopy, FT-IR and Electrical Studies. The XRD result shows that no sharp peak which indicates the samples is amorphous nature. The band gap energy for the films prepared in different concentration ammonia varies from 2.51 to 2.62 eV. The small peaks observed from 400-487 cm^{-1} are due to Cd-S band stretching. The electrical resistivity of the CdS thin film deposited on the glass substrate plotted between the variations of logarithm of resistivity (ln ρ) with reciprocal of temperature (1000/T). The resistivity observes that decreases with increases temperature.

Keywords: CdS thin film, XRD, UV, FT-IR, Electrical studies

INTRODUCTION

Cadmium Sulphide is an II-IV group semiconductor with a direct band gap of 2.4 eV [1] it has been used as a suitable window layer, solar cells, gas sensors photo dectors and lasers. CdS has been fascinated by many research communities due to its useful optoelectronics and photoconductive properties. It has also been used in other applications in photo resistors, optical filters and multilayer light emitting diodes, photo detectors, gas sensors, transparent, conducting semiconductors, optical wave-guides, Non-linear integrated optical devices, light amplifiers, image intensities, phosphors, electroluminescent devices and radiation detectors [2]. Various techniques have been used to make CdS thin film such as closed space sublimation [3], chemical bath deposition [4], vacuum evaporation [5], magnetron sputtering [6], spray pyrolysis [7] Thermal evaporation, chemical pyrolysis deposition and metal organic chemical vapour deposition [8-10] and each method has its own characteristic merits and demerits in producing homogeneous and defect free CdS thin films.

Among these techniques, chemical bath deposition technique is chosen for the present study, due to its easy, economical, reproducible quality and it is uncomplicated to control the growth rate. Thin film properties are sturdily dependent on the method deposition, concentration of precursor, the substrate materials, temperature, rate of deposition and the background pressure. In this study influence of different concentrations of ammonia on CdS thin film and their structural, optical, electrical and morphological changes are discussed.

In this study, influence of ammonia concentration and temperature of the mixer was maintained at 92°C, the deposition time was 2 h and the pH of the solution was maintained at 11.8 to deposit CdS thin films by chemical bath deposition method and to understand the growth mechanism and its impact of structural, optical and electrical properties. The films were characterized using X-ray diffraction analysis (XRD), optical analysis, fourier transform infrared (FT-IR) and electrical analysis to understand the CdS morphology and structure. The band gap energy (Eg) was determined from UV-Visible spectrometry.

EXPERIMENTAL

Substrate cleaning

The CdS thin films were growing on 7.5 × 2.5 × 0.1 cm microscope glass slides. The glass substrates were cleaned in an ultrasonic cleaner using acetone and alcohol. They were soaked in a chromic acid cleaning solution for 20 min. Further, they were cleaned ultrasonically in an isopropyl alcohol. Finally they were washed in deionized water and dried by flowing with dry nitrogen for 30 min.

Sample preparation

All the chemicals used in the present investigation were analytical grade purchased from Merck. CdS samples were prepared by silar method. For deposition of the films 30 ml of 0.004 M $CdCl_2$ solution is used as cationic precursor, 20 ml of 0.005 M $SC(NH_2)_2$ solution is used as anionic precursor, 30 ml of 0.3 M NH_4Cl serves as a buffer and 26 ml of (0.5, 1.0, 1.5 and 2.0 N) NH_3 is the complexing agent. The temperature of the mixer was maintained at 92°C, the deposition time was 2 h and the pH of the solution was maintained at 11.8 with the pH meter for the film deposition. The glass substrates were immersed in solution contained in glass beaker placed inside a water bath. The CdS thin films were prepared on glass substrate. After the formation of the films the substrates were removed from the bath and rinsed several times in distilled water to remove any adherent particles and unreacted materials. Samples were dried at room temperature. The prepared thin films were examined and characterized by means XRD, UV, FT-IR and Electrical Studies.

