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Cu-doping effects on the physical properties of cadmium sulfide thin films

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ABSTRACT

Thin films of CdS were fabricated by close spaced sublimation technique under vacuum of $\sim 10^{-5}$ mbar at a source temperature of 550 °C for various periods of time. These as-deposited thin films were immersed into $Cu(NO_3)_2$ solution at 80 ± 5 °C for variety of time to ensure Cu doping. The structural, surface, optical and electrical analyses were completed with the help of X-Ray Diffraction, Scanning Electron Microscope with Energy Dispersive X-Ray, UV-VIS-NIR Spectrophotometer and Hall Measurement System respectively. The transmittance of as-deposited sample is reduced from 80% to 30% with increasing copper immersion time. The mobility increased from 6.67×10^1 to 1.15×10^3 cm^2/Vs due to the change in the carrier concentration.

1. Introduction

Cadmium sulfide is II–VI compound semiconductor [1] having good transmittance [2], wide band gap (2.42 eV) [3] with useful electrical properties making it an ideal material for the fabrication of solar cells [4]. This material is used as an efficient window layer for the solar cell fabrication due to its low resistivity [5]. For this reason, it is very important to control the resistivity of cadmium sulfide thin films [6]. Cadmium sulfide is a direct band gap material which has a great potential in light-emitting diodes and other electronic devices also [7].

Cadmium sulfide thin films have been prepared by a variety of methods including chemical bath deposition, thermal evaporation, solution growth, vapor transport, close spaced sublimation technique [4,8–10] etc.

Close spaced sublimation (CSS) technique is one of the standard techniques for thin film deposition with encouraging results. This technique is very effective for the efficient solar cells as it allows the film to grow at high substrate temperature (400–600 °C) under vacuum. The efficient thin film solar cells are obtained using cadmium sulfide as an n-partner. The highest efficiency so far reported for cadmium sulfide thin film solar cells is 16.5% [11].

2. Experimental procedure

Thin films of CdS were fabricated by CSS technique under vacuum of $\sim 10^{-5}$ mbar at source temperature of 550 °C for various periods of time. The substrate temperature was 450 °C. Thin films were deposited on the soda lime glass slides of dimension 0.5 cm × 3 cm × 8 cm and the optimized annealing temperature was about 450 °C under the vacuum for 30 min. The source material cadmium sulfide powder (99.99% pure) by Aldrich chemical company was used for preparation of thin films. Material of interest was put in the graphite boat, a halogen lamp (1000 W) connected to the main power through temperature controller with K-type thermocouple, is used to heat the source material. The substrate was set at a distance of about 5 mm from the source. It was heated by a halogen lamp (500 W), while another thermocouple was inserted into the substrate to control its temperature. The chamber was evacuated $\sim 10^{-5}$ mbar with the help of rotary pump and diffusion pump. The deposition time in each film was different at the source temperature of 550 °C, then the source and substrate lamps were switched off to allow cooling down to 50 °C before opening the chamber.

After the deposition of cadmium sulfide thin films, the annealing that is, very necessary to improve the crystallinity as well as morphology of samples. As the atoms of the as-deposited thin films are not arranged, to arrange them it must be supply the energy. All the samples are annealed at 450 °C for half an hour. A set of five as-deposited thin films were immersed into the solution of $Cu(NO_3)_2$ with distilled water at 80 ± 5 °C for several periods of time. The structural, surface, optical and electrical analysis was completed with the help of XRD, SEM with Energy Dispersive X-Ray, UV-VIS-NIR Spectrophotometer and Hall Measurement System respectively. In this research work, the results of as-deposited and Cu-doped samples are presented and discussed in detail. To our knowledge this research work is a novel report on CdS semiconductor by CSS technique not reported earlier.

