

Structural, Electrical and Optical Properties of Chlorine Doped CdS Thin Films

¹Amanullah Fatehmulla, ²A.S. Al-Shammari,
¹A.M. Al-Dhafiri, ¹W.A. Farooq and ³F. Yakuphanoglu

¹Department of Physics and Astronomy, College of Science, King Saud University,
P.O. Box: 2455, Riyadh-11451, Saudi Arabia

²Department of Physics, College of Science, University of Hail, P.O. Box: 2440, Hail, Saudi Arabia

³Department of Physics, Faculty of Science, Firat University, Elazig, 2311, Turkey

Abstract: The chlorine doped CdS thin films were prepared by high vacuum evaporation (HVE) technique at room temperature. The structural, electrical and optical properties of the films were investigated. The electrical resistivity of the CdS films is found to be in the range of 10^{-2} - 10^{-4} Ω .cm. The carrier concentration and mobility values of the CdS films are increased with Cl doping. The CdS films exhibit high optical transmittance (70-90%) and the optical band gap of the CdS films were changed with Cl doping and was in the range of 2.45-2.48 eV. It is evaluated that the structural, electrical and optical properties of the CdS films are controlled by Cl dopant.

Key words: CdS film • Thermal evaporation • Grain size • Optical properties • Electrical properties

INTRODUCTION

The metal chalcogenide (II-VI) semiconductor compounds, particularly CdS, CdSe, CdTe etc., have long been of interest for having a photo-conductivity in the visible region and CdS has the best photoconductivity [1, 2]. Cadmium sulphide (CdS) thin films are widely used in a large number of solid state device applications such as photoconduction, Xerography, electroluminescent devices, piezo-electric transducers, laser material, optical detectors [3], ultrasonic transducers, photovoltaic solar energy conversion, thin film transistor electronics and other optoelectronic devices. Presently, CdS is considered as the best suited window material for CdTe and CuIn(Ga)Se₂ solar cells [4, 5]. Different deposition techniques have been utilized to obtain CdS. These preparation techniques include vacuum evaporation [6], spray pyrolysis, sputtering, molecular beam epitaxy (MBE), metal organic vapor phase epitaxy (MOVPE) and metal organic chemical vapor deposition (MOCVD), close spaced sublimation (CSS), VPE, CSVT, CVD, successive ionic layer adsorption and reaction (SILAR), physical vapor deposition (PVD), screen printing, chemical bath deposition (CBD), anodization, laser ablation, electrodeposition and electrophoresis [7-9]. The widest

application for vacuum coating has been for decorative purposes. Thin bright metallic-looking films can be deposited on conductors and non-conductors alike at relatively low cost [10]. Furthermore, vacuum evaporation technique is a simple and convenient method for large-area and low cost deposition [11]. As deposited CdS thin films exhibit high resistivity (of the order of 10^{6-7} Ω .cm) which limits their use for photovoltaic applications [12]. However, the optoelectronic properties of these films can be improved using different methods including preparation parameters, thermal treatment, doping, etc. Podesta et al. have doped CdS thin films by fluorine and they have noticed a great effect of fluorine doping on the optical properties of the film and as a result an improvement in the efficiency of CdS/CdTe solar cell [13]. Hiie *et al.* have studied the effect of annealing on the physical properties of CdS:Cl thin films prepared by SP and CBD techniques and they have observed a significant improvements in the film properties [14]. Furthermore, some work have been carried out to investigate the effect of CdCl₂ treatment on the performance of CdS/CdTe solar cells [15, 16]. In our previous work, it was found that chlorine co-activation strongly affected the physical properties of chemically deposited CdS thin films [17].

Corresponding Author: F. Yakuphanoglu, Department of Physics, Faculty of Science, Firat University, Elazig, 2311, Turkey.
Tel: +90 424 2370000-3621, Fax: +90 424 2330062.

In present paper, we have investigated the effects of chlorine doping on the structural, electrical and optical properties of CdS thin films.

