Optical, Structural and Electrical Properties of Cu Doped CdS Thin Films Fabricated by SILAR Method

D. Pradhabhan[*1] & Dr. A. Sakthivelu[2]
[1,2]PG & Research Department of Physics,
Periyar E.V.R College, Trichy, Tamilnadu.

***Abstract*:- Cu doped CdS nano crystalline thin films were deposited using one of the simple Successive Ionic Layer Adsorption and Reaction (SILAR) method. The result and impact of Cu doping concentration of 3, 6 and 9 Mol% on the optical, structural, morphological and electrical properties of Cu doped CdS films were studied. XRD studies exhibited that the Cu doped CdS thin were polycrystalline with cubic phase crystal structure. FESEM results show that the surface morphology of the prepared films changes with Cu doping concentration. A blue shift in the optical band gap was found in the UV visible spectroscopy. Hall measurements clearly indicate the result and impact of Cu doping concentration on electrical resistivity and conductivity and it shows comparatively high electrical conductivity at 9Mol% of Cu doping concentration.**

Keywords: Copper doped Cadmium Sulphide, SILAR, Thin films, UV & XRD.

1. INTRODUCTION:

Cadmium sulphide (CdS) is an n-type semiconducting material that has been used in several applications, including low cost solar cells, light emitting diodes, photo resistance sensors, nonlinear optical devices and optical waveguides [1-4]. Different deposition techniques have been used to fabricate the cadmium sulphide thin films, such as chemical bath deposition, vacuum evaporation, spray Pyrolysis, sputtering, electro deposition [5] and Successive Ionic Layer Adsorption and Reaction (SILAR) [6,7] method. Among all the deposition methods, SILAR method is an important, cost effective and simple technique for the fabrication of multi-component thin films. The Cu doped CdS thin films have many possible applications, such as high efficiency photovoltaic cells and light emitters because the thin films of Cu doped CdS thin films are known to be extremely sensitive to absorb the electromagnetic radiation that on coverage to any type of radiation is capable of stimulating electron-hole pairs and can display a notable structural changes. Moreover, the doping of Cu modifies the band gap energy of CdS and also enhances its photoelectrical properties. Aim of the present work is to study the result of doping cu on the structural, electrical and optical properties of the CdS thin films synthesised by SILAR method.

2. EXPERIMENTAL PROCEDURE

All the chemicals used to prepare the Cu doped CdS thin films were of analytical grade and all the solutions were prepared in the millipore water. To deposit the Cu doped CdS thin films, cationic precursor (0.1M) cadmium acetate (50ml) and (0.003M) Copper Sulphate were taken in a beaker and the anionic precursor (0.1M) Thiourea (50ml) was taken in a separate beaker. For the deposition of Cu doped CdS thin film, well cleaned glass substrate was immersed into the cationic precursor for 40 sec for the adsorption of Cd^{2+} and Cu^{2+} ions on the surface of the glass substrate, and then the substrate was dipped into the double distilled de-ionized water for 10 sec to avoid precipitation and also to remove the weakly bounded cations. The substrate was then immersed into the anionic precursor bath for 40 sec for reaction of S^{2-} ions with Cu^{2+} and Cd^{2+} ions on the substrate. This process was carried out at ~75°C temperature. Successive dipping cycles repeated up to 75 times, to get the well adherent and homogeneous Cu doped CdS thin films [8]. Then the same procedures were carried out for 0.006 and 0.009 mol of Cu. Doping of Cu is carried out the following molar ratio and they are 3, 6 and 9 respectively. The samples were annealed at 200°C for 1 hour in atmospheric air. Phase identification and crystalline properties of the films were studied by XPERT-PRO X-ray powder diffractometer with CuKα radiation (λ = 1.5418Å). Scanning electron microscopy FE-SEM 6701 F used to study the surface Morphology and to illustrate the formation of crystallites on the film surface. UV–VIS spectrophotometric measurements were performed using a Unico UV-2102PCS spectrophotometer at room temperature. The electrical parameters were measured using Hall measurements setup (ECOPIA-HMS 3000) at room temperature with the permanent magnet of 0.57 Tesla.