3. Results and discussion

3.1. Structural analysis

The structural characterization of cadmium sulfide thin films was performed by XRD with a wavelength 1.5406 Å in the

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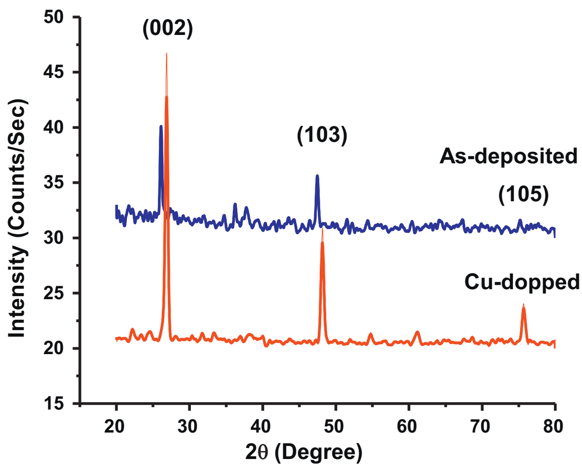


Fig. 1. XRD trace of as-deposited and Cu-doped CdS samples.

diffraction angle ranging from 20° to 80°. Peaks relating to CdS are identified by using standard card JCPDS-00-041-1049. Cadmium sulfide has hexagonal structure with effective parameters $a = b = 4.1409$ Å, $c = 6.7198$ Å. The crystallite size (*CS*) can be calculated with the help of Scherer formula

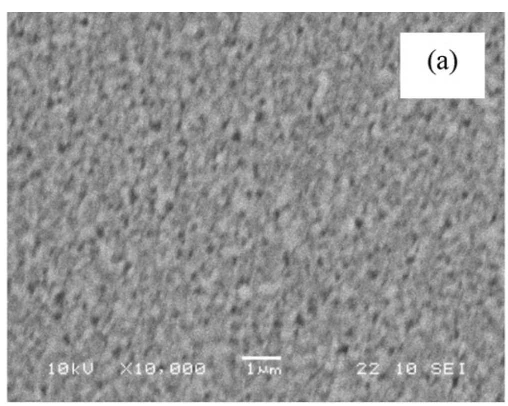
$$CS = \frac{(0.9)\lambda}{B\ \cos\theta} \quad (1)$$

where λ is wavelength of X-rays, θ is angle of diffraction and B is full width at half maximum (FWHM). The texture co-efficient (*T.C.*) was also investigated with the help of following formula

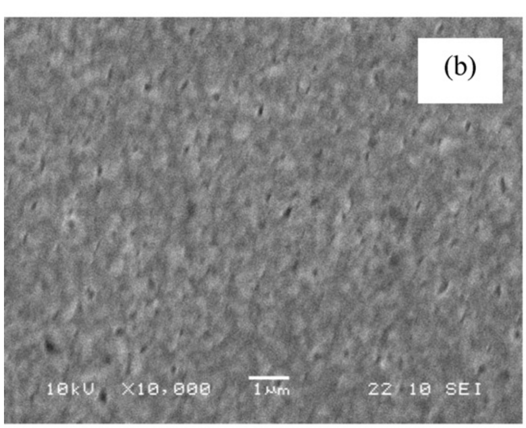
$$T.C. = \frac{(I/I_0)}{(1/N)\sum(I/I_0)} \quad (2)$$

where I represent the intensity of X-rays trace, I_0 is standard intensity and N is number of peaks [12]. The texture co-efficient and crystallite size are calculated as 1.84 and 90 nm for the peak (0 0 2) respectively, which is the preferred orientation of the growth.

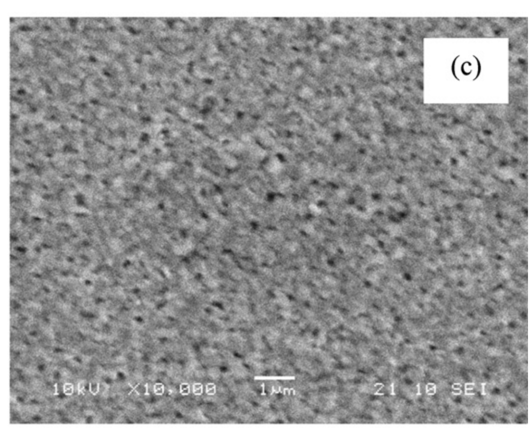
The copper is considered as one of the lowest resistive element. The copper-doping in cadmium sulfide thin films by ion exchange process is a new doping process giving encouraging results. While immersing thin films of cadmium sulfide into the copper nitrate solution, the copper either diffuses interstitially or substitute the Cd atom; the XRD results of Cu-doped CdS samples shows no peak corresponding to any copper compound, thus the volume of unit cell increases with copper doping, which is confirmed by shifting of peaks towards right as observed in Fig. 1. The texture co-efficient and crystallite size for Cu-dopped sample are calculated as 2.57 and 156 nm respectively. The preferred orientation of the growth is still along (0 0 2) plane. It was observed that the peak shift also increases with increasing copper doping concentration. The mass% of copper in cadmium sulfide thin films increases as well as the intensity of the preferred orientation also increases showing the reorientation of planes after copper doping.



