OPTICAL, STRUCTURAL AND ELECTRICAL PROPERTIES OF SILAR DEPOSITED Al DOPED CdS THIN FILMS

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

Abstract.
Successive Ionic Layer Adsorption and Reaction (SILAR) technique was used for reparation of Al doped CdS thin films. Al doped CdS films were annealed at 200°C for 1 hour in air. Al doped CdS films with various doping concentration were characterized using XRD, Field Emission Scanning Electron Microscopy (FESEM) and UV-Visible spectrophotometer. The XRD study shows that the zinc blend cubic structure of CdS is not much affected with respect to Al doping. The micro structural properties and grain size with various Al doping concentration were investigated from XRD data. The percentage of transmittance and optical band gap were investigated from optical data. The optical band gap of Al doped CdS films decreases for the increase in Al doping concentration.

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

1. Introduction

The II-VI compound semiconductors are having great importance due to their applications in various electro-optic devices. Cadmium sulphide (CdS) is a wide band gap semiconductor belonging to II-VI group compounds [1-3]. For the application of CdS thin films in solar cells, it is necessary to have layers with the following characteristics which are uniformity, transparency, crystallinity, and good electrical properties. Cadmium sulphide (CdS) is a wide band gap (2.42 eV) and direct transition semiconductor [4]. Consequently, it is potentially an important material to be used as an antireflection coating for heterojunction solar cells [5]. It has been widely used as a window material in high efficiency thin film solar cells based on CdTe or CIGS [6]. The addition of trace amount of transition metal ion into CdS host plays an important role in modifying the structural, optical and electrical transport properties of the binary alloy material [7]. Metal chalcogenides are attracting a great deal of attention because of their many fold importance in a wide spectrum of optoelectronics devices [8]. Al-doped CdS thin films show low electrical resistivity of about 48 Ω cm and high carrier density of about 1.1×1019 cm^{-3}. The doping of group III elements has been found to decrease the resistivity of CdS thin films. The effect of Al incorporation on the structural and electrical properties of CdS has been investigated to determine the feasibility of CdS films for the potential technological application [9, 10]. Different techniques have been used to prepare the cadmium sulphide thin films, such as vacuum evaporation, chemical bath deposition, sputtering, spray Pyrolysis, electro deposition [11] and Successive Ionic Layer Adsorption and Reaction (SILAR) [12,13]. Among all the methods, SILAR method is an important, simple and cost effective technique for the fabrication of multi-component thin films. The present article deals with investigations of synthesis of Al doped CdS films, structural, morphological and Optical properties of Al doped CdS thin films.

2. Experimental

All the chemicals used for the preparation of thin films were of analytical grade. It includes cadmium acetate, thiourea and aluminium nitrate. All the solutions were prepared using double distilled water. For the preparation of Al doped CdS thin films, cationic precursor (0.1M) cadmium acetate (50 ml) and (0.003 M) aluminium nitrate were taken in a beaker, and the anionic precursor (0.1M) thiourea (50 ml) was taken in a separate beaker. For the deposition of Al doped CdS thin film, well cleaned glass substrate was dipped into the cationic precursor for 40 sec for adsorption of Cd^{2+} and Al^{2+} ions on the surface of the glass substrate, and then the substrate was dipped into the de-ionized water for 10 sec to avoid precipitation and also to remove the loosely bounded cations. The substrate was then immersed into the anionic precursor bath (S^{2-}) for 40 sec. The procedure was carried out at ~75°C temperature. Successive dipping cycles were repeated up to 75 cycles, to get the well adherent and homogeneous Al doped CdS thin films. Then the same procedures were repeated for 0.006M and 0.009 M aluminium nitrate. Al was doped with CdS in the following mol % and they are 3, 6 and 9 respectively. The prepared samples were annealed in air at 200°C for 1 hour. 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.

