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Structural, Optical and Electrical Properties of Thermally Deposited CdS Thin Films

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Abstract: Thermal evaporation technique is used to deposit CdS thin films on glass substrates using CdS powder. Various characterization techniques have been used to investigate the structural, optical and electrical properties of the prepared thin films. The results of XRD analysis showed that the as-deposited and annealed (at 200℃ for 1 hour) CdS films were single crystalline having a cubic structure with (111) plane orientation according to International Center for Diffraction Data (ICDD) card number 10-0454. The crystallite size is found to be 37.32 nm and 39.78 nm for the as-deposited and annealed films respectively. The "AFM" outcomes show uniform, homogeneous and tightly adherent films over the entire glass substrate surface without any voids, pinholes or cracks and having a large number of grains. The UV-Visible-NIR absorbance spectra were recorded in the range of (400- 1100) nm to investigate the optical characteristics. The results have shown that the CdS films have a low absorbance in the visible-near infrared region from ~ 500 nm to 1100 nm. The energy gap was calculated using Tauc's plot and it was around 2.4 eV for the as-deposited and annealed films. The electrical characterization included D.C. conductivity and Hall Effect measurements were carried out. From D.C. measurements, it was found that the deposited films have two transport mechanisms of free carriers and two activation energies were estimated. Hall measurement results showed that the deposited films are n-type, and the carrier concentration and mobility have been estimated.

Keywords: Thermal Evaporation, CdS Thin Films, Structural Properties, Optical Properties, Electrical Properties.

1. INTRODUCTION

In recent years, there has been growing interest in II–VI semiconductor materials for their potential applications in optoelectronic and photovoltaic industries. One of the most promising alternative materials is cadmium sulfide (CdS), which is a chalcogenide n-type semiconductor having a direct energy band gap between 2.28 eV and 2.45 eV[1]. Owing to their interesting structural, optical and electrical properties that are much different compared to bulk materials, CdS thin films can be applied in many technologies such as window layer in solar cells[2], optical sensors[3], transistors[4], diodes[5], etc. Various methods such as electro-deposition[6], spray pyrolysis[7], successive ionic layer adsorption and reaction (SILAR)[8], pulsed-laser deposition[9], vacuum evaporation[10], chemical bath deposition (CBD)[11], and thermal evaporation[12], etc. are used to prepare CdS thin films. Among these, thermal evaporation under vacuum is one of the well-established techniques. CdS thin films can exist in either cubic or hexagonal phase or as a mixture of both phases. Some of the physical properties of vacuum evaporated CdS thin films are reported by various authors[13-15], but little information on electrical properties of CdS film has been reported. CdS films prepared with thermal evaporation have an excellent photoconductivity as well as permeability in the visible range, but usually the resistivity is very high (> 10^8 Ω.cm), which limits their use as optical window in solar cells. Annealing or chemical doping could solve this problem[16]. In the present study, CdS thin films are deposited by thermal evaporation under vacuum and annealed at 200℃ for 1 hour. The films are characterized by X-ray diffraction (XRD), AFM, UV-VIS-NIR spectroscopy and electrical measurements and the results were discussed to investigate their possible applications.

2. EXPERIMENTAL DETAILS

CdS thin films were deposited by thermal evaporation technique at a vacuum pressure of (5×10^{-5} mbar) on highly pre-cleaned glass substrates using high purity CdS powder (Fluka AG) placed in molybdenum boat. The film thickness was measured by gravimetric method and was found to be ~ 200 nm. After that the films were annealed at 200℃ for 1 hour. For electrical investigation, pure aluminum was used for the preparation of the electrodes.

