



Effect of annealing on structural and optoelectronic properties of CdS thin film by SILAR method

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ABSTRACT

CdS thin films were deposited by simple and easy successive ionic layer adsorption and reaction (SILAR) method. Prepared thin film were annealed at 250°C in air for 30 minutes. The crystallographic structure and the crystallite size were studied by the X-ray diffraction (XRD) pattern and optical band gap were studied by optical absorption spectroscopy and electrical measurements by means of I-V measurement in dark and illumination condition, electrical resistivity studied by using two probe method. The crystallite sizes were found to increase, and it shows the hexagonal structure. The optical energy band gap observed to be decreased from 2.45 to 2.42 eV for as deposited and annealed film respectively. The electrical properties of these films were studied by I-V measurement in dark illumination (100W) condition. As the light intensity increases the photo current goes on increasing and the resistivity decreases. So film exhibits photoconductivity phenomena suggesting its useful for sensors and photovoltaic device and from thermoemf measurements, the electrical conductivity was found to be of n-type conductivity.

Keywords: CdS, Thinfilms, Opto-electronic properties; Photosensor.

INTRODUCTION

In the past few years, the deposition and characterization of cadmium sulphide semiconducting thin films has been received a considerable amount of interest due to their potential application in the area of electronic and opto-electronic devices fabrications [1-4]. Polycrystalline CdS thin films possess good optical transmittance, wide band-gap (2.43 eV) and electrical properties makes

it as one of the ideal material for their application to solar cell fabrication [4] CdS is one of the important materials for application in electro-optic devices such as photoconducting cells, photosensors, transducers, laser materials, optical wave-guides and non-linear integrated optical devices, also used as photo catalyst [5, 6]. There are various technique available for the deposition of the CdS film such as chemical bath deposition (CBD)[1, 7-9], spray pyrolysis[2, 10, 11], pulsed laser deposition[12], but recently, deposition of CdS thin films was carried out by a new chemical method, successive ionic layer adsorption and reaction (SILAR) [13-15]. The SILAR method for preparation of thin films is attractive, easy to control over growth rate, cost effectiveness, less time consuming compared to other methods[16]. It is based on immersion on substrate on separately placed cationic and anionic precursors and rinsing between every immersion with ion exchange water to avoid homogenous perception[17].

In the present case, preparation, characterization and measurement of optical and electrical properties are reported for CdS thin film were deposited by SILAR method. The preparative parameters such as concentration of precursor's solutions, immersion time, rinsing time, number of deposition cycles, etc. are optimized.

MATERIALS AND METHODS

CdS thin film was carried out by a new chemical method, known as SILAR method using by cadmium acetate [$\text{CH}_3(\text{COO})_2\text{Cd}_2\text{H}_2\text{O}$] as the cationic precursor were maintained at pH ~11 [13]. Substrate immersed in solution where Cd^{2+} get adsorbed onto glass substrate and it rinsed in ion exchange water for 40s, to avoid the excess of ions. Then it immersed in anionic precursor of sodium sulphide [$\text{Na}_2\text{SH}_2\text{O}$]. The S^{2-} ions reacts with Cd^{2+} again rinsing the substrate in ion exchange water to remove the unreacted. S^{2-} ions. Thus the layer of CdS film was formed. This process was carried out up to good quality of the film was obtained. The reaction mechanism was observed to be

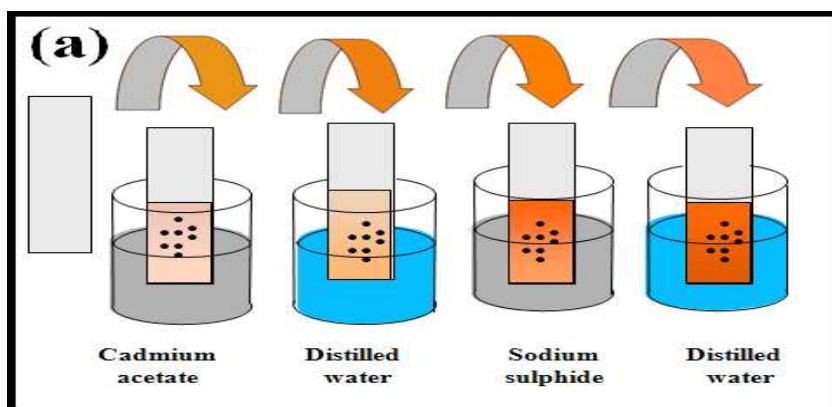
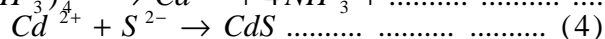
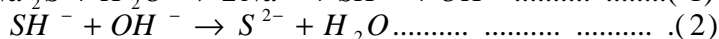
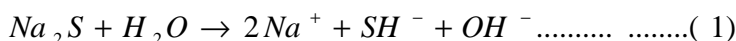