Experimental Details: Thin Films were prepared by HVE (high vacuum evaporation) technique using the Hindhivac model A-12D4 coating unit evacuated at 10^{-6} Torr. The chlorine doped CdS films were prepared on cleaned substrates. CdCl₂ of 99.99% purity mixed CdS of 99.999% purity powders were placed in a molybdenum boat connected to a current source by two stainless-steel electrodes. Since CdS and CdCl₂ have similar vapor pressures at high temperatures (845°C) [18], it is expected that the films would have a similar vapor pressure over the substrate, when the mixture is heated evenly. The boat was filled by CdS powder mixed with 0.05%, 0.10%, 0.15%, 0.20% and 0.25% CdCl₂ by weight using the percent composition formula [19]:

$$\text{Mass \%}X = \left(\frac{\text{Mass of } X \text{ in the mixture}}{\text{Mass of the whole mixture}} \right) \times 100 \quad (1)$$

The weight of each compound was taken by a microbalance. The mixture was placed in the evaporation system and the base pressure was reduced to 5×10^{-6} Torr. The substrate temperature was kept constant at 300 K. When the film thickness is reached 100 nm on the digital thickness monitor, the evaporation shutter was closed and the source current was reduced slowly to zero. The rate of deposition was maintained at 7 Å/sec. The thickness of the film was confirmed also through MBI technique (multiple beam interferometry). The chemical analysis was done through wet chemical methods. The films were tested by a DPD colorimetric method using a Hach photometer. The samples were cut into 6×6 mm and ohmic contacts were made by evaporating high purity indium exactly to the corners of these samples. Electrical measurements were carried out by Van der Pauw technique using HMS-2000 from Ecopia. For Hall measurement, a magnetic field of 0.51 T was applied perpendicular to the current flow direction. Conductivity type was determined through Hall effect measurement and it has been reconfirmed using hot point probe technique as well. All measurements were made at room temperature. Perkin-Elmer Lambda 40 UV/VIS Spectrophotometer was used for optical studies.

RESULTS AND DISCUSSION

Structural Properties of Chlorine Doped CdS Films: The obtained films from the HVE technique on glass

substrates were flat, homogeneous, transparent and green-yellowish, with very good adherence to the substrate. The XRD patterns for chlorine doped CdS thin films ($d = 1000 \text{ \AA}$) prepared by HVE technique on glass substrates are shown in Figure 1. The presence of two peaks can be observed from the figure CdS:Cl films at $2\theta = 26.5^\circ$ and $2\theta = 15.1^\circ$. The peak at $2\theta = 26.5^\circ$ corresponds to either cubic (111) or hexagonal (002) planes with more intensity which indicates good crystallinity of the film. With regard to the peak appeared at $2\theta = 15.1^\circ$, the comparison with ASTM data revealed that this peak corresponds to the (100) plane of orthorhombic structure of CdCl₂ indicating the presence of chlorine. This has been confirmed also through wet chemical method and it has shown a strong presence of chlorine in our films [17]. Thus, we believe that the chlorine works as a dopant in these films. From the figure, it can also be seen that as the concentration of CdCl₂ increases the intensity of CdCl₂ peak also increases while the intensity of CdS peak decreases. This indicates that the doping concentration has increased as the CdCl₂ concentration increases in the evaporated mixture. The decrease in the intensity of the most intense peak of CdS thin films with increasing the dopant concentration has been also observed by F. Atay *et al.* for indium doped CdS thin films and M. Urrahman *et al.* for silver doped CdS thin films [20,21].

The crystallite size of the films was calculated using Scherrer formula [22]:

$$t = \frac{\lambda}{\beta \cos \theta_\beta} \quad (2)$$

where λ is the X-Ray wave length, β is the full-width at half-maximum (FWHM) values of the diffraction peaks and θ_β is the Bragg angle. Table 1 shows the effect of CdCl₂ concentration on the grain size of CdS thin films prepared by HVE techniques on glass substrates. As seen in Table 1, the chlorine increases the crystallite size resulting in a good crystallinity of CdS thin films. The presence of chlorine in the films did not affect the growth direction, but it assists to form the bigger crystallites. Thus the role of chlorine in this process is significant.

Figure 2 shows SEM images for doped CdS films prepared by HVE technique. With 0.05% concentration, the grains observed under the microscope are as a cluster of submicroscopic crystallites. The average grain size increases from about 0.5 μm upto 3 μm , when the chlorine concentration increases from 0.05% to 0.20% and grain boundaries become very well defined. Thus chlorine enhances the grain size.