3. RESULT AND DISCUSSION

3.1. Structural Analysis

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 8 Issue 07, July-2019

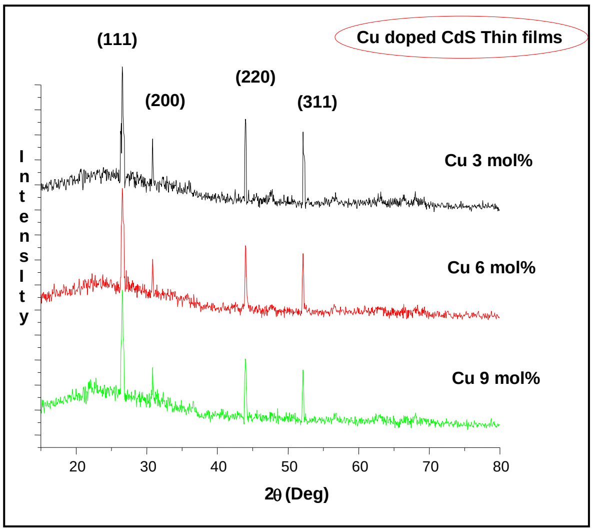


Fig.1-XRD patterns of Cu doped CdS thin films

The crystalline nature of Cu doped CdS films was examined by X-ray diffraction spectra obtained by grazing incidence X-ray diffraction. Fig.(1) shows the XRD spectra of the SILAR deposited Cu doped CdS films, which exhibits the X-ray diffraction spectra of CdS. The diffraction pattern exhibits the entire characteristic peaks of the cubic (zincblende) phase, which is good agreement with the reported standard values (ICDD No. 10-0454). In the diffraction pattern, (111) reflection was the prominent peak than the other intensity peaks. Intensity of the (200) , (220) and (311) diffraction peaks were decreased with increasing the Cu doping concentration, which indicates that excessive doping level of Cu deteriorates the crystallinity in the prepared films, which might be due to the improvement of stress caused by the smaller ionic radius of Cu^{2+} compared with Cd^{2+} ions. In order to determine lattice parameter of the prepared thin films, JANA2006 code was used in the Le-Bail mode. The calculated lattice parameters of Cu doped CdS thin films were tabulated in Table.1. It can also observed that, for the increase in the Cu doping concentration from 3Mol% to 9 Mol% lattice constant (a) decreased linearly from 5.9309 to 5.8760 Å. Th a ght change in lattice parameter 'a' of Cu doped CdS thin film, prove that the Cu ions were incorporated successfully into the CdS lattice. This slight drop in the intensity peaks of the deposited thin films are attributed to the reduction in the crystallinity of the thin films. The well known Scherer formula [9] given in equation (1) used to determine the crystallite size of the SILAR deposited Cu doped CdS thin films and the average lattice strain has been calculated using Stokes Wilson equation [10] given in equation (2), The FWHM values of the prepared films were determined from their highest intensity peak broadening by pseudo-voigt peak fitting.

Crystallite size $D_{ave} = 0{\cdot}94\lambda/\beta \cos\theta$ ----- (1)

Micro Strain $\varepsilon = \beta / 4\tan\theta$ ----- (2)

Where D_{ave} is the mean crystallite size, ε is the average micro strain *(Δd/d)*, *β* the full width at half maximum of the diffraction line, θ angle of diffraction, and *λ* the wavelength of the X-ray radiation. The minimum crystallite size of ~14.36 nm is found for 9 Mol% of Cu doped thin film and the maximum crystallite size of ~18.87 nm is found for 3 Mol% of Cu doped thin film which is shown in Table.01.

Cu doping concentration (Mol. %)	Crystallite size, D (nm)	'a'(Å)	Micro Strain- €
3	18.87	5.9309	3.13 x10^{-3}
6	16.69	5.9100	3.51 x10^{-3}
9	14.36	5.8760	3.72x10^{-3}

Table .1 - Structural parameters of Cu- doped CdS thin films

3.2. Surface Morphology and EDAX by FESEM Analysis

Surface Morphology and EDAX by FESEM Analysis
The FESEM micrographs of SILAR deposited Cu doped CdS thin films for the various Mol% of Cu (3 Mol %, 6 Mol % and 9 Mol %) on well cleaned glass substrates are shown in Fig. 2 (a), (c) and (e) respectively. It is observed that the surface morphology of the prepared thin films are strongly depends on the concentration of the Cu dopant. The grains almost cover the surface of substrate uniformly. However, Cu doped CdS thin film shows particles with partially spherical like shape in 3 mol% of Cu doping concentration. Fig. 2(c) shows particles on the surface of substrate were seemed to be agglomerated with better surface coverage in 6 mol% of Cu doping concentration. The surface of the 9 Mol % of Cu doped CdS film shows nearly completes substrate coverage and decrease in grain size.