Fig. 1 SILAR technique for CdS thin film

The obtained films were annealed for half an hour at 250⁰C. Films were characterize by means of X-ray diffraction (XRD) was used to investigate crystalline phases of as deposited and annealed (250 °C) thin films. The surface morphology were studied by scanning electron microscopy. UV-Vis spectrophotometer (Perkin Lambda-25) in the range from 400-1100 nm was used to measure its optical properties. I-V characteristic were calculated by Lab-equipped model 24 (2004) computer interface and electrical resistivity studies were performed by two probe method, thermoelectric properties studied by thermoemf measurement unit.

RESULTS AND DISSCUSSION

3.1) Structural study

Fig. 2 shows XRD patterns of annealed and deposited film. The XRD pattern of as-deposited thin films is amorphous or consists of small grains. CdS films were annealed at 250^oc in air for 30 minutes. Annealed films show the well resolved peaks justifying improvement in crystallinity[15].CdS structure exhibiting lattice planes (002), (110) and (200) confirmed with the standard data card JCPDS 80-006.The CdS film deposited by the SILAR method shows a hexagonal crystal structure.

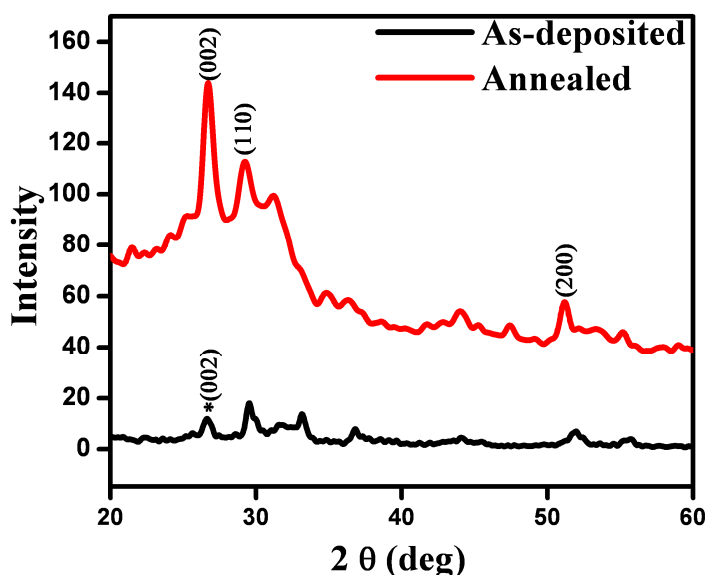


Fig. 2 XRD patterns of as deposited and annealed CdS thin films

The average crystallite size has been calculated by using Scherer's equation [18] as where the constant K is a shape factor usually 0.94, λ the wave length of X-ray (0.15418 nm), β the FWHM in radians and θ is the Bragg's angle We use the standard (0 0 2) H reflection at $2\theta \approx 26.66^\circ$. It has been observed that the grain size of the film increases from ≈ 11 to ≈ 13 nm when film were annealed at 250^oc.

$$D = \frac{K \lambda}{\beta \cos \theta} \dots \dots \dots (1)$$

3.2) Optical Studies

Fig. 3 shows the plot of absorbance against wavelength for CdS thin film. The absorption spectra of as-deposited and annealed samples were studied by using equation [19]

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^n}{h\nu} \dots\dots\dots (1)$$

where E_g is the separation between the valence and conduction bands, and n is a constant equal to 1 for direct gap materials and 4 for indirect gap materials. The plot of $(\alpha h\nu)^2$ against $h\nu$ is linear, the graph satisfies the condition for a direct transition in the excitation process hence we can conclude that the transition is direct [15]. The absorption edge found to occur in the range 500-520nm. Figure 4 shows the plot of $(\alpha h\nu)^2$ vs $h\nu$ to derive the energy band gap of CdS thin film. The energy band gap for as deposited and annealed film were calculated using the following equation.

$$(\alpha h\nu^2) = \beta^2 (h\nu - E_g) \dots\dots\dots (2)$$

Where α is absorption coefficient, β is constant, E_g is band gap energy. The energy band gap was observed to be 2.45 eV to 2.42 eV for as deposited and annealed films which is in good agreement with that reported by other authors [1, 11]. The decrease in band gap values are due to increase in grain size on annealing. [20] The observed decrease in energy band gap in annealed films can be attributed to the improved crystallites size of the material when compared to the as deposited thin film [7].

