



Optical study of effect of thiourea on CdS thin films

KEYWORDS

Cadmium sulphide thin films, Hexagonal structure, Grain size, Spray Pyrolysis, Optical band gap

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ABSTRACT This paper presents the results of the structural and optical analysis of CdS thin films prepared by Spray of Pyrolysis (SP) technique. The deposited CdS films were characterized using spectrophotometer and the effect of Sulfide on the structural properties of the films was investigated through the analysis of X-ray diffraction pattern (XRD). The growth of crystal became stronger and more oriented as seen in the X-ray diffraction pattern. The studying of X-ray diffraction showed that; all the films have the hexagonal structure with lattice constants $a=b=4.1358$ and $c=6.7156\text{\AA}$, the crystallite size of the CdS thin films increases and strain (ϵ) as well as the dislocation density (δ) decreases. Also, the optical properties of the polycrystalline thin films examined by the UV-VIS spectroscopy. The band gap of thin films was found to be direct transition and decreases with the increase of sprayed number in the range of (3.57-2.38) eV.

I. Introduction

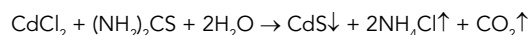
Over the years, chalcogenide semiconductors of II- VI group have attracted considerable attention because of their applications in optoelectronic devices [1] such as solar cells [e.g., CdS/CdTe, CdS/CuInSe₂] and photo-conductive devices [2]. CdS is one of such compound in this group and its physical properties have been investigated extensively for both fundamental and practical purpose. In recent years, thin CdS films deserve attention because of their expected gap emission which lies very close to the highest sensitivity of the human eye [3]. There had been an increasing in research and development of CdS films, which are widely used in devices. Cadmium sulfide (CdS) with hexagonal structure was highly favorable for solar cell applications as a window layer because of its suitable band gap (a wide band gap $E_g= 2.4$ eV) and stability [4] also, its high transmittance and low resistivity [5]. CdS also been used in other applications including photovoltaic devices [6], Light emitting diodes and thin films FET transistor [7]. However due to the high cost of such a material, studies were developed towards polycrystalline compound semiconductors and particularly thin polycrystalline films [8].

Many techniques had been reported for the deposition of CdS thin films. They included chemical bath deposition (CBD) [9], molecular beam epitaxial technique (MBE) [10], sputtering [11], thermal evaporation [12], metal organic chemical vapor deposition (MOCVD) [13], successive ionic layer absorption and reaction (SILAR) [14] and spray pyrolysis [15,16]. In this work, spray pyrolysis technique has been chosen for deposition of CdS thin films because it is very low cost and simple technique that enables intentional doping and getting large area also uniform thin films [17]. The present studying is centered over the effect of increasing the ratio of thiourea to CdCl₂ on the CdS thin films on the structural and optical properties of polycrystalline thin CdS films. X-ray diffraction (XRD), Ultraviolet- visible (UV-VIS) absorption spectroscopy is used to characterize the sample.

II. Experimental Method

The CdS thin films were prepared by from 0.1 M aqueous solution of thiourea and 0.1 M aqueous solution. CdS thin films were prepared from these solutions with ratio of CdX-S2X (where 25 ml of CdCl₂ and 50ml of thiourea). The usual cleaning of the glass slides was first carried out and after that prepared the films from different numbers of sprays (6 sprays, 12 sprays, 15 sprays). The solutions were mixed thoroughly, and the final solution was sprayed on to heated substrates which were kept at temperature 400°C. The substrates are microscopic plane glass slides of area 2.5 x 7.6 cm². The time of spraying was short about 4 seconds, and the distance from

the heater to the end of the capillary tube was 20cm. When the solution was sprayed the following reaction takes place at the surface of the heated substrate.



This yield is a yellow-orange deposit layer, and uniform growth of CdS films on substrates. The deposited CdS films were characterized for structural and optical properties under different growth conditions. The crystallographic structures of the films were analyzed with X-ray diffractometer using Cu-K radiations (1.54060 Å) operated at 40 kV and 30 mA. For optical studies, optical absorbance spectra recorded by using UV-Visible spectrophotometer (UV-2601) in wavelength range (300-800 nm), the thickness of the CdS thin films was measured by using Stellar Net Inc spectrometer.