3. Result and Discussion

3.1. Structural Analysis

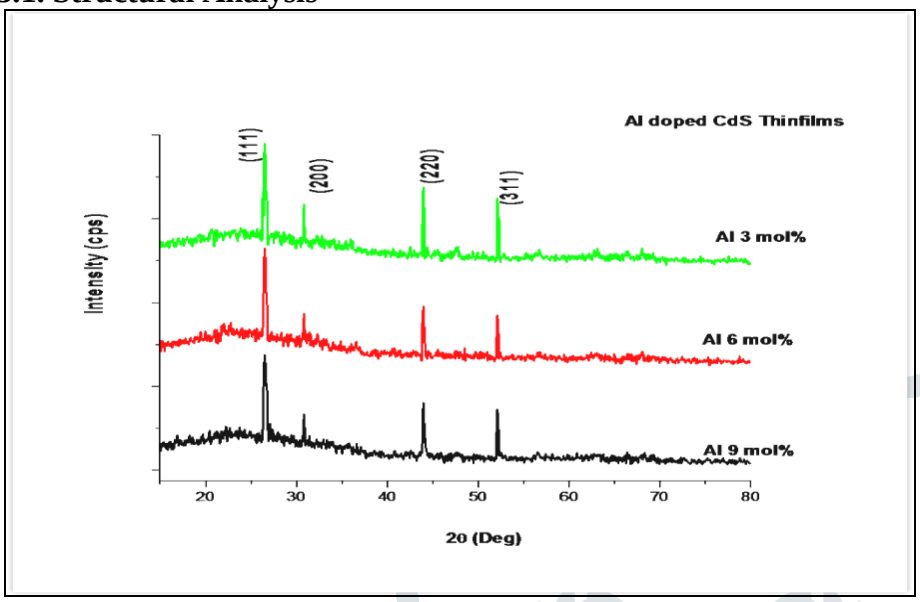


Fig.1-XRD patterns of Al doped CdS thin films

Al doping concentration (Mol. %)	Crystallite size, D (nm)	'a'(Å)	Micro Strain- Є
3	17.23	5.9300	3.19×10^{-3}
6	16.17	5.9006	3.57×10^{-3}
9	14.86	5.8760	3.78×10^{-3}

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

The crystal structure of Al doped CdS films were determined by XRD spectra obtained by grazing incidence X-ray diffraction. Fig.(1) shows the X-ray diffraction spectra of the SILAR deposited Al doped CdS films. In the diffraction pattern, peaks corresponding to the (111), (200), (220) and (311) planes of Cubic CdS are observed. The diffraction pattern exhibits the entire characteristic peaks of the Zincblende CdS Cubic structure, 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 peaks. Intensity of the (200), (220) and (311) diffraction peaks were decreased with increasing the Al concentration, which indicates that excessive Al doping deteriorates the crystallinity of the films, which may be due to the formation of stress by the smaller radius of Al^{2+} (0.53 Å) ions compared with Cd^{2+} (0.95 Å) ions[14]. In order to determine lattice parameter of the thin films, JANA2006 code was used in the Le-Bail mode. The calculated lattice parameters of thin films were tabulated in Table.1. The calculated values of lattice parameter a for 3mol% of Al doped CdS is 5.9300Å and these values are found in good agreement with the corresponding value 5.818Å [ICDD No. 10-0454]. It can also found that, with the increase of the doping concentration of Al from 6 mol% to 9 mol% , lattice constant (a) decreased linearly from 5.9006 to 5.8760 Å. The slight change of lattice parameter of Al doped CdS also prove that the Al ions were incorporated into the CdS lattice. The 2θ of the (111) was shifted to higher values of 2θ (from 34.40 to 34.47°), when Al was incorporated and indicates reduction of inter-planar spacing "d" in the films. Also the crystallographic (111) peak becomes broad with increasing concentration. The literature reveals that the reduction in the intensity of the crystallographic peak is attributed to the reduction in the crystallinity of the films. The crystallite size of the SILAR deposited Al doped CdS thin films has been calculated using Scherer formula [15] given in equation (1), The FWHM values of the samples were derived from their highest intensity peak broadening by pseudo-voigt peak fitting. The average lattice strain has been calculated using Stokes Wilson equation [16] shown in equation (2)

