Characterization of Pb Doped CdS Thin Film Fabricated by Spray Pyrolysis Deposition Technique

Mousumi Kundu[1], Mst. Halima Khatun[2], Sajal Khan[3], Md. Shahjahan[4]

Bangabandhu Sheikh MujiburRahman Science & Technology University, Department of Applied Physics Electronics and Communication Engineering, Bangladesh

Abstract: ***Undoped and Pb-doped CdS (Pb:CdS) thin films were prepared by a spray pyrolysis technique on glass substrates at 300^{0}C substrate temperature for different doping concentrations. The physical properties of the films were studied as a function of increasing lead dopant concentration. Structural, optical and electrical properties of these films have studied for photovoltaic applications. The structural and optical properties of the prepared films were characterized using XRD and UV-VIS spectroscopy. X-ray diffraction (XRD) patterns revealed that the samples have hexagonal crystal structure. The particle size of the crystallites was found to be in the range 20-62 nm for CdS film. The optical properties of the Pb:CdSthin films have been studied at room temperature in wavelength range 400 nm to 1100 nm.The variation of energy band gap for the films with different doping concentrations was studied. The resistivity decreases with increase of the temperature which confirms semiconductor behavior and it depends on the doping concentrations.Hall measurements were done in air ambient at room temperatureand the samples are found n-type semiconductor.***

Keywords: Spray pyrolysis, Dopant, Band gap, CdS

1. Introduction

Thin films of polycrystalline semiconductors has extremely wide range of physical and chemical properties makes them important material both for technological and industrial applications. Cadmium sulfide (CdS) belongs to II - VI compound semiconductor which has a wide direct band gap of E_g.=2.36−2.45 eV at room temperature. CdS is currently used as a window layer in thin film solar cells**[1]**, because of its large band gap and high transparency **[2]**.The deposition of CdS films has been explored by different techniques: sputtering, thermal evaporation, chemical bath deposition, and molecular beam epitaxy**[3,4]**. Spray pyrolysis deposition (SPD) technique provides a simple route of synthesizing thin films because of its simplicity, low cost experimental set up from an economic point of view**[5,6]**. Lead doped cadmium sulfide ($Cd_{1-x}Pb_xS$) films are getting attention in recent years due to their promising applications in fabricating blue and green light emitting diodes**[7]**, laser diodes, waveguide**[8],** logic gate and field emitter, photoconductor**[9],**nano-rods and thin films in energy conversion.

This work presents the influence of Pb doping on the structure of CdS thin films, by using the spray pyrolysis technique. The effect of Pb incorporation in CdS on the structural, optical and electrical properties has been investigated to determine the feasibility of CdS films for the potential technological applications.

2. Experimental Details

The working solution was prepared by taking cadmium chloride [$CdCl_2.H_2O$], Lead acetate [Pb $(CH_3COO)_2.2H_2O$] and NH_2CSNH_2 as a source material and distilled water was used as solvent. All the precursor solution was prepared in the molar concentration of 0.1 M for spraying. The Pb doping concentrations were varied from 1% and 2% (% wt.). The prepared solutions were maintained under continuous magnetic stirring at room temperature for one hour.

Before spraying on the glass substrates were first cleaned with liquid detergent, dipped into chromic acid mixture and then cleaned thoroughly in a stream of cold water. The temperature of the substrate was controlled by controlling the heater power by using a variac. The substrate temperature was measured by placing a copper constant thermocouple on the substrate. The substrate temperature was adjusted at 300ºC for film deposition.After deposition the films were annealed at 450ºC for an hour.

The crystalline structure of the films were determined XRD (Bruker D2) CuKα radiation of wavelength λ= 1.54185 Å for 2θ values over 20°- 70°. Peak positions were identified with JCPDS card No.41e1049.The optical transmission and absorption spectra of the CdS:Pb thin films have been studied at room temperature in wavelength range 400nm to 1100nm usingUV–Vis spectrophotometer. Resistivity of the films has been measured within the temperature range 305 K to 465 K using Van der Pauw configuration and Hall measurement system reveals the type of the semiconductor.