III. Results and discussion

We have studied the effect of increase volume ratio of thiourea to CdCl₂ on the CdS thin films. We can observe that at high amount of sulfide the thickness of the films decreases as 61.7nm, 56.4nm and 33nm respectively with increasing of the number of sprays (6, 12, 15 sprays), because the sublimation of the sulfide during the sprayed process, which was due to the reaching of CdS films to CdX Sx stability state. Also the effect of the ratio of thiourea on the structural properties and optical properties were presented in following confirms:

III.1. Structural properties

The structural properties of the CdS thin films have been investigated by X-ray diffraction technique, Fig. 1 shows the X-ray diffraction pattern of the three CdS thin films deposited on glass substrate. Many Peaks were observed at 24.838, 26.523, 28.200 and 36.686 deg, corresponding to the (100), (002), (101) and (012) planes of the hexagonal phase of CdS. The intensity of the peaks was observed to increase as the ratio of S was decreased. A strong peak with 2θ value about 26.523 corresponds to the (002). Crystalline plane of CdS was present in all the three XRD which could be indexed hexagonal structure of CdS and it had a good agreement with standard X-ray diffraction data, which reported in card (JCPDS powder diffraction file no. 96-901-1664). We can observe also other peaks appear with increasing number of sprays (as S was decreases), the degree of preferred orientation increased with the increases number of sprays. Thus the film prepared at 15 sprays had a better crystalline quality, as indicated from its XRD pattern. The average grain size was calculated from the scherrer formula [18]:

$$D = K\lambda / \beta \cos \theta \quad (1)$$

Where K is a constant taken to be 0.94, λ the wavelength of X-Ray used ($\lambda=1.54060 \text{ \AA}$), β the full width at half maximum of (002) peak of XRD pattern, and 2θ is the Bragg angle. The values of crystallites sizes are found to be in the range (23.7-27.0) nm, an increase in grain size has been observed as shown in fig. 2 which illustrates the variation in average grain size, that's caused by the effect of decreases sulfide. Using the Miller indices of these planes, the lattice parameters a=b and c of the unit cell are evaluated according to the relation:

$$1/d^2=4/3 (h^2+hk+k^2/a^2) + l^2/c^2 \quad (2)$$

Where d is the inter-planar spacing, and (h, k, l) are the Miller indices. The calculated values of the lattice parameters are given in table I.

The values of 2θ , thickness, interplanar spacing d, grain size, dislocation density (ρ), strain and intensity of the XRD peak in the thin films of different number of sprayed are given in table II.

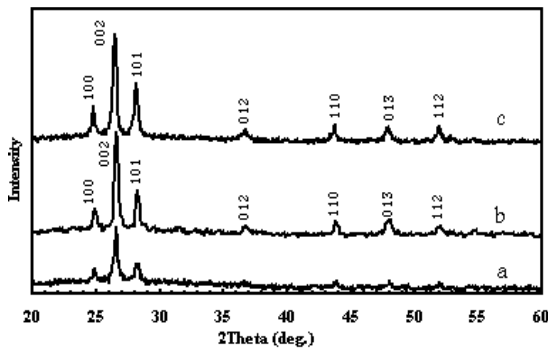


Fig.1. XRD patterns of CdS thin films of different spray (a) 6 sprays, (b) 12 Sprays and (c) 15 sprays.

Table I: The lattice parameter of the CdS film

Number sprays	Lattice constant a=b A0		Lattice constant c A0	
	Exp.	Sta.	Exp.	Sta.
6	4.1238	4.1370	6.7169	6.7144
12	4.1188	4.1370	6.6830	6.7144
15	4.1358	4.1370	6.7156	6.7144

Table II: Comparison of structural parameters, interplanar spacing's, Grain size and peak intensity of the CdS thin films of the different number sprayed