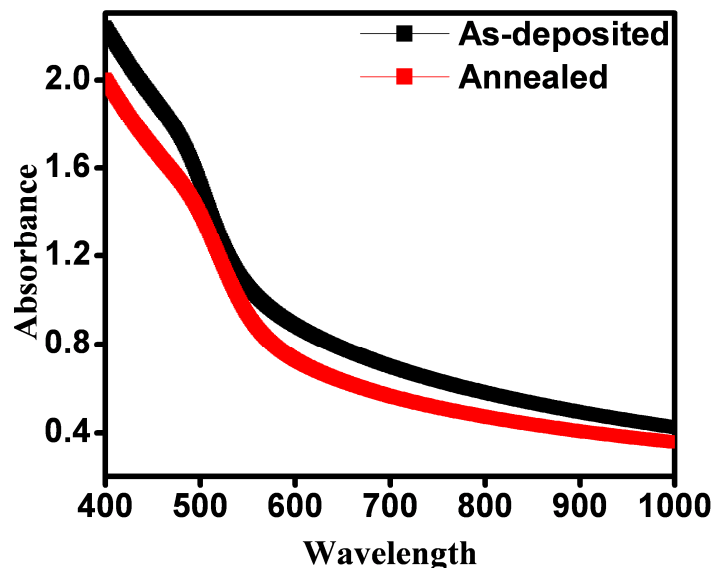


Fig. 3 Optical absorption spectra of as deposited and annealed CdS thin film

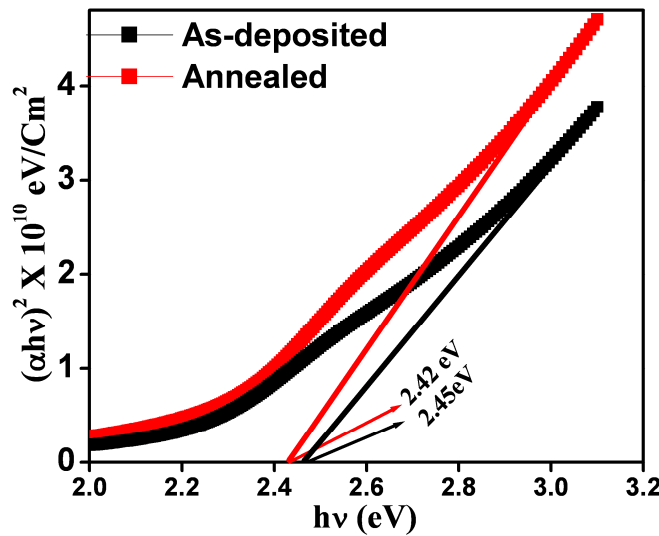


Fig. 4 Energy band gap of as deposited and annealed CdS thin films

3.3) I-V Measurement

Figure 5 shows I-V characteristic of as deposited and annealed in dark & illumination condition (100mw/cm²).The photogenerated charge carrier's increases with increase in power. The photogenerated current increases due to an increase in conductivity and resistivity decreases. The excitations of valence electrons into the conduction band significantly improves the electrical conductivity of the semiconductors; this phenomenon is known as photoconductivity. Therefore, observing the variation in the I-V plots with respect to the intensity with which the optimized samples were illuminate suggests that CdS films exhibits photoconductivity.