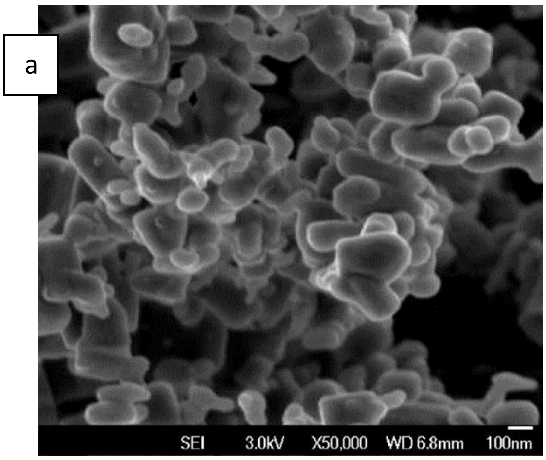


Fig.2(a). Surface morphology of Cu (3 mol%) doped CdS thin films

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 8 Issue 07, July-2019

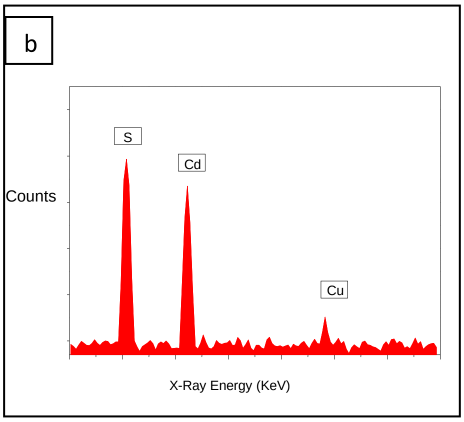


Fig.2(b). EDAX analysis of Cu (3mol%) doped CdS thin films

The prepared samples, the grain size decreases and grain orientation occur randomly when Cu incorporated with CdS lattice. The surface of Cu doped CdS thin films are seems to be formed by the stacking with self-aligned nanoparticles. The incorporation of Cu in the CdS films was verified by the EDAX result. Figure 2 (b), (d) & (f) shows the energy-dispersive X-ray analysis of Cu doped CdS film for 3 Mol %, 6 Mol % and 9 Mol % respectively. The EDAX result evidently reveals the presence of Cd, S and incorporation of Cu in the deposited thin films.