(a) SEM Images of As-deposited Sample before annealing



(b) SEM Images of As-deposited Sample Annealed at 300°C



(c) SEM Images of As-deposited Sample Annealed at 400°C

Fig. 2. SEM images showing effect of annealing temperatures on grain size of CdS samples.

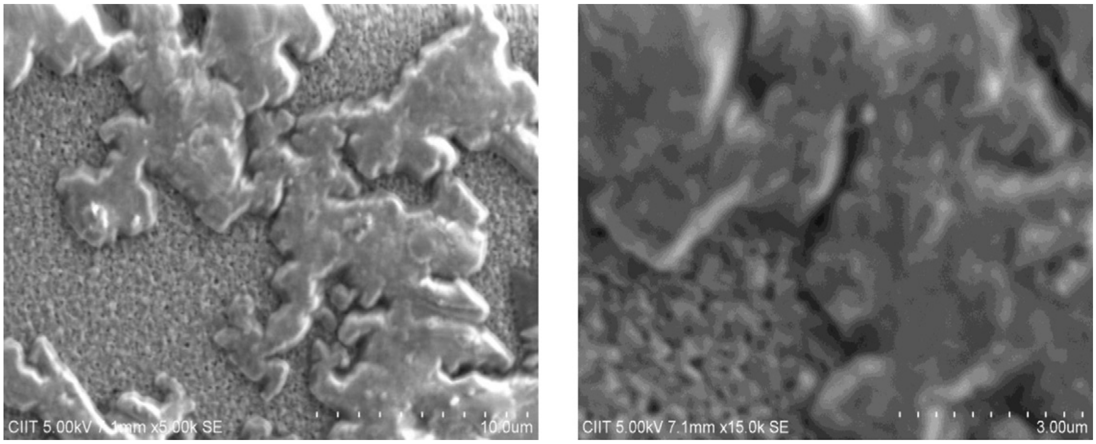


Fig. 3. SEM images of the Cu-doped cadmium sulfide thin films before annealing.

3.2. Surface analysis

The scanning electron microscopic images of as-deposited CdS samples are shown in Fig. 2. The grain size of the as-deposited CdS samples depends on the annealing temperature. The grain size of as deposited sample was 300 nm which was increased to 350 nm after annealing at temperature of 300 °C for half an hour and further reached to 500 nm at annealing temperature of 400 °C for half an hour. SEM images of copper deposited on the CdS surface are shown in Fig. 3. The samples were annealed at 450 °C, the copper was diffused into the sample and the grain size of the Cu-doped sample was increased after doping as shown in Fig. 4. The annealing temperature facilitates the copper to diffuse and reorient the structure as evident in the XRD pattern.

The EDX attached with SEM provides the compositional analysis. The ratio of S to Cd in as-deposited samples is found 0.68, which is significantly below to the required ratio of 5 for a good efficiency solar cell as reported by Hernandez et al. [13]. The reason behind is that the average optical transmission is also low in smaller S/Cd ratio. The cadmium is enriched in as-deposited samples. As thin films of cadmium sulfide were immersed in the solution of $Cu(NO_3)_2$ and further annealed at 450 °C, the Cd-composition was significantly changed as the Cu replaced the Cd atoms. The concentration of copper atoms increases with increasing immersion time which is according to Table 1. The SEM images and XRD results show that the grain size increases with Cu-doping.

Table 1
The change in composition of copper with immersion time.

Sample no.	Immersion time (min)	Copper (mass %)
1	0	0%
2	5	0.10%
3	10	1.38%
4	15	3.32%
5	20	8.92%

3.3. Optical properties

The optical properties including transmission, refractive index and energy gap are of great importance for the study of window layer material for the application in solar cell. The transmission spectra of as-deposited with increasing thickness samples are shown in Fig. 5. The transmittance decreases with increasing the thickness. As-deposited CdS samples show the transmission from 60% to 80% in the visible region, which suddenly fall at about 500 nm. This is due to the energy gap of the cadmium sulfide which is about 2.42 eV. Due to extremely good transmittance in the visible region as well as in IR region, CdS is considered as very good window material in solar cell fabrication.