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

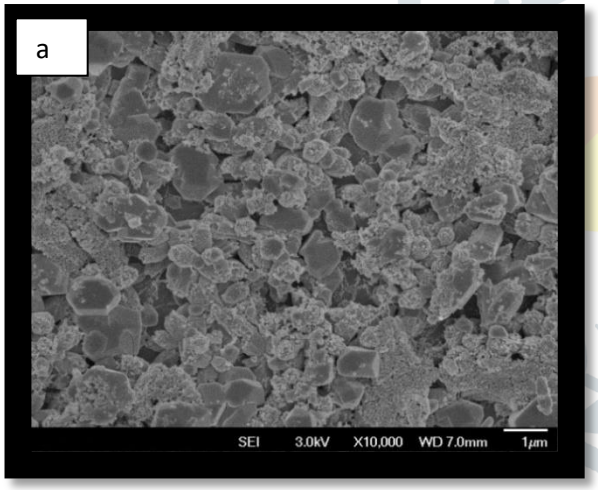
Micro Strain $\varepsilon = \beta /4\tan\theta$ ----- (2)

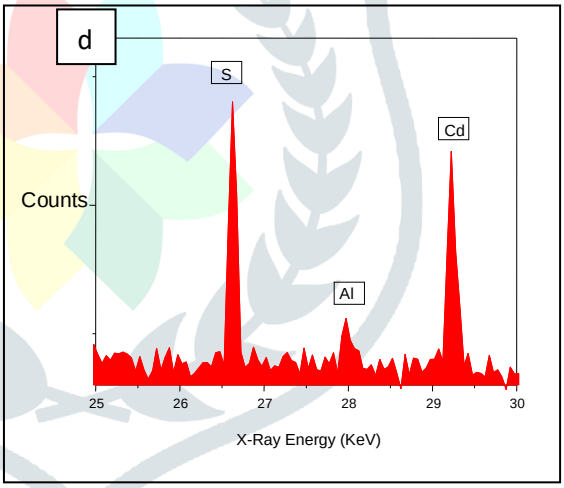
Where D_{ave} is the mean crystallite size, ε is the average micro strain $(\Delta d/d)$, β is the full width at half maximum of the diffraction line, θ angle of diffraction and λ the wavelength of the X-ray radiation. The maximum crystallite size of ~17 nm is found for 3 mol% Al doped CdS film and the minimum crystallite size of ~14 nm is found for 9 mol% of Al doped CdS film which is shown in Table.01.

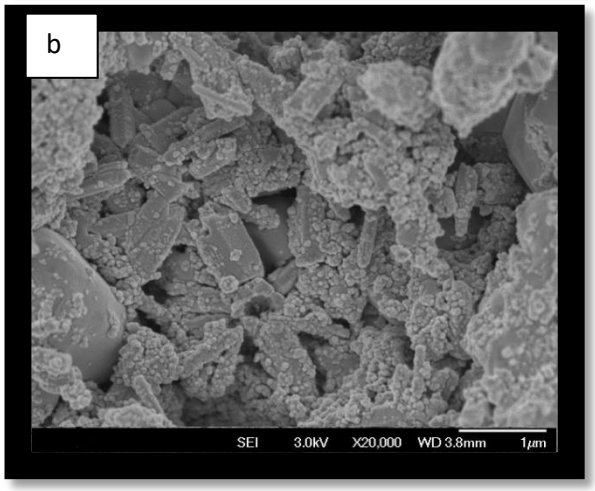
3.2. Surface Morphology and EDAX by FESEM Analysis

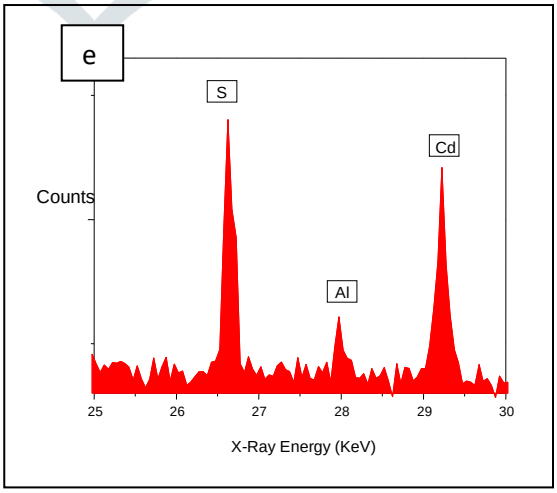
The FESEM micrographs of Al doped CdS thin films with the various mol% of Al (3 mol %, 6 mol % and 9 mol %) on glass substrates are shown in Fig.2. It can be seen that the surface morphology of the films strongly depends on the concentration of the dopant. The grains are almost cover the substrate surface uniformly. In 3 mol% of Al, particles mixed with rod like and cube like shapes are observed. Particles on the surface of substrate were seemed to be agglomerated. Fig. 2(b) & 2(c) show 6 mol% and 9 mol% of Al doped CdS thin films, there seems to be an increase in the surface coverage of grains and reduction in grain size. Al doping seems to have modified the shape of the grains. In comparison with XRD analysis, the reduction of crystallite size is in good agreement. These observations suggest an incomplete nucleation step with irregular growth rate of the grains. The result shows accelerated grain growth with the Al doping. The grain size reduces and randomizing of grain orientation occurs easily when Al dopants were incorporated with CdS. The surface seems to be formed by the stacking of self-aligned nanoparticles.