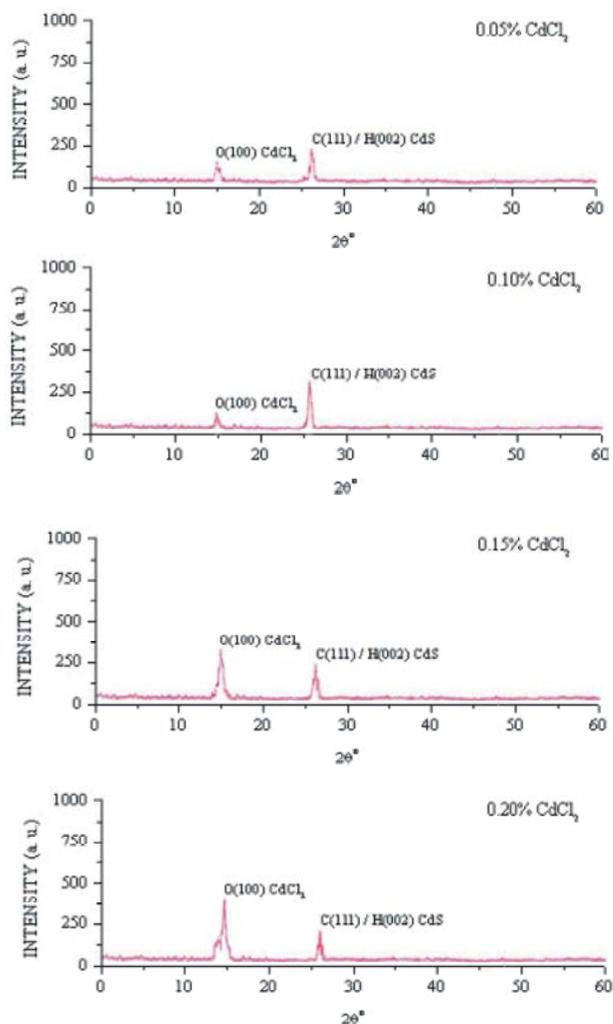


Fig. 1: XRD patterns of HVE grown CdS thin films with different CdCl₂ concentrations

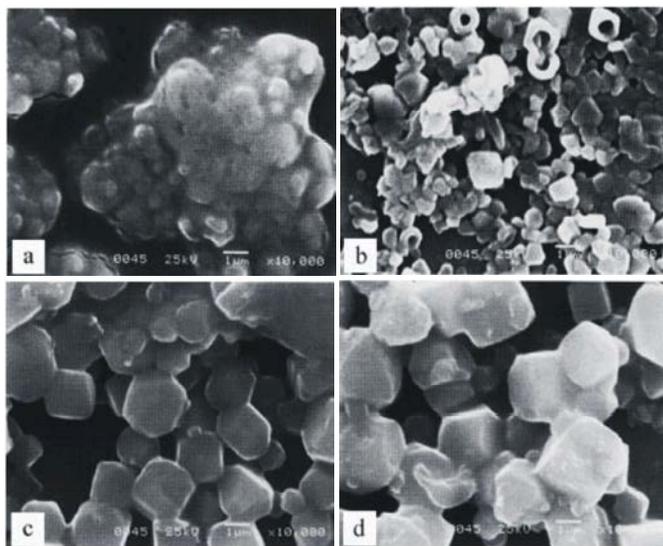


Fig. 2: SEM images of HVE grown CdS thin films (a) 0.05% CdCl₂, (b) 0.10% CdCl₂, (c) 0.15% CdCl₂ and (d) 0.20% CdCl₂

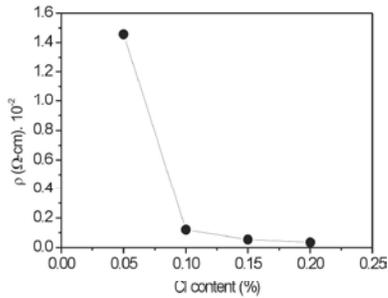


Fig. 3: Variation of resistivity of CdS thin films with CdCl₂ concentration

Table 1: Crystallite size and optical band gap values of doped CdS thin films

Cl Content(%)	t (nm)	E _g (eV)
0.05	75.5	2.45
0.10	129.6	2.46
0.15	181.5	2.47
0.20	226.8	2.48

The crystallite sizes calculated through XRD results (using Scherrer formula) are smaller than the grain sizes obtained by SEM images because the grains are formed by the crystallites.

Electrical Properties of Chlorine Doped CdS Thin Films:

The electrical conductivity properties of the films were investigated by Hall effect measurement and hot point probe techniques. The obtained results indicate that all the CdS films have n-type conductivity. It is well known that the sulfur vacancies give rise to the n-type nature of the as-deposited CdS films. Doping with chlorine didn't change the conductivity type, because, the atomic radii of chlorine and sulfur atoms are comparable. It is believed that while doping, chlorine atom will knockoff the sulfur and sits in its lattice position making a bond with cadmium atom which results in a free electron, contributing to the n-typeness of the films. The sulfur atom may replace at the interstitial position in the lattice.