The Swanepoel model gives us the calculation for refractive index and thickness of the thin films [14].

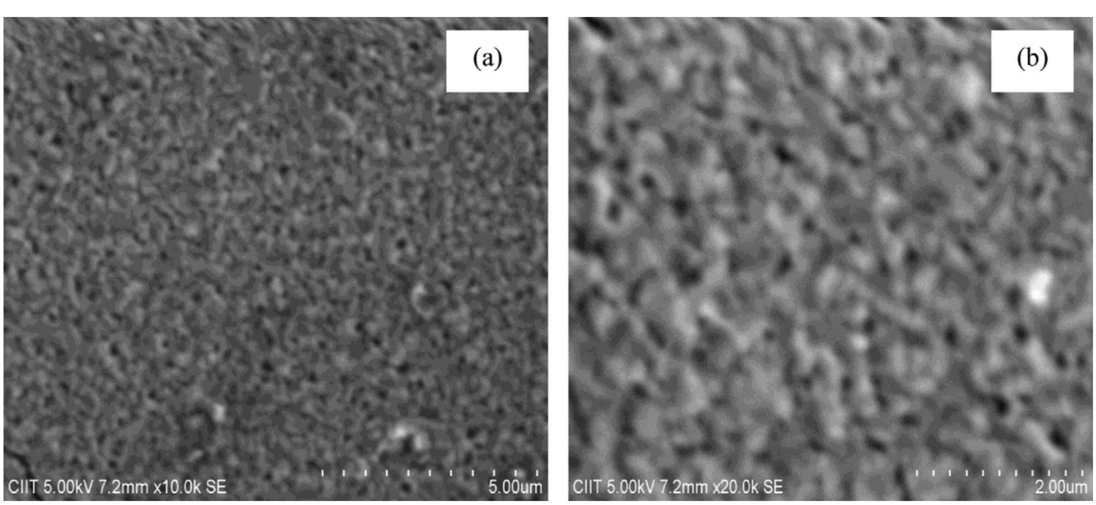


Fig. 4. SEM images of the Cu-doped cadmium sulfide thin films after annealing at 400 °C.

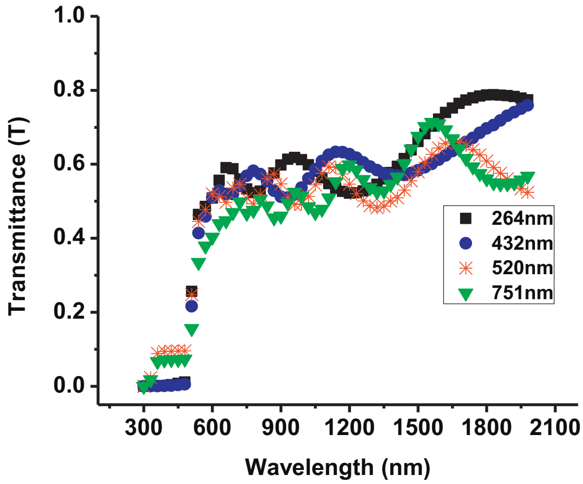


Fig. 5. Transmittance (*T*) curves of as-deposited samples.

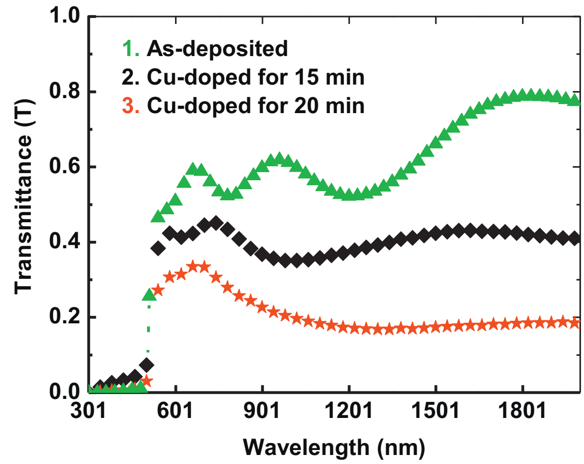


Fig. 7. Transmittance (*T*) decreases with increasing cu-doping time.