Sample characterization

The structural, optical and electrical properties of the CdS film were characterized by using a X-ray Diffraction studies were carried out XPERT-PRO, PW3071 and PW 3050/60 (Cu-Kα radiation of average wavelength 1.5405 Å), UV-VIS-NIR spectrophotometer (HR 4000 Ocean Optics), FT-IR spectrum of the powder (KBr pellet**)** was recorded using Perkin Elmer 1600. FT-IR spectrophotometer with a resolving power of 4 cm^{-1} and working ranges from 400 cm^{-1} to 4000 cm^{-1}, electrical resistivity measurement was carried out with Four Probe method.

RESULTS AND DISCUSSION

XRD analysis

XRD pattern can provide an effective method for determining the phase and crystallite size of the thin film. The basic principles of X-ray diffraction are found in text books by e.g. Buerger [11], Klug and Alexander [12]. Figure 1 shows the schematics of X-ray diffractometer. Diffraction in general occurs only when the wavelength of the wave motion is the same order of magnitude as the repeat distance between scattering centres. This condition of diffraction is nothing but Bragg's law is given as: $2d \sin\theta = n\lambda$, where, d=Interplaner spacing, θ=diffraction angel, λ=wavelength of X-ray and n=order of diffraction for the thin films, the powder technique in conjunction with diffractometer is most commonly used. In this technique the diffracted radiation is detected by the counter tube, which moves along the angular range of reflections. The intensities are recorded on a computer system. The'd' values are calculated using relation for known values of 'θ', λ and n. X-ray diffraction data thus obtained is printed in tabular form on paper and is compared with joint committee powder diffraction standards (JCPDS) data to identify the unknown material. The sample used may be powder, single crystal or thin film. The crystallite size of the deposits is estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Scherrer's formulas as follows: $D=0.9\ \lambda/\beta \cos\theta$, where, D is crystallite size, λ is wavelength of X-ray used, β is Full Width at Half Maxima of the peak (FWHM) in radians, θ is Bragg's angle. The X-ray diffraction data also can also be used to determine the dimension of the unit cell.

The typical XRD diffraction peaks of CdS thin films with different concentration of 0.5, 1.0, 1.5 and 2.0 N of NH_3 are shown in Figure 1. CdS can crystallize in four different crystal structures, namely hexagonal (wurtzite), cubic, (zinc blende) Cubic rock salt and distorted rock salt [13]. The crystalline structure of CdS thin films has been investigated by the X-ray diffraction measurements. All films deposited on glass substrate are no sharp peak which indicates the samples are in amorphous nature as illustrated by the X-ray scattering curves.

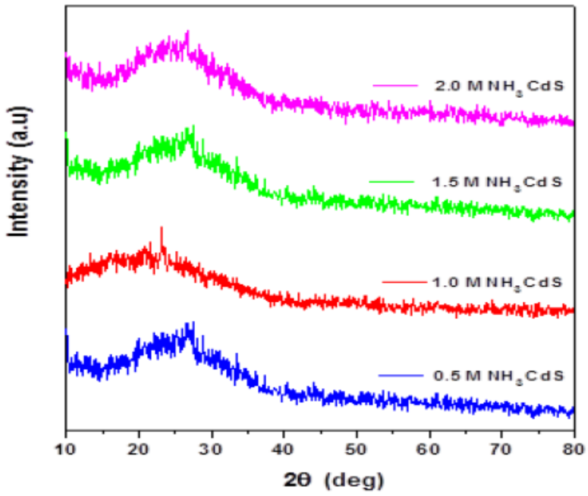

Figure 1: XRD pattern of CdS thin film with 0.5, 1.0, 1.5 and 2.0 N of NH_3

The XRD spectra are obtained by scanning of intensity versus 2θ. The broad hump in the wide angle region from 10-80°. The presence of small peaks in the X- ray diffractogram reveals the formation of nanocrystalline CdS thin films. The peaks are not sharp indicating that the average crystallite size is small. Due to size effect the peaks in the diffraction pattern broaden and their widths become large as the particles become smaller and also similar trend was observed by Jafarov et al. [14]. XRD patterns of CdS thin film without annealing has no diffraction peaks, which shows that in this condition CdS cannot crystallize reported by Jiankang [15].