Although no compositional analysis was attempted in the present study, the incorporation of Al in the films was verified by the EDAX result. Figure 2(d), (e) &(f) shows the energy-dispersive X-ray spectrum of Al doped CdS film for 3 mol %, 6 mol % and 9 mol % respectively. The EDAX reveals the presence of Cd, S and incorporation of Al in the deposited films.









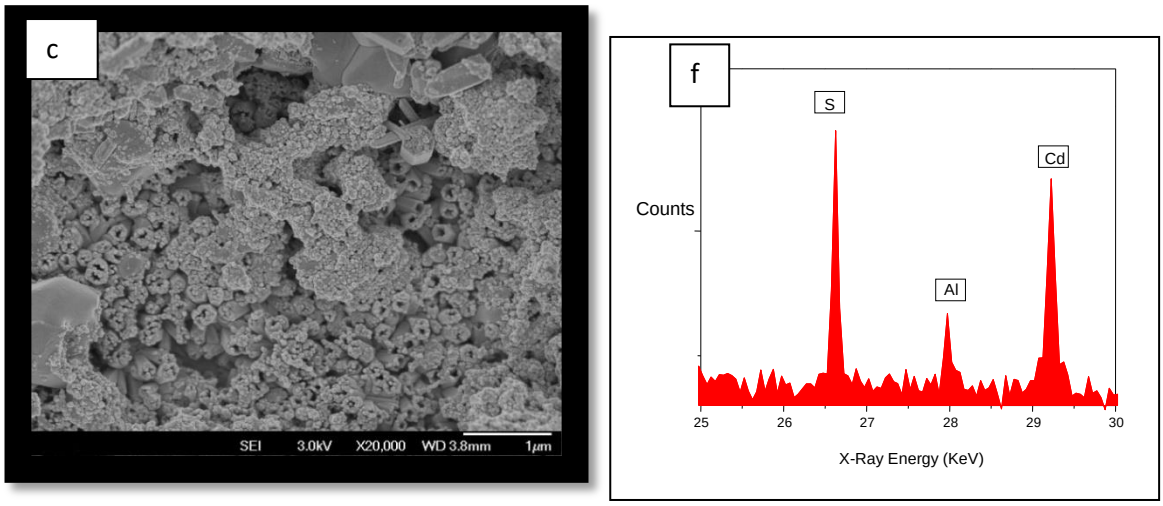


Fig.2. Surface morphology and EDAX analysis of Al doped CdS thin films for various doping concentration

3.3. Optical studies

The transmittance spectra of Al doped CdS thin films in the wavelength range of 300–1100 nm are shown in Fig. 3(a). It is observed that the transmittance of 6 and 9 mol% of Al doped films is lower than that of 3 mol% films. The transmittance of 6 and 9 mol% of Al doping concentrations is decreased, it may be due to the increased scattering of photons caused by rough surface morphology as well as crystal defects in the prepared sample. This result is in good agreement with structural and surface morphology analysis of the present work. The optical band gap Eg can be estimated by plotting (hν) versus photon energy $(\alpha h \nu)^2$ 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[17]. The calculated band gap with respect to Al doping concentration is plotted in fig. 3(b), clearly indicates decrease of band gap with increase in Al concentration. The optical band gap for 3 mol % Al doped CdS film is 2.44 eV. For 6 and 9 mol % Al doped CdS film the band gaps are 2.40 eV and 2.35 eV respectively, which are lower than 3mol % Al doped CdS film. The optical band gaps presented in Fig. 3(b) clearly exhibit a blue shift in band edge towards lower wavelength with the increase in the Al doping concentration, which indicating the reduction of the optical band gap with increase in doping concentration of Al with CdS.