The refractive index (n) can be calculated as

$$n = \frac{[N + (N^2 - 4s^2)^{1/2}]}{2} \quad (3)$$

where s is refractive index of the substrate, N is number of oscillations

$$N = 1 + s^2 + 4s\left(\frac{T_M - T_m}{T_M T_m}\right) \quad (4)$$

Thickness of the films can be calculated with the help of formula

$$d = \frac{1}{4n}\left[\frac{\lambda_m \lambda_M}{\lambda_M - \lambda_m}\right] \quad (5)$$

where d is the thickness, λ_m is the minima and λ_M is the maxima value of the wavelength taken from the transmission curves as shown in Fig. 6.

The energy gap of the material can be calculated by Eq. (6) [9].

$$\alpha h\upsilon = A(h\upsilon - E_g)^{N/2} \quad (6)$$

where A is constant, $h\upsilon$ is the photon energy, E_g is the energy gap and N depends on the nature of transition. The absorption co-efficient can be calculated as

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (7)$$

where d is the thickness and T is the transmittance. The energy gap of 2.42 eV was found in all the CdS thin films. The thickness of as-deposited CdS samples varies from 200 nm to 1000 nm. The transmission spectra changes with level of Cu-doping. Energy gap E_g and n also changes with the increase of copper concentration [15]. Fig. 7 shows that the transmittance of as-deposited sample is reduced up to 30% with increasing copper immersion time.

The energy gap varies with the change in several parameters like grain size, structural parameters, carrier concentration and lattice strain. The film thickness has direct dependence on the lattice parameters, grain size and strain. The energy gap of CdS samples changes with respect to thickness due to lattice strain [16].

By extrapolating $(\alpha h\upsilon)^2$ versus the incident photon energy ($h\upsilon$) plot, the band gap can be calculated. The energy gap of as-deposited sample was about 2.42 eV [17] as shown in Fig. 8, which was minutely reduced to 2.41 eV due to low Cu concentration.

3.4. Electrical properties

Electrical properties of CdS samples such as resistivity, mobility and sheet concentration are reported here. The Hall Measurement system is used in this study [18]. The electrical properties of as-deposited CdS samples are measured at 1 nA current and 300 K temperature given in Table 2.

The resistivity varies from 6.17×10^4 Ω-cm to 1.50×10^6 Ω-cm. This variation is due to the thickness and the dimension of the CdS samples. The value of sheet concentration varies from 9.3×10^5 to $9.63 \times 10^6/\text{cm}^2$ and the value of mobility varies from 6.67×10^1 to 1.15×10^3 cm²/Vs. At the lowest value of sheet concentration,

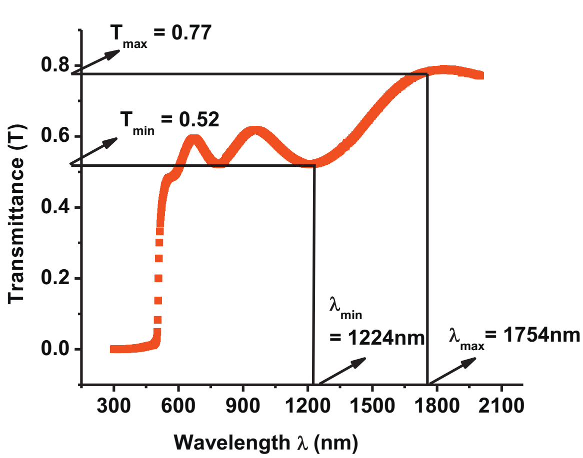


Fig. 6. Transmittance (*T*) curve of a as-deposited CdS sample.

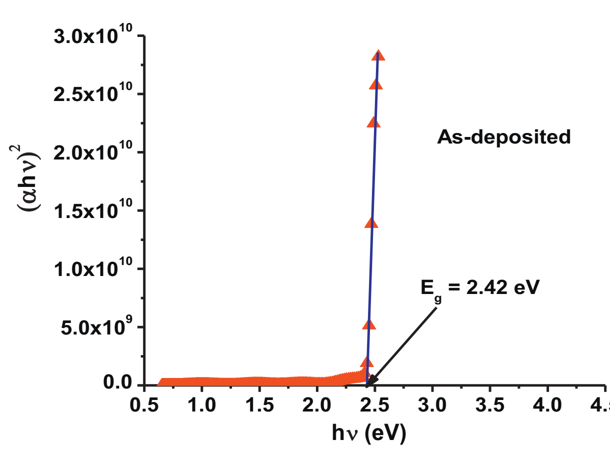


Fig. 8. Energy gap of As-deposited sample.