The XRD patterns of the CdS thin films were recorded by using X-ray diffraction model (XRD-6000), in the range between 20°and 70°, using CuKα radiations with wavelength of 1.54060 Å. The surface property measurements were done using atomic force microscopy (AFM) model (SPM-AA3000). Absorbance spectra were recorded using UV- VIS-NIR spectrometer model UV-2610. Digital electrometer (Keithley model 2450) and electrical oven were used to measure the electrical conductivity as a function of temperature in the range of (293-423) K. Hall effect measurements system type HSM-300 was used to determine Hall Effect parameters.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction analysis: The structure of the films was studied by X-ray diffraction analysis. XRD patterns of the prepared CdS thin films are shown in **Figure 1**. It can be seen that the diffraction peak is sharp and well defined indicating that the films are single crystalline with peak diffraction at ~26.53° having cubic structure with (111) plane orientation according to International Center for Diffraction Data (ICDD) card number 10-0454. This result agrees with the previous observations reported by[17,18]. It is clear from **Figure 1** that annealing leads to increase in the peak intensity. The increase in the peak intensity as a result of annealing suggests improvement in the film crystallinity[19-22]. The Scherrer's relation was used to find out the crystallite size of the films from XRD patterns[23]. The crystallite size for the (111) direction is found to be 37.32 nm and 39.78 nm for the as-deposited and annealed films respectively.

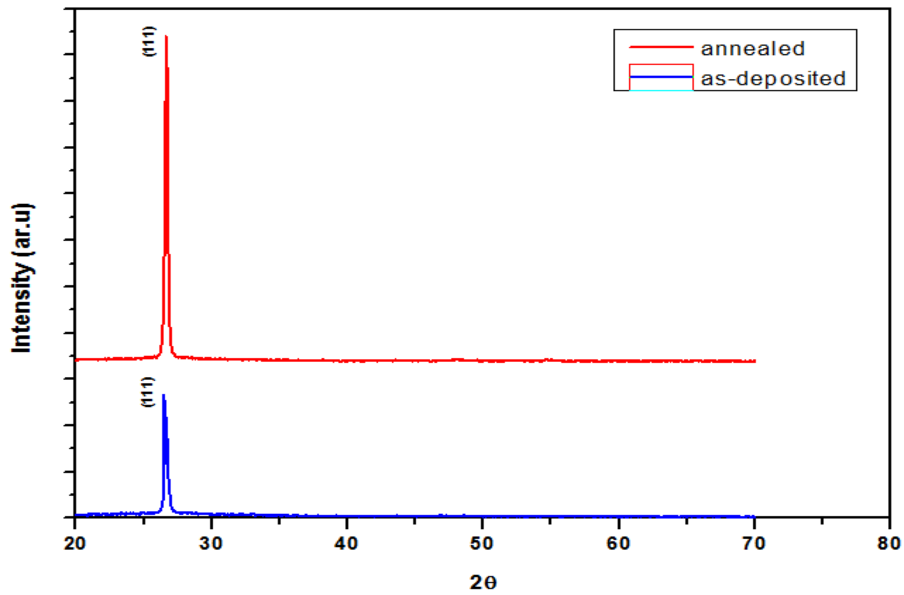
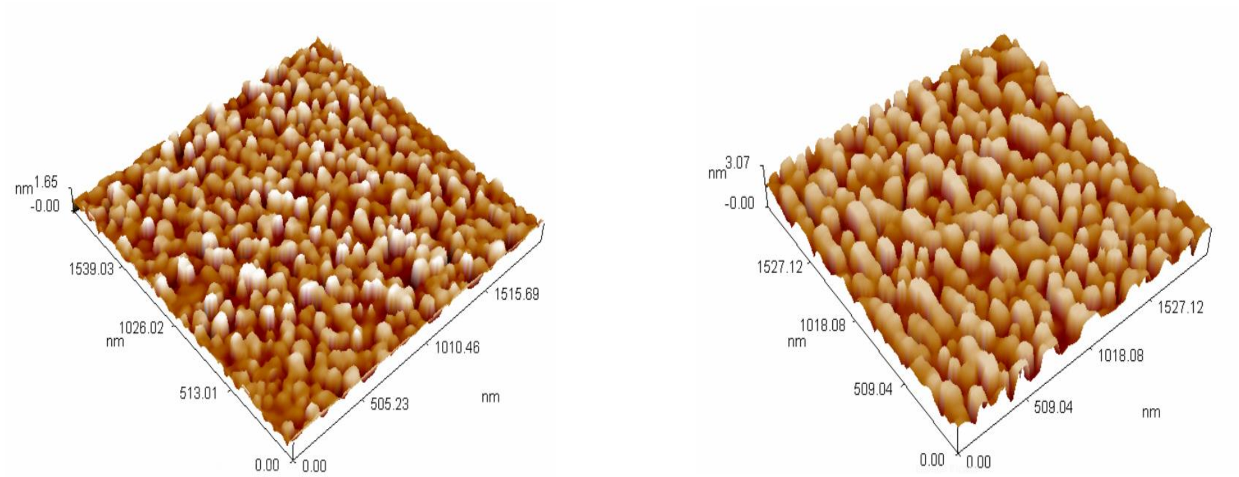