Optical analysis

Absorbance

Data obtained from the optical characterization of the CdS thin films in the wavelength range 200-1200 nm.

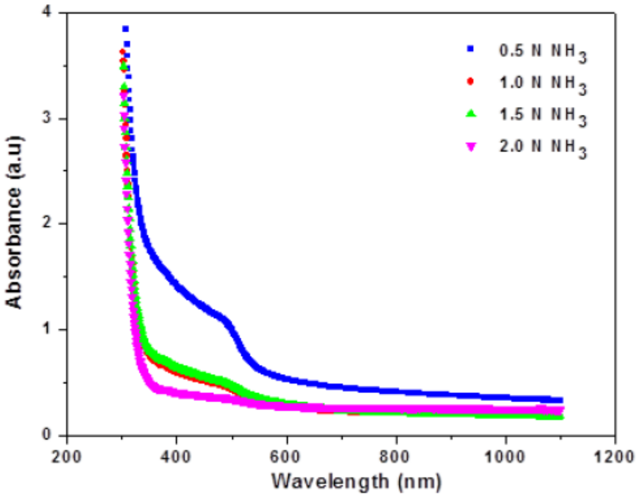

Figure 2: absorbance spectra of CdS thin film with different concentration of NH_3

In spectroscopy, the absorbance (also called optical density) of a material is a logarithmic ratio of the amount of radiation falling upon a CdS thin film material to the amount of radiation transmitted through the material [16]. Optical absorption study of CdS materials provides useful information to analysis some features concerning the band structural of materials.

The optical absorption and transmission spectrum was recorded at room temperature. The Figure 2 shows that absorbance decreases exponentially with an increase in wavelength. The absorption peaks were centered at 351 nm for the samples of 0.5, 1.0, 1.5 and 2.0 N of NH_3. The spectrum also showed that absorbance was high in the UV and low in VIS-NIR region. Hence, absorbance of the film decreases with increasing wavelength and decreasing the photon energy. The high absorbance in UV region makes the film good material for screening off UV portion of electromagnetic spectrum which is dangerous to human and animal health. It can also be used for anti-reflection coating [17,18]. Absorption edge of CdS thin films shows a clear shift to the lower wavelength as compared to its bulk counterpart. This blue shift of the absorption edge indicates decrease in the crystallite sizes and confirms the formation of CdS thin film.

Transmittance

Figure 3 shows the transmittance spectra of the CdS thin film. The optimum transmittance of 60.14% was obtained at pH 11.8. while the minimum transmittance of 30.23% was obtained. The transmittance increases with the increase in ammonia concentrations. It is also observed that the transmittance was low in the UV region which gradually increased in the visible and NIR regions. The high transmittance in VIS-NIR provides heat and visible light into the house. This high transmittance in the visible region makes CdS thin films useful aesthetic window glaze materials. However, the present study high transmittance of the film makes it suitable for solar energy collection because if coated on the surface of the collector, it will reduce reflection of solar radiation and transmits radiation to the collector fluid [19]. The optical transmittance of all samples was investigated with various concentration of ammonia, the reason of decreasing and increasing in optical transmittance can be related to voids and increase of spherical particle on surface on thin films [20].

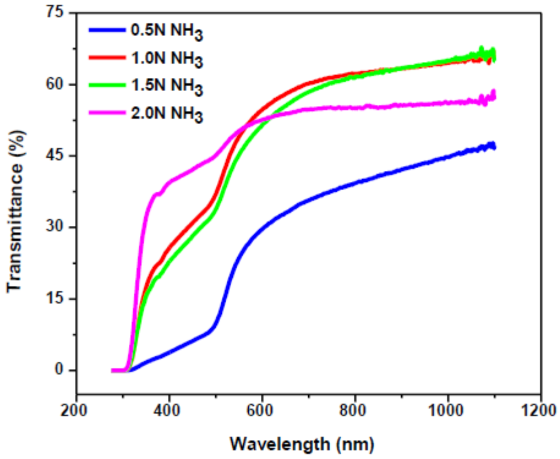

Figure 3: Transmittance spectra of CdS thin film with different concentration of NH_3