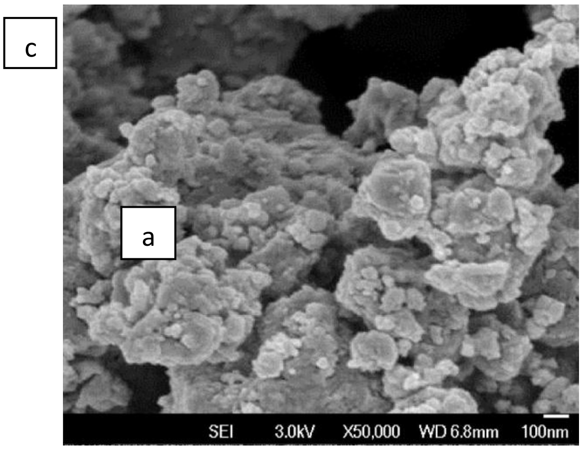


Fig.2(c). Surface morphology of Cu (6 mol%) doped CdS thin films

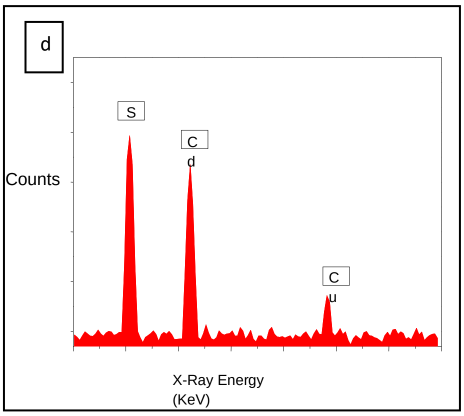


Fig.2(f). EDAX analysis of Cu (6 mol%) doped CdS thin films

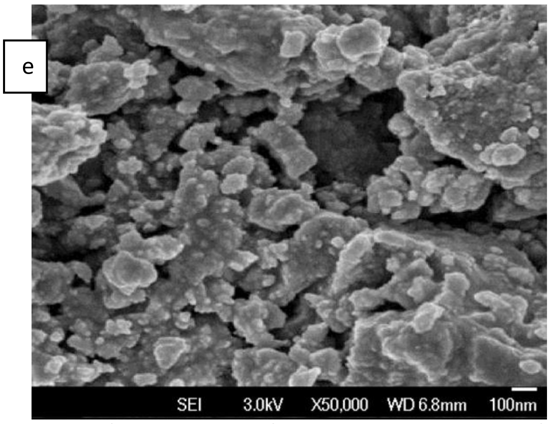


Fig.2(e). Surface morphology of Cu (9 mol%) doped CdS thin films

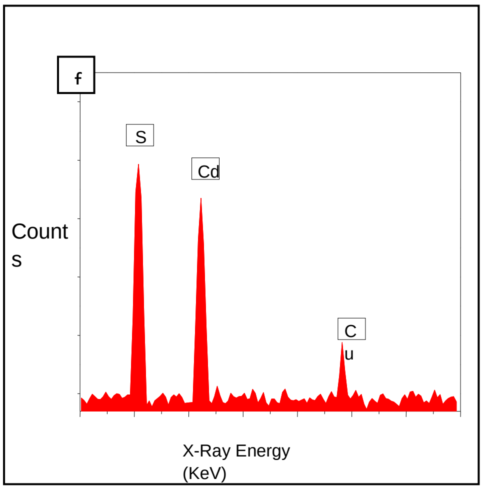


Fig.2(f). EDAX analysis of Cu (9 mol %) doped CdS thin films

3.3. Optical studies

The transmittance spectrum in the wavelength range of 300 to1100 nm for Cu doped CdS thin films are shown in Fig. 3(a). It shows that the transmittance of 6 mol% and 9 mol% of Cu doped thin films is lower than that of 3 Mol% of Cu doped films. This reduction in transmittance at higher Cu doping concentrations may be due to the increase in the scattering of photons caused by crystal defects as well as its irregular surface morphology.