3. Results and Discussion

3.1 Structural properties

The XRD pattern of undoped and doped CdS thin films shown in Fig.1gives the information of different crystallographic phases and preferred orientations. The films have remarkable peaks and so, it can be concluded that the films are crystalline in nature in all the cases. The corresponding (hkl) values of (100), (002), (101), (102), (110), (103) and (112) planes confirms the hexagonal crystal structure of pure CdS (JCPDS card No.41e1049). It has been reported in the literature that the probability that CdS dissolves in the PbS lattice at room temperature is very low **[10].**

Comparing the intensities and full width at half maximum (FWHM) of (002) peak for undoped and doped samples, it is found that the intensity of three major peaks for 2 % Pb doped sample is much higher than others which indicates the best crystalline quality of 2% Pb doped samples. The peak intensity of (002) is higher compared to other peaks of Pb doped samples. There is a small competition of intensities of (100) and (002) for Pb doped sample which indicates that the crystal structure habit is mainly along (002) direction.

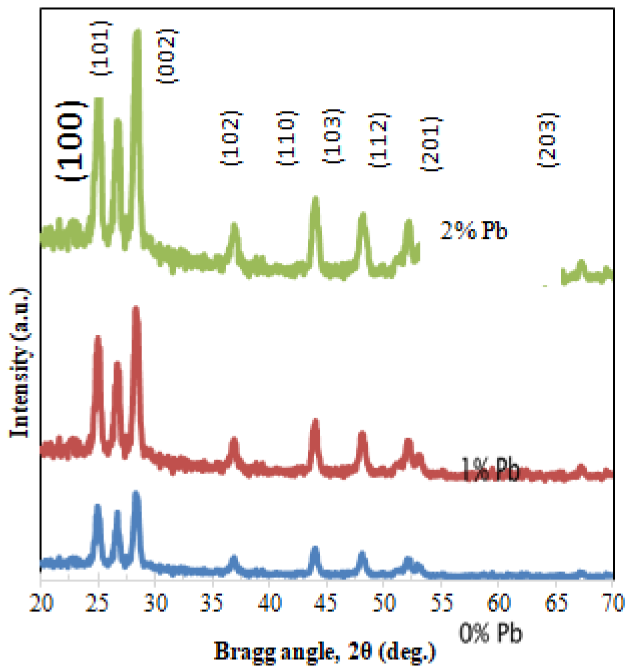

Figure 1: X-ray diffraction pattern for undoped and Pb:CdS thin films.

The crystallite size of the films was calculated by using Debye Scherer formula **[11]**

$$\zeta = \frac{0.94\lambda}{\beta \cos\theta}$$

where ζ is the crystallite diameter, λ is the wavelength, θ is the Bragg's angle and β is the full-width at half-maximum (FWHM) of the peak.

Itis found that the crystallite size in the corresponding planes for undoped and Pb:CdS thin films does not vary in a regular pattern with Pb doping concentration. The lattice parameter values of all the films show a slight deviation from the standard values which might be due to the strain introduced in the samples due to excess Cd interstitials or S vacancies present in the samples**[12]**. So our synthesized films are wurtzite hexagonal structure. As the ionic radius of Pb^{2+} (1.18Å) larger than that of Cd^{2+} (0.97Å),thus Pb^{2+} ions substituted into the crystal lattice of CdS and brought distortion in CdS lattice.