Band gap energy

The optical band gap values (Eg) were calculated from the Taue relationship [21]. The optical band gap can be calculated by extra plotting the linear portion of the plot $(\alpha h\gamma)^2$ versus hγ'.

$$(\alpha h\gamma)=A\ (h\gamma - Eg)^n$$

In which ‘hγ’ is the photon energy, Eg is the optical band gap of the semiconductor, A is a constant and n=1/2 for direct band gap semiconductor for CdS. the band gap energy (Eg) is estimated by a interpolation of each curve to energy axis.

From the plot, the variation of $(\alpha h\gamma)^2$ versus photon energy for different concentration of ammonia, CdS thin films are shown from the Figure 4 it is observed that a slight variation in the band gap values as the concentration of ammonia increases. This variation in the band gap is depends upon the grain size and lattice parameters [22,23]. The band gap energy for the films prepared in different concentration ammonia varies from 2.51 to 2.62 eV. This is in agreement with the value reported by other authors (Table 1) [24-26].

Table 1: The Band gap energy and corresponding concentration of NH_3

concentration of NH_3 (N)	Band gap energy (eV)
0.5	2.51
1.0	2.55
1.5	2.61
2.0	2.62

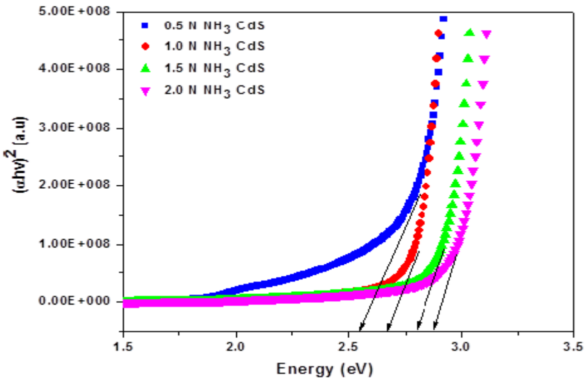

Figure 4: The Band gap value of CdS thin film with different concentration of NH_3

Cadmium sulfide (CdS) thin films were prepared by Ersin et al. [27] on glass substrates by CBD technique under different pH with influence of ammonia. The ‘Eg’ values of the CdS thin films were obtained in between 2.36 eV and 2.65 eV the band gap of the sample increases from 2.36 to 2.65 eV. It is close to the present study.

The direct band gap [28] value of CdS films by CBD method and CdS films by CSP method are found to be 2.42 eV and 2.55 eV respectively, this is close to the band gap value of the present study. The variation of band gap energy may be useful to design a suitable window material in fabrication for solar cells [29]. The optical band gap value of CdS thin film was estimated and found to be 2.40 eV less than present study (Figure 5).

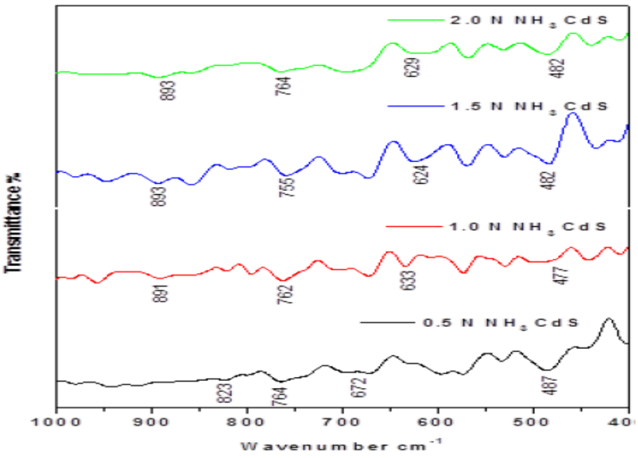

Figure 5: FT-IR Spectrum of of CdS thin film with different concentration of NH_3

Fourier transforms infrared spectroscopy (FT-IR)

The FT-IR spectrum is used to understand and analyze more elegantly the structure and molecular arrangements of thin film. Type of functional groups present in the substance is indicated by the adsorption that occurs at various frequencies.