Fig.1: X-ray diffraction patterns of the as-deposited and annealed CdS thin film.

3.2. AFM analysis: The surface morphology of CdS thin films deposited on glass substrates is carried out using AFM. The size of scanned area was (2×2) μm^2. **Figure 2** shows uniform, homogeneous and tightly adherent films over the entire glass substrate surface without any voids, pinholes or cracks and having a large number of grains. The as-deposited film has a rough surface and irregular grain size and the morphology was not changed much for the annealed film but showed better uniformity in grain size. The grain size of thin films is in the range of several tens of nanometers which indicates the crystalline nature of the films. The average roughness value, the grain size, and root mean square roughness of the films are shown in **Table 1.**



(a) (b)

Fig. 2: 3-D AFM images of (a) as-deposited and (b) annealed CdS thin films.

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Table 1: Average roughness, root mean square roughness, and grain size of the as-deposited and annealed CdS thin film.

Samples	Roughness (nm)	Root Mean Square (nm)	Grain Size (nm)
As-deposited	0.272	0.336	73.80
Annealed	0.469	0.555	84.45

3.3. Optical studies: The optical properties of the deposited CdS thin films have been investigated by using UV-Vis-NIR absorbance spectra in the region of (400-1100) nm. The variation of absorbance with wavelength for CdS thin films is shown in **Figure 3**. From the figure, it is observed that the absorbance decreases as the wavelength increases. The CdS films show low absorbance in the visible-near infrared region from ~ 500 nm to 1100 nm, this result agrees well with other reports[24].

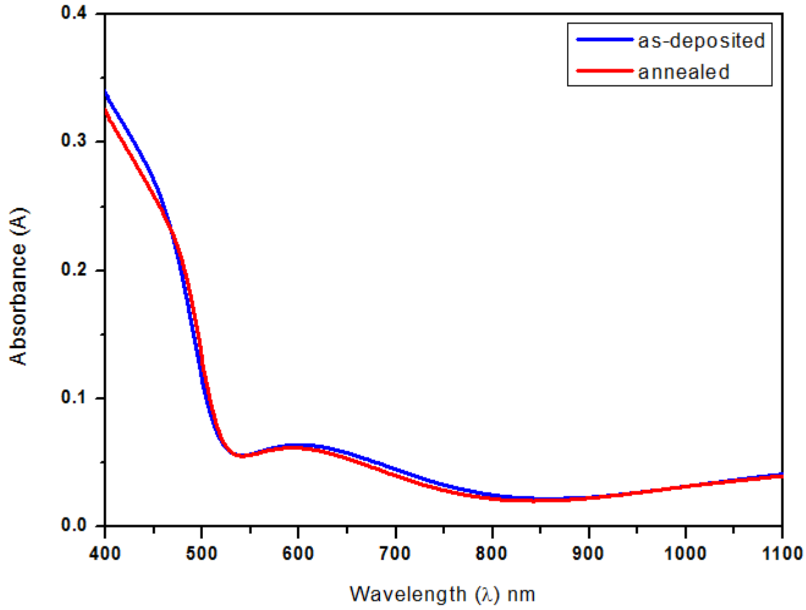

Fig. 3: Absorbance of CdS thin film as a function of wavelength.