No. of sprays	Thickness (nm)	Angle 2θ deg.	Interplanar spacing (d) A0		Grain size (nm)	Peak Intensity (a.u)	Strain $\epsilon \times 10^{-4}$ (line-2 m-4)	Dislocation density 10^{14} δ (line / m2)
			Exp.	Sta.				
6	61.7	26.618	3.3461	3.3572	23.7	350	18.18	17.80
12	56.4	26.560	3.3415	3.3572	26.8	522	16.21	13.92
15	33.0	26.523	3.3578	3.3572	27.0	534	15.38	13.71

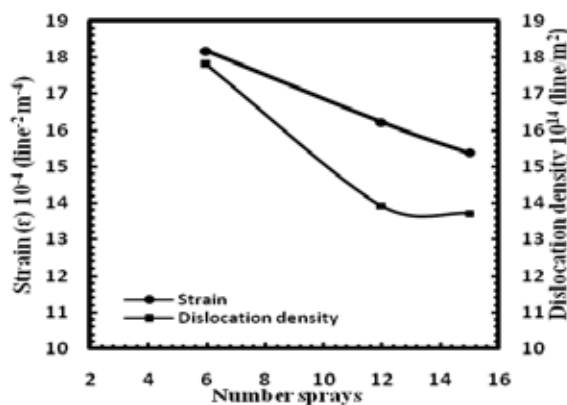


Fig.3. Effect of number of sprays on strain and dislocation

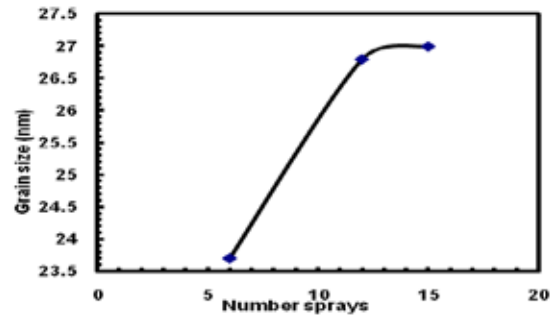


Fig. 2. Effect of number sprays on the grain size of CdS thin films

The increase of the grain size may be due to the coalescence of small crystals. Large grain size minimizes the imperfect regions of the film; this is also supported by the smaller strain and dislocation densities.

The stain, ϵ was calculated by using the formula [19]:

$$\epsilon = \beta \cos \theta / 4 \quad (3)$$

The dislocation density, δ of the CdS thin film is defined as the length volume of the crystal, was evaluate from the formula [19]:

$$\delta = 1/ (D)^2 \quad (4)$$

Figure 3 shows the variation dislocation density and strain. Since dislocation density and strain are manifestation of dislocation network in the films, the decrease in the dislocation density indicates the formation of high quality films [20]. As shown in Table II, the dislocation density and strain of CdS thin films were decreased with increasing the number of sprays.

Figure 4 shows the strain and dislocation density of CdS thin films as a function of the crystallite size. The strain and dislocation density decrease with increasing the crystallite size. The maximum in the crystallite size at 15 sprays is considered to be due to decrease in the strain, which was caused by change in the crystal structure. The strain and dislocation density decreases with increasing the crystallite size in the film attributed to the sublimation of the sulfide during the sprayed process. Therefore, we may conclude that there is a decrease in the lattice imperfections with increase in the crystallite size [21].

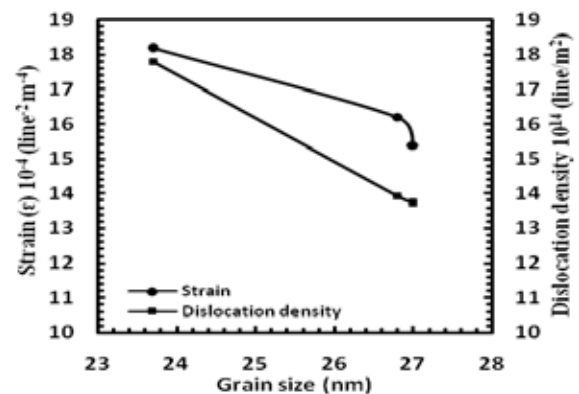


Fig.4. Strain and dislocation density of CdS thin films density of CdS thin films as a function of grain size

III.2. Optical properties

The optical transmittance and absorbance spectra of the films are given in figs.5 and 6, respectively. The transmission coefficient strongly depends on the film structure, which is determined by the preparation methods, film thickness and deposition conditions. Increasing the number of sprays induces the reduction of transparent.