3.2 Optical Properties

Optical properties of CdS thin film are influenced mainly by the deposition conditions and thickness. The optical transmission spectra recorded for undoped and Pb doped CdS thin films as a function of the wavelength range 400-1100 nm using UV-visible spectrophotometer. The transmittance spectra are shown in Fig.2(a).It is observed from this figure that the transmittance in the visible range rise sharply and relatively slow in the higher wavelength region. Again, it is seen that the transmittance of CdS thin films decreases with the increase of Pb concentration. This result may be caused by the scattering of photon by the crystal defects created by doping**[13].** A sharp increase in transmittance is observed at 520 nm and attributed to the band edge absorption and transition is direct. This strong absorption means that the incoming photons have the sufficient energy to excite electrons from the valance band to conduction band.

The absorption spectra are shown in Fig.2(b) shows that the absorbance of the film decrease sharply at the band edge with the increase of wavelength and then becomes nearly constant for a wide range of wavelength. It is also seen that the absorbance increases with the increase of Pb doping concentration.

The optical band gap energy of the films has been obtained from the intercept on the energy axis after extrapolation of the straight line section from the energy curve is shown in Fig.2(c). The optical band gap energy of this film has been calculated using the Tauc's relationship**[14,15]**

$$(\alpha h\nu) = A(h\nu - E_g)^m$$

where, α *is* the absorption co-efficient, A is a constant, hv is the photon energy, E_g is the optical band gap of the semiconductor and m is the index related to the density of states for the energy band.

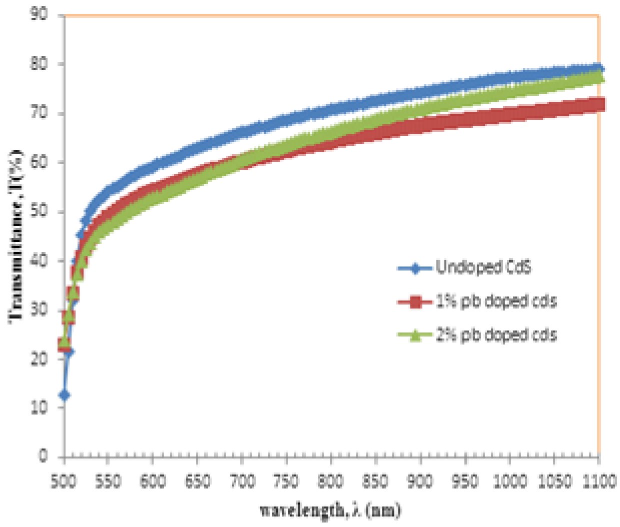

Figure 2(a): Variation of optical transmittance with wavelength for undoped and Pb:CdS thin films.

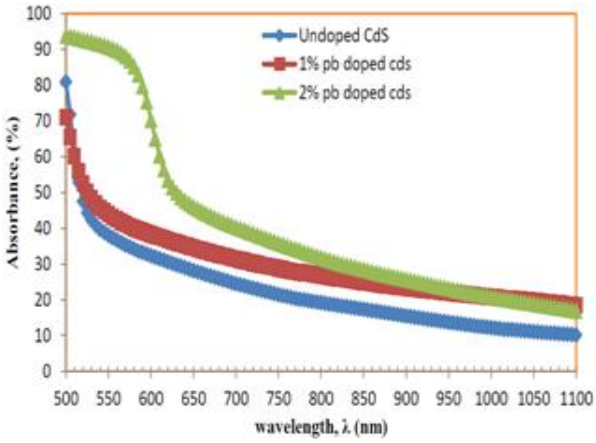

Figure 2(b): Variation of optical absorbance with wavelength for undoped and Pb:CdSthin films.

From the study it is clear that the band gap energy for direct transition decreases with the increase of Pb doping concentration. The optical band gap of Pb:CdS found to be 2.36eV to 2.42eV depending on the doping concentrations.