FT-IR frequencies were used to evaluate the chemical bonding and to characterize and identify the organic species present in the CdS thin films. The presence of chemical bonding oxidized CdS thin films were studied by an FT-IR spectrometer in the ranges from 400 to 4000 cm^{-1}. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The small peaks observed from 400-487 cm^{-1} are due to Cd-S band stretching.

Similar result was confirmed that the formation of CdS, as this region was assigned to metal-sulphur (M-S) by Devadoss et al. [30]. The peak from 755-762 cm^{-1} is due to bending vibration of CdS, it is close to the reported by Esakkiraj et al. [31]. The peak noticed around 823 -892 cm^{-1} is assigned to S-S-S bending [32]. The Cd-S bond is mainly electrovalent; the FT-IR spectra do not show strong bands associated with Cd-S stretching and bending vibrations [33].

Electrical resistivity

The electrical resistivity of CdS thin film measurement was carried out in the temperature range 32-200^{o}C using D.C four probe methods. The measurement shows that the as deposited CdS films have the resistivity at 32°C.

The variation of ln ρ with 1000/T is shown in Figure 6. It observed that resistivity decrease with increase in temperature suggesting the semiconductor behavior of CdS. The activation energy for the as deposited CdS film is calculated from slope of Figure and is found out from 1.3797-2.5800 eV (Table 2).

Table 2: Electrical property parameters of CdS thin film with different concentration of NH_3

Concentration of NH_3	Resistivity (× 10^{-3} Ω cm)	Activation energy
0.5	3.683	1.3797
1.0	2.918	0.0011
1.5	2.532	0.4391
2.0	3.582	2.5800

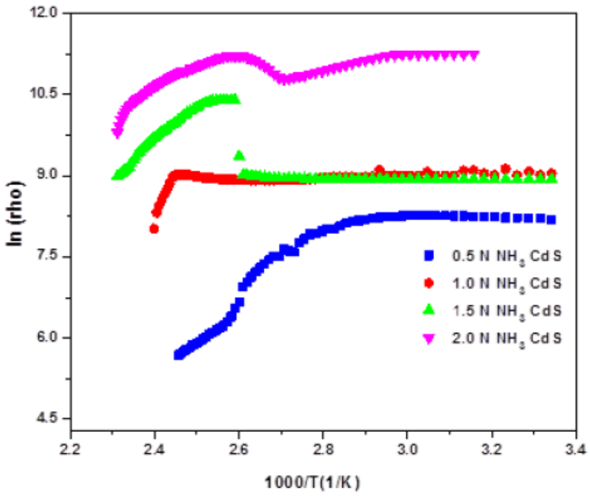

Figure 6: Electrical properties of CdS thin film with different concentration of NH_3

CONCLUSION

CdS thin film was successfully prepared by chemical bath deposition method. XRD analysis reveals that peaks are not sharp indicating that the average crystallite size is small. Due to size effect the peaks in the diffraction pattern broaden and their widths become large as the particles become smaller. All films deposited on glass substrate are no sharp peak which indicates the samples are in amorphous nature. The CdS thin films suitable for aesthetic window glaze materials. The band gap energy for the films prepared in different concentration ammonia varies from 2.51 to 2.62 eV. The small peaks observed from 400-487 cm^{-1} are due to Cd-S band stretching. The peak from 755-762 cm^{-1} is due to bending vibration of CdS. The electrical resistivity of the CdS thin film deposited on the glass substrate plotted between the variations of logarithm of resistivity (ln ρ) with reciprocal of temperature (1000/T). The resistivity observes that decreases with increases in temperature.

ACKNOWLEDGEMENTS

The authors are grateful to the Alagappa University, Karaikudi, Sastra University, Thanjavur and National College, Tiruchirappalli for their help with XRD, UV, FT-IR and electrical analysis.

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