We can see from the absorbance spectra, which the films at high number of sprays the absorbance increase and thus caused by the effect of sulfide, which is due to the reaching of CdS films to stability. It is seen from the optical spectra that the absorption edge shifts towards the higher wavelength side indicating the reduction in the band gap values, as shown below. The optical band gap E_g of the films has been calculated using the absorption spectra by using the Tauc relationship, which is given by the formula [22] [23]:

$(\alpha hv)^m = A (hv - E_g)$ (5) Where, A is a characterize parameter independent of photon energy, hv is the incident photon energy and $m = 2$ for direct band gap energy material. By plotting $(\alpha hv)^2$ versus the incident photon energy (hv) and extrapolating the straight line portion of the curve to intercept the energy

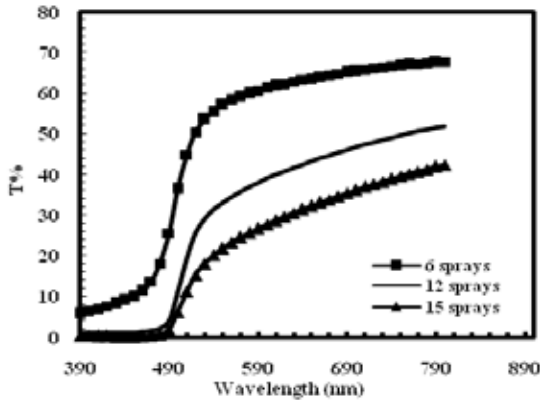


Fig.5. Transmission spectra of CdS thin films of different spray

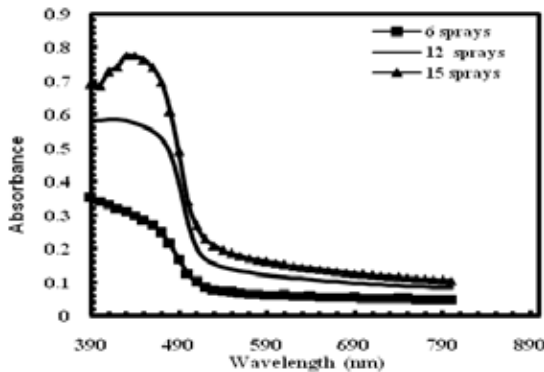


Fig.6. Absorbance spectra of CdS thin films of different sprays

axis, the optical band gap can be obtained as shown in fig. 7; the value of the band gap energy has been calculated as shown in table (III).

The optical band gap of the films is found to decrease with the decreases sulfide and due to the increase of grain size as show in table (II), this agreement with the results which reported by others[24][25]. The decrease in band gap energy may be due to enhancement in the crystal properties. We can see that at low numbers of sprays the optical band gap which calculated is greater than the bulk band gap (2.42eV), as reported by earlier workers [26].

Fig.8 indicates the relation between the refractive index and the wavelength in order to give us on information on the

electronic polarizability, local field and for determining the density of colors inside the material [27]. We can see from the spectrograph that refractive index increases as the number of sprays increase.

The absorption coefficient of these films at different energy is shown in fig.9, reveals that exhibits the variation of the absorption coefficient as a function of energy for CdS films in different sprayed numbers, and this suggest that crystalline nature of the thin films increase with the decrease amount of sulfide, and further supports increased crystalline nature as implied from the enhanced peak intensity of the XRD peaks for low film thickness.

The extinction coefficient (k) also calculated from the relation of [28]:

$$k = \alpha \lambda / 4\pi \tag{6}$$

Where, k is the extinction coefficient. Fig.10 shows the variation of the extinction coefficient (k) versus the wavelength of the as deposited CdS thin films.