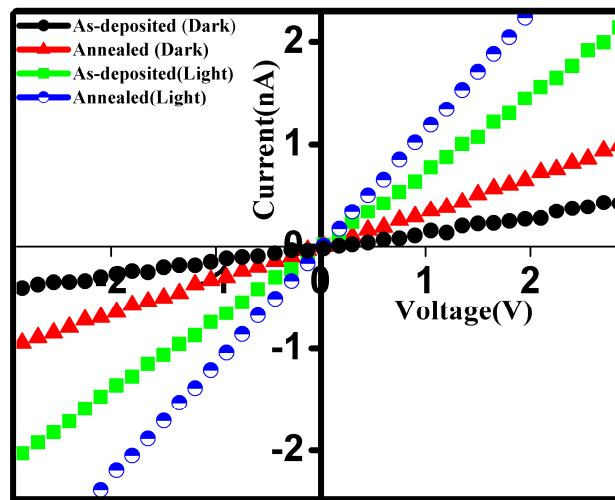


Fig. 5 I-V characteristics of as deposited and annealed CdS thin films

CdS thin films plays an important role in photo sensor applications. Its photosensitivity[21] was calculated by the equation.

$$S = \frac{R_d - R_l}{R_d} \dots\dots\dots (3)$$

Where R_d and R_L is the resistance in dark and under light, respectively.

Figure 6 shows the plot of photosensitivity verses intensity of light obtained when the CdS thin films exposed to different source of lights such as 40, 60 and 100 mW/cm^2 . It is clear from the figure that the charge carrier density increase with increase in light intensity and the photosensitivity also increases in annealed film as compared to deposited film. The photoresponse and photosensitivity in annealed film is found to be excellent in CdS films suggesting its utility in photosensitive material and photovoltaic devices.

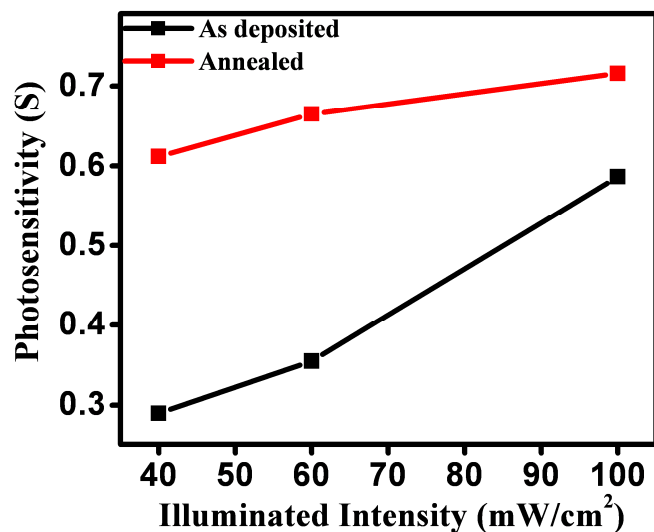


Fig. 6 photosensitivity verses illuminated intensity of CdS film

Fig. (7) represents the current response as a function of exposure time. From the fig it confirms that for long term exposure the current in the thin film increases which may be related to generation of more number of free charge carriers.

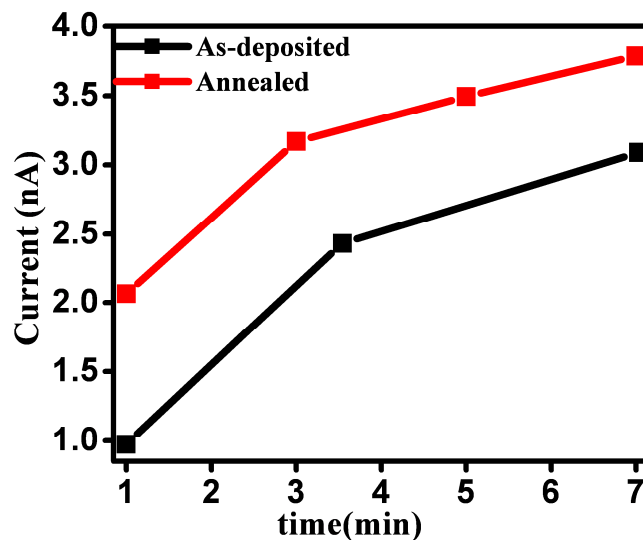


Fig. 7 Current verses time of CdS film

3.4) Electrical Resistivity

The variation of $\text{Log } \rho$ with $1000/T$ is as shown in Fig. 8 The dark electrical resistivity of CdS thin films were studied at room temperature using dc two-point probe method. It is observed that the resistivity decreases with increasing temperature, indicating the semi conducting nature of the film[1]. Annealed films showed lower resistance compared to that of as deposited films, an effect that could result from improved film structure [9]and possible due to decrease in band gap and can also be related to increased mobility of charge carrier for lower gap material.

$$\rho = \rho_0 \exp(E_a / KT) \dots \dots \dots (4)$$

Where ρ is resistivity at temperature at T , ρ_0 is a constant, k is Boltzmann constant E_a is the activation energy, which is estimated by the slope of the $\text{Log}(\rho)$ versus $1/T$

Activation energies for as deposited and annealed CdS thin films were found to be 0.5053 eV, and 0.3594eV, respectively. The decrease in activation energy is mainly attributed to the removal of defect states present in the film[22].