Figure 4 shows the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ and the energy gap (E_g) value is calculated by using the absorption coefficient values and (Tauc's equation) by assuming allowed direct transition between valance and conduction bands. From the figure, it is observed that the energy band gap slightly decreases after annealing from 2.45 eV to 2.41 eV. This is in good agreement with that reported by other authors[20, 24-27]. The decrease in band gap values is due to the increase in crystallite size on annealing[24], as supported by XRD results.

3.4. Electrical studies: The electrical characterization included D.C. conductivity and Hall Effect measurements. **Figure 5** shows the plots of lnσ versus $10^3/T$ for the deposited CdS thin films in the range of (293-423) K. The activation energy of electrical conductivity was found by using the relation $\sigma = \sigma_o \exp(- Ea / KT)$[28]. From the figure, one can note that there are two transport mechanisms for the as-deposited and annealed CdS thin films, giving two activation energies, (E_{a1}) in the range of (293-353) K and (E_{a2}) in the range of (363-423) K. The conduction mechanism of the activation energy (E_{a2}) at higher temperature range is due to carrier excitation into the extended states beyond the mobility edge, and at the lower range of temperatures; the conduction mechanism of the activation energy (E_{a1}) is due to carrier excitation into localized states at the edge of the bands[29].

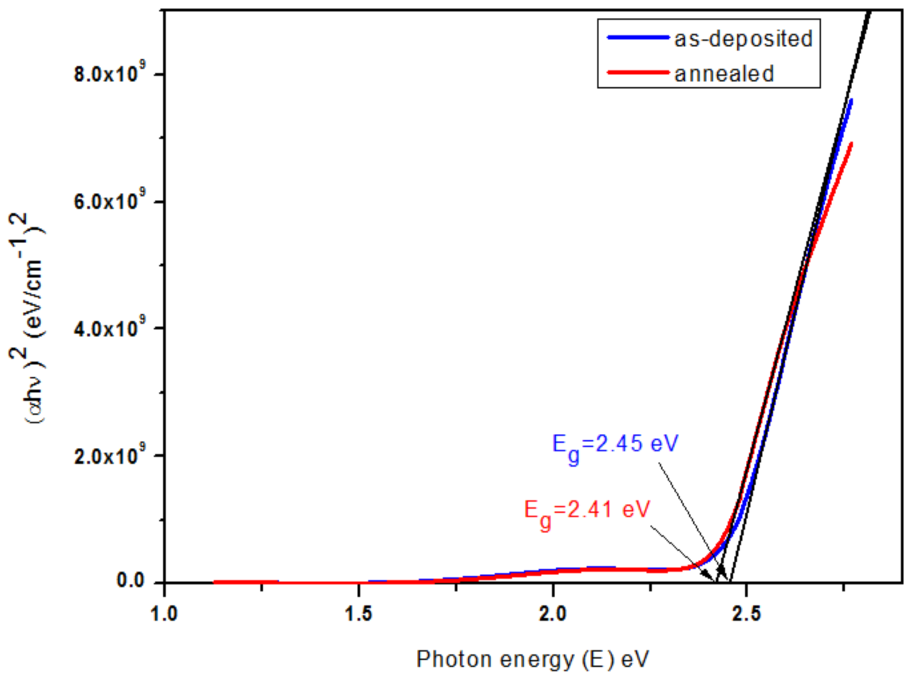

Fig. 4: The relation between $(\alpha h\upsilon)^2$ and ($h\upsilon$) of CdS thin films.