Table III: The band gap of CdS thin films of different sprays

Number sprays	Band gap (eV)
6	3. 57
12	2. 43
15	2. 38

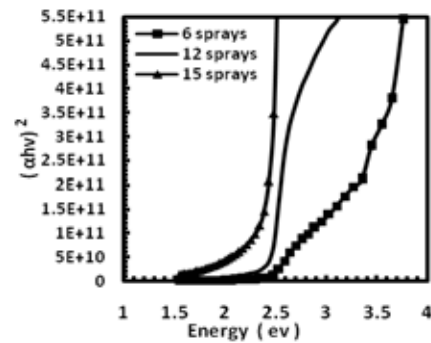


Fig.7. $(\alpha hv)^2$ versus hv of CdS thin films of different sprays

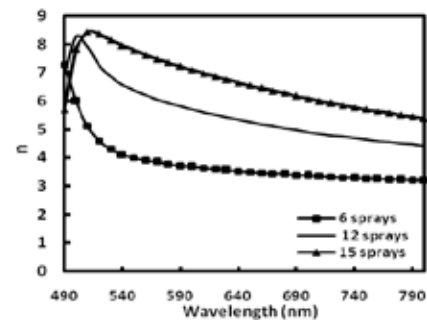


Fig.8. Reflective index as a function of the wavelength with sprays different sprays

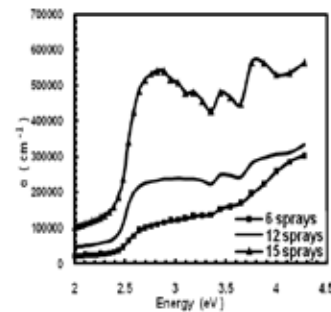


Fig.9. Absorption coefficient as a function of wavelength

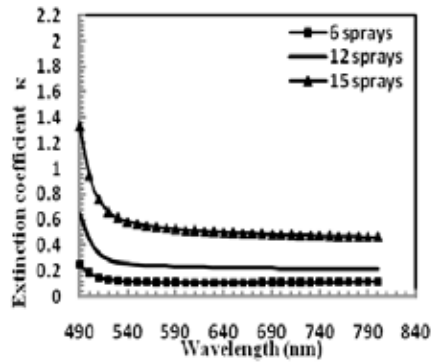


Fig .10. Extinction coefficient as a function of the wave- for CdS films for different sprayed length with different sprays

The real part of dielectric constant and the imaginary part of the dielectric constant as a function of photon energy as illustrated in figs.11 and 12 respectively. It is seen that both ϵ_1 and ϵ_2 decreases with increasing energy. The deposition parameters cause important changes in real part and imaginary parts of the dielectric constant of the films.

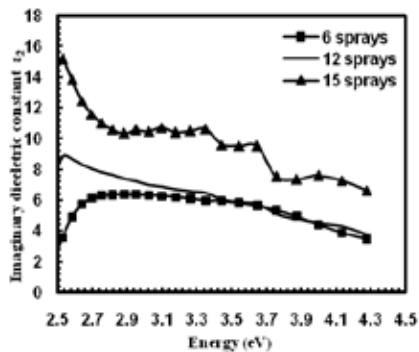


Fig.11. Real dielectric constant as a function of Photon energy

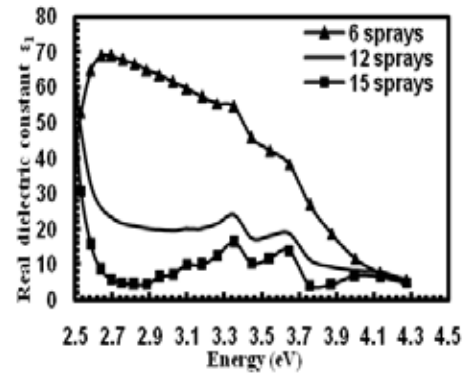


Fig.12. Imaginary dielectric constant as a function of energy the different sprayed with the different sprayed

IV. Conclusions

The CdS thin films were prepared by spray pyrolysis technique on glass substrate using the solution of cadmium chloride and thiourea. Films have been characterized using optical and structural measurements. The films have hexagonal structure with a preferential orientation of (002) plane. The crystallites size measured by XRD studies was found to be within 23.7–27 nm. The deductions were made to obtain the optical and structural parameters such as the dislocation density, strain, optical band gap energy and absorption coefficient etc. Energy gap was deduced from the optical absorption spectra; they show a direct transition in the range 3.57–2.38 eV. The variations of these with the effect of thiourea on the CdS films had been studied.

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