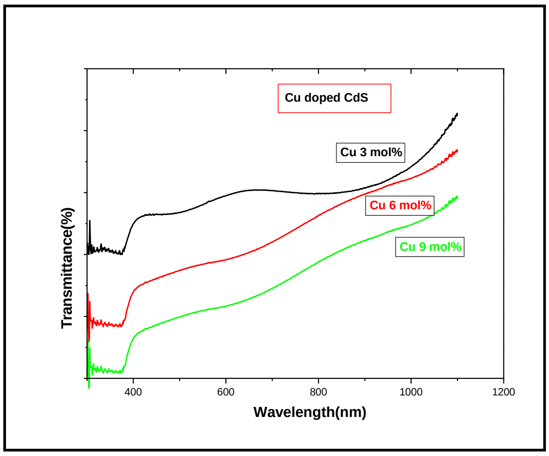


Fig.3 (a) - Transmittance graph of Cu doped CdS films

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 8 Issue 07, July-2019

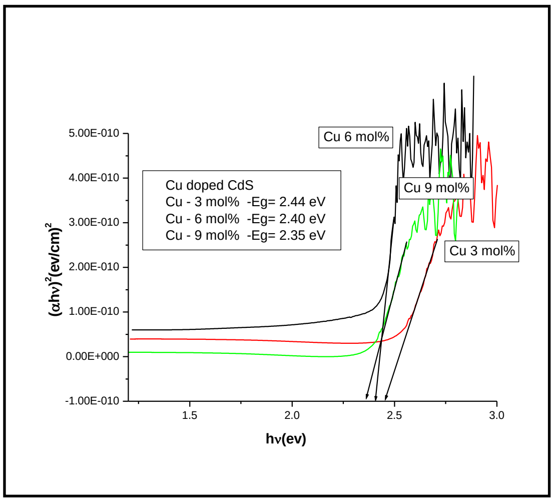
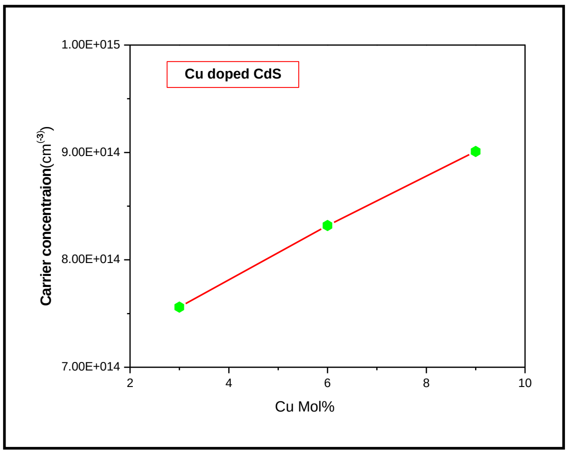


Fig. 3 (b) - Band gap of Cu doped CdS thin films

The optical band gap Eg can be calculated by plotting (hν) versus $(\alpha h\nu)^2$ based on the relation h = A (h - Eg)$^{n/2}$ where α is the absorption coefficient, A is a constant and n is the exponent depending on quantum selection rule for a particular material[11]. The calculated band gap value with respect to Cu doping concentration is plotted in fig. 3(b), which clearly indicates the considerable decrease in band gap value with increase in Cu doping concentration. The optical band gap for 3 Mol % Cu doped CdS film is 2.44 eV which is higher than the remaining two samples. For 6 Mol % Cu doped CdS film the band gap is 2.40 eV and for 9 Mol % Cu doped CdS film 2.35 eV. This reduction in band gap value with respect in increase in Cu doping concentration clearly indicates the effect of Cu doping level on the CdS thin films. Fig. 3(b) clearly exhibit a blue shift in the higher Cu doping concentration, indicating the narrowing of the optical band gap value. This narrowing of Eg value for Cu-doped CdS thin films suggests the successful incorporation of Cu in CdS structure.

3.4. Electrical Studies



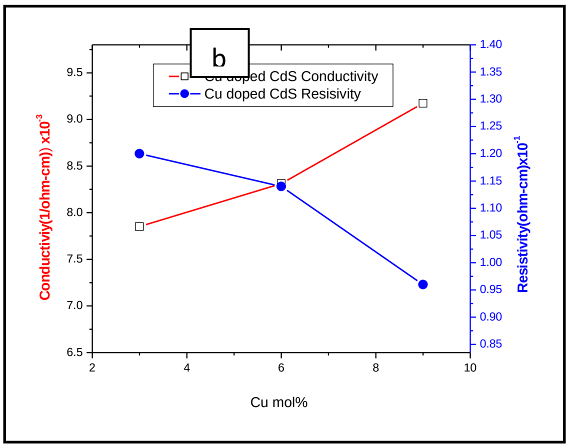


Fig.4. (a) & (b) shows variation of Resistivity, Conductivity & carrier concentration of Cu doped CdS films

Table.02-Resistivity, Conductivity & carrier concentration of Cu doped CdS films

Film	Resistivity (ohm-cm)	Conductivity (1/ohm- cm)	Carrier concentration (cm^{-3})	Hall Coefficient (cm^3/C)
3 mol% of Cu	6.104×10^2	2.089×10^{-03}	6.501×10^{16}	4.159×10^7
6 mol% of Cu	5.322×10^2	3.110×10^{-03}	9.518×10^{16}	1.774×10^6
9 mol% of Cu	4.787×10^2	4.154×10^{-03}	1.950×10^{17}	7.301×10^5