Table 2
Resistivity, Mobility and Sheet concentration of as-deposited CdS samples at 300 K.

Sample no.	Resistivity (Ω cm)	Mobility (cm^2/Vs)	Sheet concentration (/cm^2)
1	6.17E+04	2.10E+02	9.63E+06
2	1.94E+05	5.36E+02	1.49E+06
3	1.76E+05	1.15E+03	9.30E+05
4	3.86E+05	4.47E+02	1.27E+06
5	1.50E+06	6.67E+01	1.64E+06

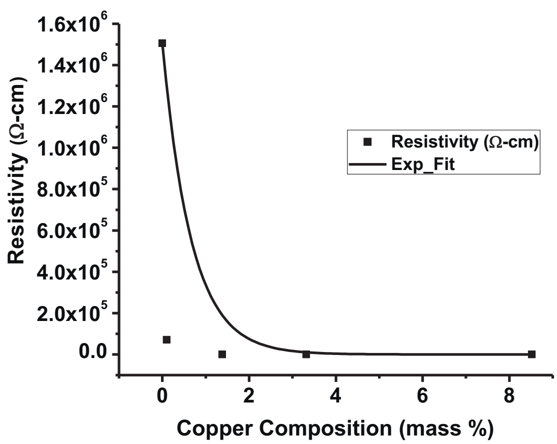


Fig. 9. Variation in resistivity with increase in copper composition.

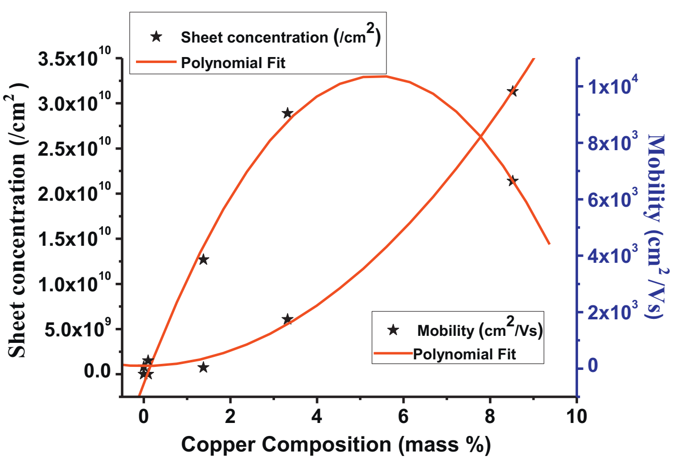


Fig. 10. Variation in mobility and sheet concentration with increase in the copper composition.

i.e. 9.30×10^5/cm^2, the highest value of mobility was found, i.e. 1.15×10^3 cm^2/Vs. Mobility increases due to the decrease in the carriers. As the doping time of as-deposited CdS samples increases, the copper concentration also increases. The highest copper composition is 8.92% after 20 min of doping at 80 ± 5 °C and the resistivity decreases with increase of copper composition. The lowest resistivity achieved after Cu-doping is 0.7 Ω-cm which is a significant change as compared to the resistivity obtained before doping, i.e. 1.506×10^6 Ω-cm as shown in Fig. 9. The mobility increases with the increase in copper composition as shown in Fig. 10. The sheet concentration is changed with the change in composition of copper. The sheet concentration increases linearly with increase in the copper composition up to some extent and then reduces sharply as shown in Fig. 10. The number of charge carriers increases with the increase of copper doping. As the copper composition increases the changes in resistivity, mobility and sheet concentration were observed.

4. Conclusions

In XRD traces, the as-deposited CdS thin films fabricated by close spaced sublimation technique exhibit hexagonal structures. The preferred orientation was found along (0 0 2) plane. Ion-exchange process has been applied for Cu-doping and the shift in peaks confirms the successful doping of Cu in CdS thin films. It was observed that the grain size of the samples increases after annealing; the same increases with Cu-doping also. An increase in texture coefficient and crystallite size for Cu-dopped sample are observed. The transmission of as-deposited CdS thin films in visible region varies from 60% to 80%; while the same reduces to about half by copper doping. A very small change in the energy gap of the material is observed while a significantly large change in electrical properties is found after Cu-doping. The semiconductor behavior of CdS samples is confirmed by using Hall Measurements. The lowest resistivity ∼0.7 Ω-cm can be achieved by copper doping by using the CSS technique, which is the several orders of magnitude reduction in resistivity.

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