The electrical resistivity of chlorine doped CdS thin films is shown in Figure 3. A decrease in the resistivity with increasing Cl concentration is observed in Fig. 3. Beyond 0.1% chlorine concentration, the resistivity undergoes a saturation trend. This behavior is explained with respect to Seto's model. The model suggests that grain boundaries in the CdS films affect the resistivity of the films [18]. Within a single grain, the carrier transport is similar to single-crystal carrier transport. As the carriers reach the grain boundary, they are faced with trapping centers. Depending on the distribution of these trapping centers and the temperature, some of the trapping centers near the grain boundary are filled with carriers and

become charged [18]. The empty centers may capture an electron from a charged center. Thus, conduction is possible by hopping of charge carriers from the filled trap center to the empty ones. However, with increased doping concentrations, more of the empty centers are filled with charge carriers, creating a potential barrier near the grain boundary. This potential barrier plays a role in limiting the conductivity of the films. Beyond 0.1% Cl concentration, however, resistivity undergoes a saturation trend. This saturation trend can be explained if we take into account the increased number of defect centers in the films, known as A-center complexes that result from increased doping. These centers are formed in the presence of doubly negative-charged Cd vacancies and chlorine atoms. The formation energy of V_{Cd}^{-2} decreases as the Fermi level increases [18]. Thus, for heavily doped films, these V_{Cd}^{-2} defects are spontaneously created. In this case, any excess chlorine atoms are trapped in the A-center complexes, limiting the number of donors in the film and giving rise to the saturation behavior.

The carrier concentration of chlorine doped CdS films is shown in Figure 4. However, the carrier concentration increases as the Cl concentration increases which indicates that the chlorine impurity atoms serve as strong donor impurities.

From the experimental results it was noticed that the carrier concentration reaches saturation as heavy doping is carried out that is for concentration > 0.20%. This saturation is explained using the A-center complex model discussed earlier. The Fermi level in this regime is so high that V_{Cd}^{-2} defects are spontaneously created. In this case, any excess chlorine atoms are trapped in A-centre complexes, limiting the number of donors in the film, hence, saturating the carrier concentration [18].

The mobility values of chlorine doped CdS films were measured and are shown in Figure 5. As seen in Fig. 5, a rapid incremental in the mobility is seen with increasing Cl concentration. This behavior begins to slow down as the doping concentration increases. This slow down in mobility is perhaps caused by the increasing number of charged defect complexes with increasing doping concentration. These defect centers increase the scattering rate for the carriers, thus degrading the mobility in the deposited films. Grain boundaries with their trapping centers offer another source of scattering for the carriers in the films, leading to a further reduction in the carrier mobility [18].

Optical Properties of Chlorine Doped CdS Films:

Transmission spectra of the films were recorded as a function of the wavelength in the range 300-800 nm.

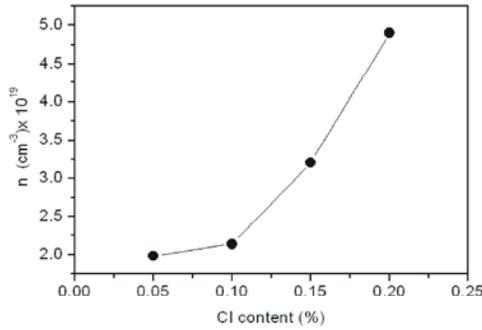


Fig. 4: Carrier density variation of CdS thin films with CdCl₂ concentration

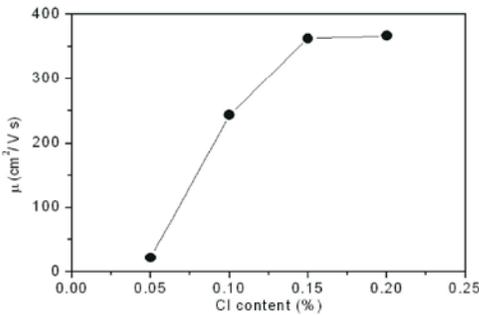


Fig. 5: Mobility variation of CdS thin films with CdCl₂ concentration

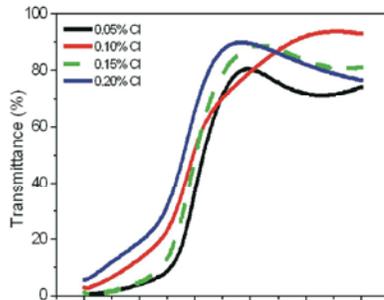


Fig. 6: Transmission spectra of CdS thin films with different CdCl₂ concentration