Table 1: Values of direct band gap energy for undoped and Pb:CdSthin films

Pb concentration in CdS (mol%)	Direct band gap, E_g (eV)
0	2.42
1	2.38
2	2.36

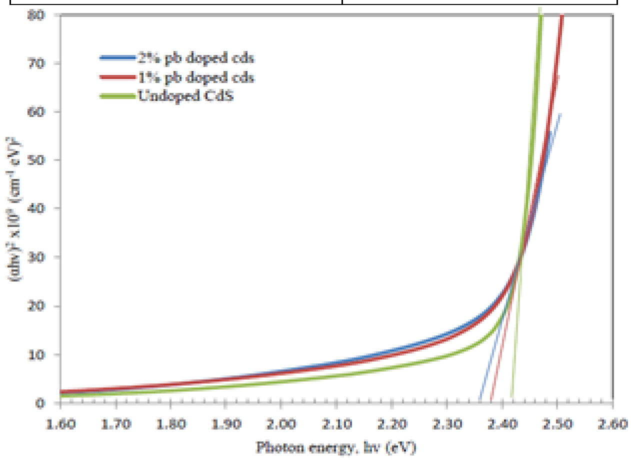

Figure 2(c): Variation of $(\alpha h\nu)^2$ with photon energy for undoped and Pb:CdSthin films.

3.3 Electrical Properties

The resistivity of all the pyrolized samples was measured by Van der Pauw method **[16].** The samples were annealed at 450°C for one hour and then cool down slowly to room temperature so that constituent atoms sits their lattice site properly and to remove any structural disorder may present during growth process. FromFig.3(a),it is observed that the resistivity decreases with the increase of temperature that confirms the semiconducting nature of the samples. It is also seen that the resistivity of the samples decreases with increasing the doping concentration of Pb. The decrease of resistivity of undoped and Pb:CdS thin films with increasing temperature may be due to increase of transition of donor electrons to conduction band. The room temperature (RT) resistivity of all the films are found to be in the order of $\mathbf{10^1}$Ω-cm.

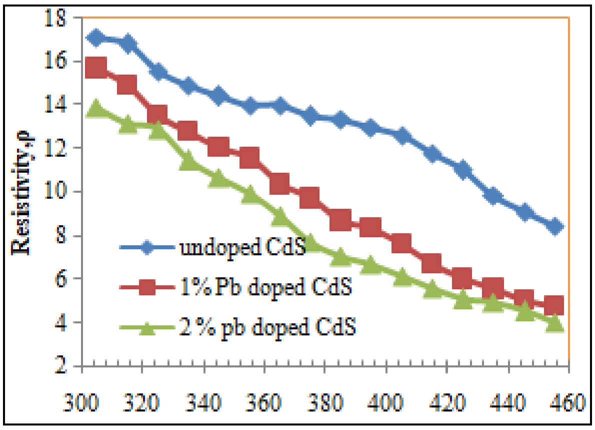

Figure 3(a): Variation of resistivity with temperature for undoped andPb:CdSthin films.

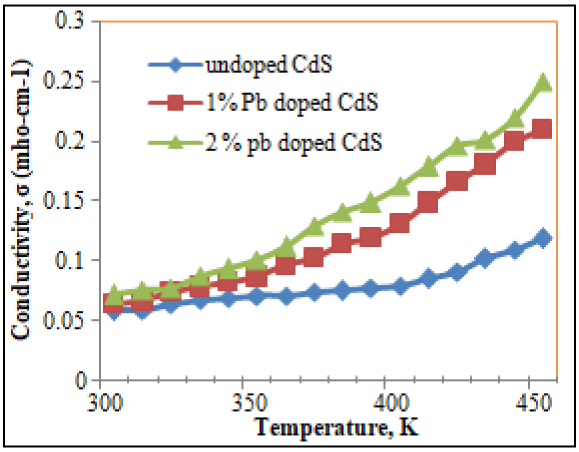

Figure 3(b): Variation of conductivity with temperature for undoped and Pb:CdS thin films

The plot of conductivity as a function of temperature for undoped and Pb:CdS thin films is shown in Fig.3(b) confirmed that the conductivity is inversely related to the resistivity and it was found to increase with the increase of temperature and with increase of Pb concentration as well.