The various Hall parameters such as conductivity, carrier concentrations (*n*), resistivity and hall coefficient have been calculated and tabulated in Table. 2. The variation of the carrier concentration with Cu doping content is shown in Fig.4 (a). It is revealed that Cu content is a factor which affects the electrical properties of the CdS thin film. It can be observed from Fig.4 (b) that the thin film shows comparatively the highest conductivity and the lowest resistivity at a Cu doping concentration of 9 Mol %.The increase in the electrical conductivity is due to the occurrence of huge number of free charge carriers introduced by Cu dopant. It can be explained as follows: when Cu is incorporated in to the CdS lattice, Cu^{2+} replaces Cd $^{2+}$ ion in the CdS crystal structure resulting in four more free electrons that contribute to the electric conduction. So, the enhancing electrical conductivity is due to the presence of large numbers of free carriers introduced by Cu dopant. The highest value of carrier concentration obtained in the present study is 1.950×10^{17} cm^{-3} and it is observed at 9 Mol% of Cu doped CdS films.

4. CONCLUSIONS

SILAR deposition method is used to prepare the polycrystalline Cu doped CdS thin films on glass substrates. The effects of Cu doping concentration on structural, optical, surface morphological and electrical characterizations of CdS films were studied. The XRD results clearly show that Cu doped CdS films have cubic structure. When the doping concentration is 3 Mol%, the intensity of (111) peak is stronger than that of other intensity peaks. This literature reveals that the decrease in the XRD intensity peaks of the deposited thin films are attributed to the reduction in the crystallinity of the thin films and also it indicates that, Cu ions were successfully incorporated into the CdS lattice. The FESEM images revealed that, up on increasing the Cu doping content, the surface morphology of the films is improved and grains are uniformly distributed throughout the surface. Optical studies reveals that, the optical band gap Eg of Cu doped CdS thin films decrease with increasing Cu doping concentration in the samples. Hence, the decrease in the optical band gap from 2.44 to 2.35 eV is observed for increasing the Cu doping concentration from 6 to 9 mol% respectively. From the electrical studies, it is observed that the variation in electrical resistivity might be directly attributed to the effect of Cu ion incorporation into the CdS lattice. At 9 Mol% of Cu doping, the thin films exhibit the highest electrical conductivity and lower resistivity. The structural, optical and electrical characterization studies of Cu doped CdS thin films clearly indicate the successful incorporation of Cu into CdS.

5. REFERENCES

[1] Kashiwaba, Y., Sato, J. and Abe, T., Appl. Surface Science, 212-213, pp 162-165(2003).
[2] Bacaksiz, E., Novruzov, V., Karel, H., Yanmaz, E.,Altunbas, M., Kopya, A.I. , J. Phys. D: Appl. Phys., 34, pp 3109-3112 (2001).
[3] Ullrich, B., Bagnall, D.M., Sakai, H. And Segawa, Y, Journal of Luminescence, 87-89, pp 1162-1164 (2000).
[4] Senthil, K., Mangalarj, D., Narayandass, S.K., Applied Surface Science, 169-170, pp
[5] 476-479 (2001).
[6] Ulrich, B., Tomm, J.W., Dushkina, N.M., Tomm, Y.,Sakai, H. and Segawa, Y., Solid
[7] State Communications, 116, pp 33-35 (2000).
[8] R.Radha, A.Sakthivelu, D.Pradhabhan, C.Ravichandiran, S.Murugesan, E.Mohandas and Geethadhevi, International Journal of ChemTech Research, Vol.6, No.6, pp 3374-3377(2014)
[9] R. Radha, A. Sakthivelu, D.Pradhabhan, C. Ravichandiran, S. Murugesan, & E. Mohandas, Journal of Scientific Research in Physical & Mathematical Science Volume (2) Issue (9) Year (2015)ISSN : 2349-7149
[10] D. Pradhabhan, Dr. A. Sakthivelu, International Journal of Advanced Trends in
[11] Engineering and Technology (IJATET), Volume 2, Issue 2, 2017
[12] S Tewari and A Bhattacharjee, Pramana – J. Phys. **76**, 153 (2011)
[13] P Shrestha, R Ghimire, J J Nakarmi, Young Sung Kim, S Shrestha, C Y Park and J H Boo, Bull. Korean Chem. Soc. 31, 112 (2010)
[14] Muhammad Nafees, Wasim Liaqut, Salamat Ali, Muhammad Ahsan Shafique Appl Nanosci (2013) 3:49–55