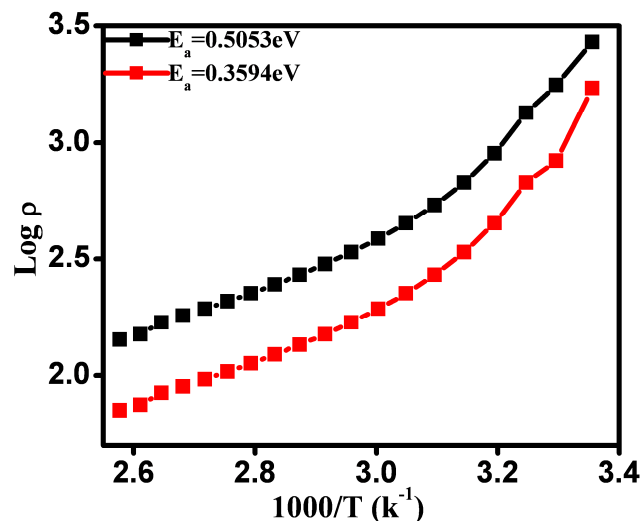


Fig. 8 Plot of $\text{Log } \rho$ versus $1000/T$ to characterize the nature of the thin films

3.5) Thermo-emf measurement

Figure 9 shows thermoemf measurements of as deposited and annealed CdS thin films. The temperature difference between ends of the samples causes transport of the carriers from the hot to the cold end and creates an electric field which gives rise to the thermal voltage, this thermally generated voltage is directly proportional to the temperature difference across ends of the semiconductor. It is found that the polarity of thin films were positive towards the hot end, indicating the CdS is n-type semiconductors. The negative sign of the thermoelectric power suggests that the major contribution to the conductivity is due to electrons. The thermoemf in annealed film is higher than that of as deposited one, which may be due to increase in crystallite size and density of defect levels [13].

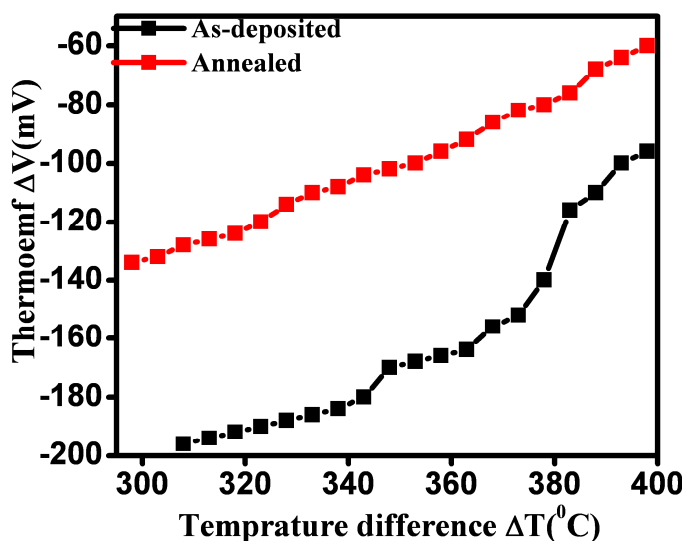


Fig. 9 Thermoemf characteristics of CdS thin films

CONCLUSION

CdS has been successfully prepared by successive ionic layer adsorption and reaction method. The X-Ray diffraction reveals that as deposited films are amorphous and improved grain size of the films after annealing. The optical study reveals decrease in energy band gap useful to fabrication of optoelectronic devices. The photosensitivity enhanced from 58 % in as deposited to 71 % in annealed thin films upon exposure to 100 mW/cm^2 was observed. CdS thin films give good response to the light and hence indicating that they can be employed in photosensor applications. The activation energy were found to be decrease in annealing thin films.

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