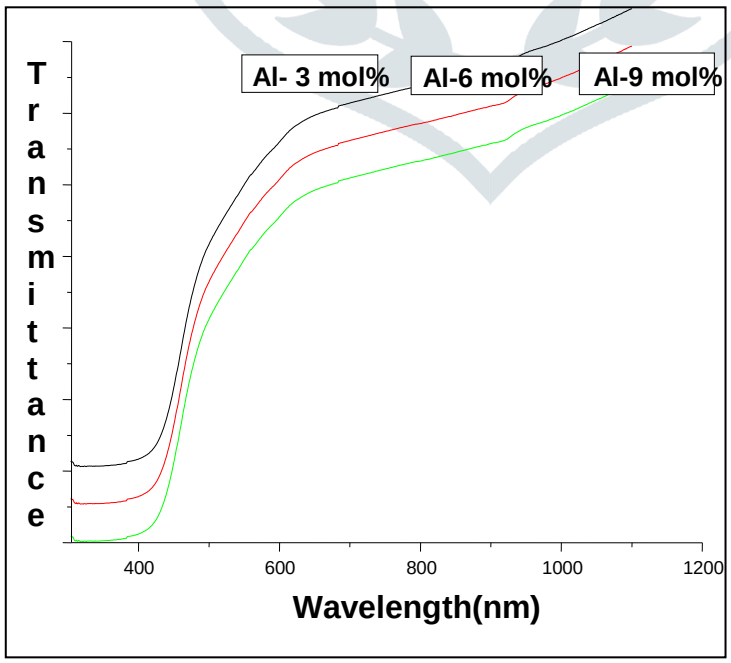


Fig.3 (a) - Transmittance graph of Al doped CdS films

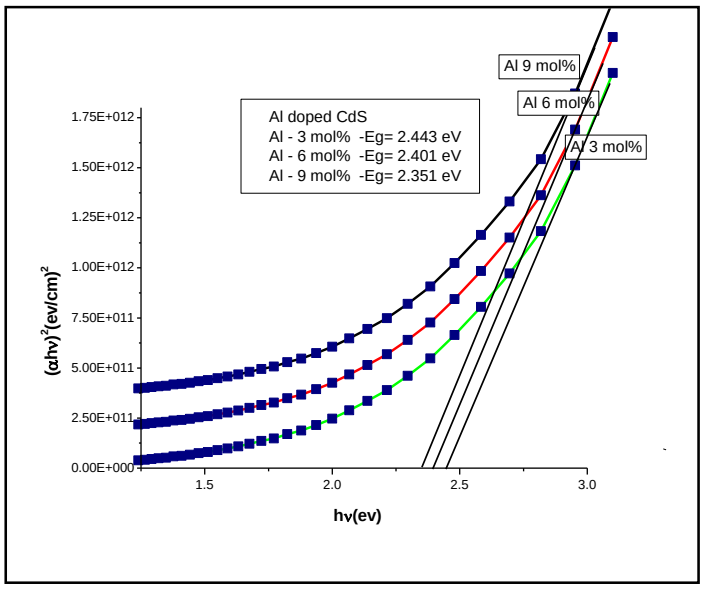


Fig. 3 (b) - Band gap of Al doped CdS thin films

3.4. Electrical Studies

Film	Resistivity (ohm-cm)	Conductivity (1/ohm- cm)	Carrier concentration (cm^{-3})	Hall Coefficient (cm^3/C)
3 mol% of Al	$1.97x10^{2}$	$7.051x10^{-03}$	6.66E14	$5.131\ x10^{7}$
6 mol% of Al	$1.92x10^{2}$	$7.712x10^{-03}$	7.82E14	$2.724\ x10^{6}$
9 mol% of Al	$1.87x10^{2}$	$8.274x10^{-03}$	8.51E14	$8.331\ x10^{5}$