The substrate absorption was corrected by introducing an uncoated cleaned glass substrate of the same size in the reference beam. The optical transmittance spectra of chlorine doped CdS films in the wavelength range 300-800 nm are shown in Figure 6. An increase in transmittance is observed for the chlorine doped films. All chlorine doped films have sharp fall at the band edge, which is an indication of good crystallinity of the film and exhibit high optical transmittance (70-90%) in the range of wavelengths above the absorption edge. A shift for the absorption edge towards the shorter wavelength with increase in the doping concentration can be observed from the spectra. This shift towards the shorter wavelength indicates the increase of optical band gap [7].

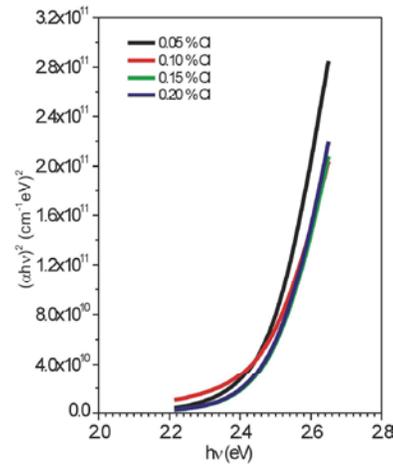


Fig. 7: Bandgap of CdS thin films

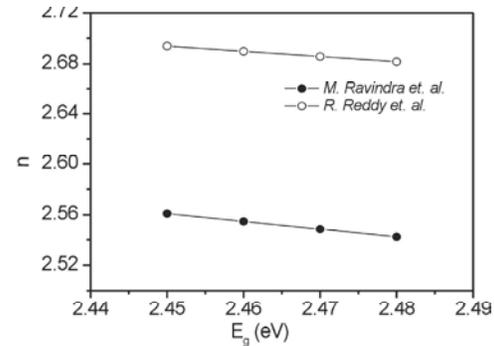


Fig. 8: Variation of refractive index of CdS thin films with the band gap energy

The absorption coefficient α at various wavelengths was calculated using the equation [23]:

$$\alpha = \frac{2.303}{d} \log_{10} \left(\frac{1}{T} \right) \quad (3)$$

The band gap of the films was determined by plotting a graph between $(\alpha h \nu)^2$ and $(h \nu)$ within an accuracy of ± 0.01 eV. The bandgap variation of chlorine doped CdS films are shown in Figure 7. The straight line behavior in the figure implies that the transition is direct. The band gap of doped films is comparable with the pure ones. Furthermore, it is clearly seen from the figure as the CdCl₂ concentration increases the band gap also increase. The increase in band gap can be attributed to the improvement in crystallinity [24]. The absence of interference patterns made it impossible to determine the refractive index of the films from the transmission spectra. However, researchers have reported some relations that govern the variation of the optical refractive index n with the band gap energy. Ravindra *et al.* [25] have proposed the following relation to calculate the refractive index:

$$n = 4.08 - 0.62E_g \quad (4)$$

Another formula has been reported also by Reddy and Anjaneyulu [26] which takes the following form:

$$n = 3.59 - \ln E_g \quad (5)$$

Figure 8 shows the Variation of refractive index of the films with the band gap energy as calculated using equations (4) and (5). As seen from the figure, both methods show that the refractive index decreases as the band gap increases. This decrease in the refractive index value can be attributed to the increase of the chlorine content in the film.

CONCLUSIONS

Chlorine doped CdS thin films have been successfully prepared by HVE technique at R.T. All the films obtained during the present investigations have resulted in n-type conductivity. The resistivity of chlorine doped CdS films decreased with the increase of CdCl₂ concentration and beyond 0.10% CdCl₂ concentration resistivity undergoes a saturation trend following the Seto's model. The carrier concentration increases as the CdCl₂ concentration is increased. A rapid incremental behavior of mobility has been noticed with increasing CdCl₂ concentration. An increase in transmittance is observed for the chlorine doped films. A shift for the absorption edge towards the shorter wavelength with increase in the doping concentration has been noticed. This shift towards the shorter wavelength indicates the increase of optical band gap.

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