The activation energy ΔE can be calculated using the relation,

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{2k_B T}\right)$$

Where, ΔE is the activation energy, $\sigma_0$is a constant and $\sigma$is the electrical conductivity, K_B is the Boltzmann constant and T is the absolute temperature.

The activation energy ΔE_1 at lower temperature region reveals thermally activated conduction and ΔE_2 at high temperature region manifests the thermally activated trapped charge conduction mechanisms is shown in Fig. 3(c).

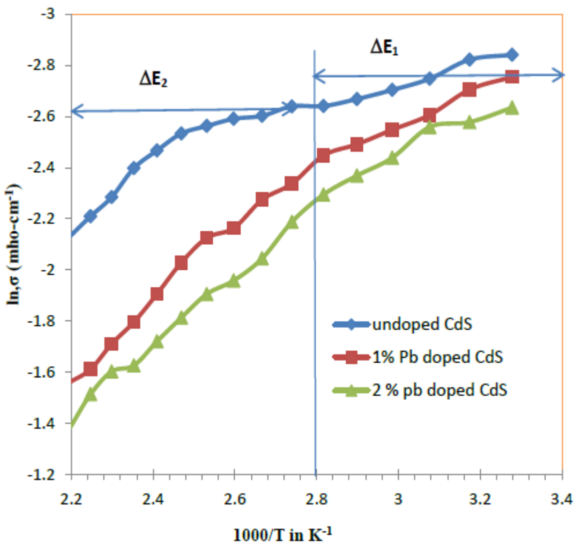

Figure 3(c): Variation of lnσ with 1000/T for undoped and Pb:CdSthin films

Table 2: Activation energy of undoped and Pb:CdS thin films

Pb concentration in CdS(mol%)	Activation energy, ΔE (ev)	
	ΔE_1 (303-358)K	ΔE_2 (358-453)K
0	0.0124	0.0375
1	0.0225	0.0636
2	0.0226	0.0626

The different Hall parameters such as Hall constant (RH), carrier concentrations (N), resistivity (ρ) and Hall mobility (μH) haves been calculatedand tabulated in Table-2for all the samples.The observed carrier concentrations and Hall mobility are comparable with that of reported [17] for Pb:CdS thin films prepared by chemical spray pyrolysis technique.

Table 3: Resistivity, Conductivity, Hall constant, Carrier concentration and Hall mobility

Pb concentration in CdS(mol%)	Resistivity, ρ at (RT) (ohm-cm)	Hall constant, R_H (cm^3/coul)	Carrier concentration, Nx10^{16} (cm^{-3})	Hall mobility, μ_H(cm^2/Vs)
0	17.12	-350.02	1.785612251	20.45
1	16.80	-202.92	3.08003154	12.08
2	14.59	-125.08	4.996841996	8.57

From the Hall study it is clear that the carrier concentrations increase with the increase of Pb doping concentrations and Hall mobility decreases with the increase of Pb doping concentration. Hall coefficient of the Pb:CdS thin films, was found negative which confirmed that the films are n-type material.

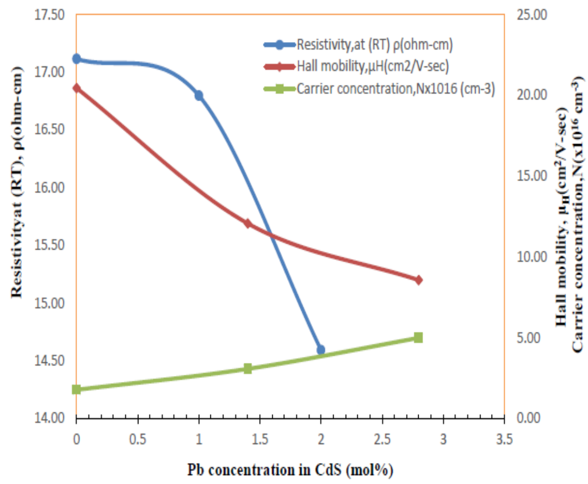

Figure 3(d): Variation of Resistivity, Carrier concentration and Hall mobility with Pb concentration in CdS films..