It is observed from **Table 2** that the conductivity of the annealed CdS films is higher than that of the as-deposited one which may be attributed to the increase in crystallite size and improvement of the CdS structure which in turn causes to decrease the energy band gap. It is clear from **Table 1** that the activation energies decrease with annealing; this is mainly attributed to the removal of defect states presented in the film[30]. This result is consistent with other reports[24, 31].

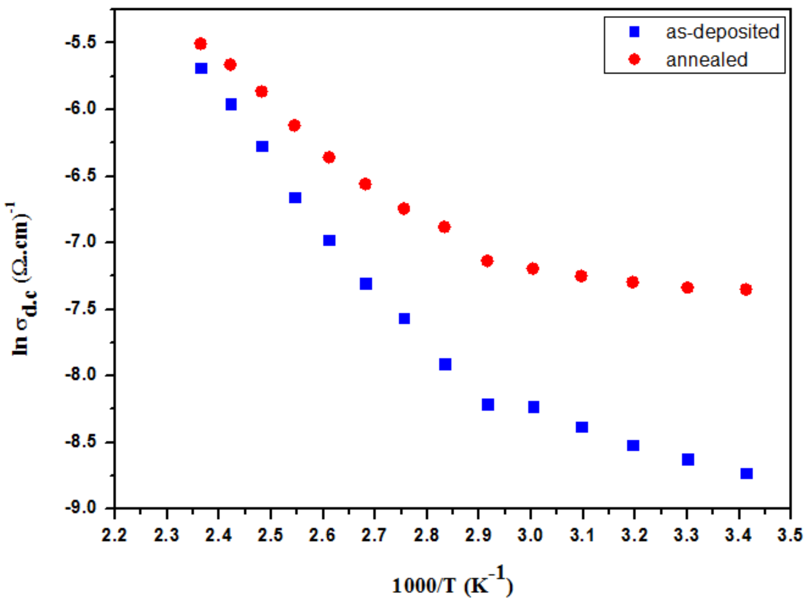

Fig. 5: Ln $\sigma_{d.c}$ versus 1000/T of as-deposited and annealed CdS thin films.

Table 2: D.C conductivity parameters of CdS films.

Sample	σ $(\Omega.cm)^{-1}$	T (K) (293-353) E_{a1} (eV)	T (K) (363-423) E_{a2} (eV)
As-deposited	1.6173×10^{-4}	0.113	0.426
Annealed	6.4251×10^{-4}	0.059	0.283

Carrier concentration and Hall mobility at room temperature of the as-deposited and annealed CdS thin film have been determined from Hall effect measurement. The results are shown in **Table 3**. CdS films exhibit a negative Hall coefficient showing n-type charge carriers; i.e. the conduction is dominated by electrons. This result is similar to that reported by other authors[24, 31]. From the table, it can be seen that the carrier concentration increases while the carrier mobility decreases after the annealing process.

Table 3: Hall measurements of CdS thin films at room temperature.

Sample	Carrier Concentration n_H cm^{-3}	Hall Mobility μ_H $cm^2/V.s$
As-deposited	1.947×10^{14}	5.19
Annealed	2.681×10^{15}	1.498

4. CONCLUSION

Thermal evaporation technique is successfully used to deposit CdS thin films on glass substrates using CdS powder. The X-Ray diffraction reveals that the as-deposited and annealed films are single crystalline with a cubic structure. The annealing leads to enhance the properties of the prepared films. The crystallite size for the (111) direction of the annealed film was found to be higher than that of the as-deposited films. The annealing process leads to increase the roughness and grain size of prepared films. It is observed that the energy band gap slightly decreases after annealing process. D.C. conductivity measurement shows that there are two transport mechanisms for the as-deposited and annealed CdS thin films.

The conduction mechanism at higher temperature range is due to carrier excitation into the extended states beyond the mobility edge, and at the lower range of temperatures; the conduction mechanism is due to carrier excitation into localized states at the edge of the bands. Hall measurements confirmed that the CdS films are n-type, carrier concentration increases while the mobility of carrier decreases after annealing process.

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