4. Conclusion

CdS thin films doped with Pb have been successfully fabricated on ordinary glass substrate using convenient spray pyrolysis technique at substrate temperature 300^0C and the experimental investigations and analysis on the structural, optical and electrical studies has been observed. The XRD result confirms the formation of CdS with a hexagonal wurtzite crystal structure. It is also observed that the crystal structure habit is mainly along (002) direction for Pb:CdS andthe shift in the diffraction angles is due to the incorporation of Pb^{2+} at the sub-lattice sites. The UV-Vis study confirms that the Pb:CdS films are direct band gap semiconductor with very high absorption coefficient ~ 10^5 cm^{-1}. The optical band gap energy is observed to vary from 2.36 eV to 2.42 eV. The Van der Pauw electrical measurements confirms Pb doped CdS thin films are semiconducting. Hall measurement reveals undoped and Pb:CdS films are n-type semiconductor and the effective carrier concentrations are found to be in the order of 10^{16} cm^{-3}.

References

[1] Kul M., Zor M., Aybek A.S., Irmak S. and Turan E., Thermally stimulated currents in CdS films produced by ultrasonic spray pyrolysis, *Thin Solid Films.*,515,8590(2007)

[2] A.F. Wells (1984) *Structural Inorganic Chemistry* 5th edition Oxford Science Publications

[3] T. C. Harmann, Mass Inst. Technol., Lincoln Lab., 3, 10 (1971).

[4] SubbaRamaiah K. and Sundara Raja V., Effect of annealing and γ-irradiation on the properties of CuInSe thin films, *Sol. Energy. Mater. SolarCells.*,32, 1 (1994)

[5] D. Perednis, L. J. Gauckler, Journal of Electroceramics. (2005) pp. 14.

[6] A. Nakaruk, C. C. Sorrell, Journal of Coatings Technology. (2010) pp. 7.

[7] T. Sivaraman, A.R. Balu, V.S. Nagarethinam, Effect of magnesium incorporation on the structural, morphological, optical and electrical properties of CdS thin films, Mater. Sci. Semicon. Proc. 27 (2014) 915e923.

[8] Iacomi, F ,Purica M. , Budianu E. , Prepelita P, Macovei D. "Structural studies on some doped CdS thin films deposited by spray pyrolysis method", Thin Solid Films, 515, p6080-6084, 2007.
[9] Rusu R.S. and Rusu G.I., On the electrical and optical characteristics of CdO thin films, *J.Optoelectronics andAdv. Mat*., 7(2), 823 (2005).
[10] J., M.Guglielmi, A.Martucci, J.Fick, G.Vitrant, Sol-Gel Sci.Technol. 11, pp. 229 (1998).
[11] B.D. Culliyy, *"Elements of X-ray diffraction",* Addition-Wesley, Reading, MA, (1972) pp. 102.
[12] PG and Research Department of Physics, AVVM Sri Pushpam College, Poondi 613503, Tamilnadu, India.
[13] P.M.RatheeshKumar,C.SudhaKartha,K.P.Vijayakumar, T.Abe, Y.Kashiwaba, F.Singh and D.K. Avasthi, Semiconductor. Sci. Technol., (2005) pp. 120.
[14] D.R. Sahu, Mcrochem Journal, 38 (2007) pp. 1252.
[15] W.E. Mahmoud, AA Al-Ghamdi, Opt. Las. Technology, 42 (2000) pp. 1134.
[16] Van-der-Pauw, Philips Tech. Rech., 20 (1958) pp. 230.
[17] Internationa Journal of Physics and Research (IJPR) ISSN (P): 2250-0030; ISSN(E): 2319-4499 Vol. 6, Issue 2, Apr 2016, pp. 31-36.