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

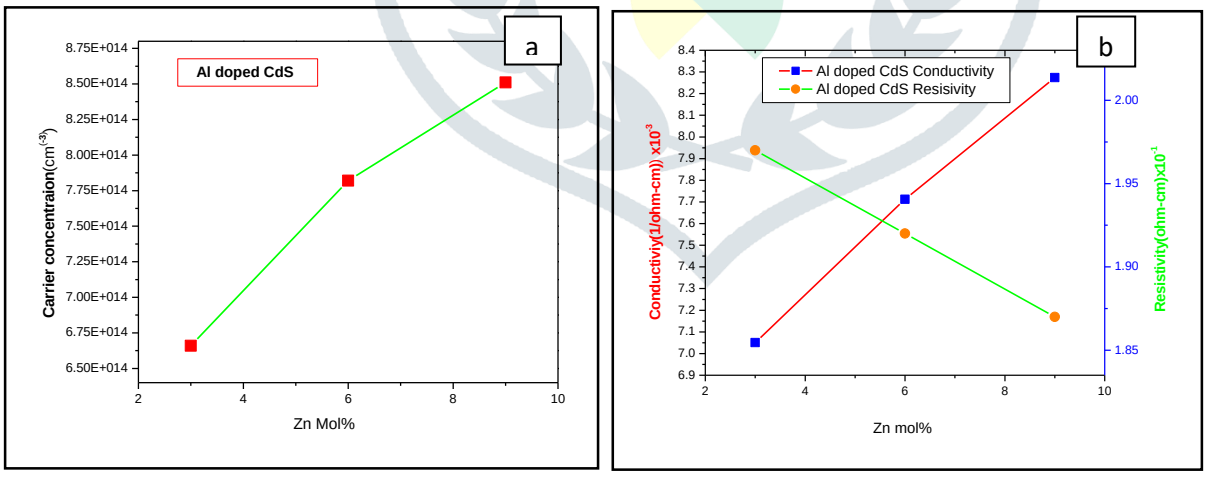


Fig.4. (a) & (b) shows variation of carrierconcenration, conductivity & resistivity with Al mol% respectively.

The Electrical properties of Al doped CdS thin films were performed at room temperature in van der Pauw configuration. The different Hall parameters, such as conductivity, resistivity and carrier concentrations (*n*) have been calculated and tabulated in Table 2. The variation of the carrier concentration with Al content is shown in Fig.4 (a). It is shown that Al content is a parameter which makes notable impact on the electrical properties of the CdS film. It can be observed from Fig. 4(b) that the film shows comparatively the lowest resistivity and the highest conductivity at Al doping concentration of 9 mol %. The increase in the electrical conductivity with Al doping concentration is may be due to the presence of large number of free carriers introduced by Al dopant. The highest carrier concentration obtained in the present investigation is $8.510x10^{14}$ cm^{-3} and it is observed at 9 mol% of Al doped CdS films.

Conclusion

Al doped CdS thin films were successfully deposited on glass substrates using SILAR deposition method. Photo acoustic and transmittance spectroscopy analysis were performed on Al doped CdS thin films, to obtain the optical absorption and transmission spectra, respectively. Then, the band gap of the films was calculated using the UV characterization results. A decreasing band gap value was observed with increasing Al doping concentration, the Eg values decreases from 2.44 eV to 2.35 eV for increase in Al doping concentration from 3 mol% to 9 mol%. XRD measurements show a change in the intensity and the broadening of the intensity peak (111) when Al doping is increased, which indicating that the incorporation of Al^{2+} ions slightly modifies the lattice structure of the CdS film. The average interplanar distance of CdS was modified with increasing Al-doping concentration, due to dislocations produced by Al^{2+} ions in the lattice, and the replacement of Cd^{2+} ions in the lattice both substitutionally and interstitially. A decrease in the crystallite size was observed for increase in Al doping concentration, the minimum and maximum crystallize values observed for 3 and 9 mol% of Al doping concentration respectively. The maximum value of conductivity and minimum value of resistivity observed in prepared samples at 9 mol% of Al doping concentration, which indicates the successful incorporation of Al with CdS.

5. References

[1] G.E. Delgado, J.E. Contreras, A.J. Mora, L. Béancourt, P. Grima-Gallardo, M. Quintero Chalcogenide Lett. 6 (12) (2009) 647.
[2] H. Chavez, M. Jorden, J.C. McClure, G. Lush, V.P. Singh, J. Mat. Sci.: Mater. Electron. 8 (1997) 151.
[3] C.S. Ferekides, D. Marinskiy, S. Marinskaya, B. Tetali, D. Oman, D.L. Morel, In: Proceedings 25th IEEE PVSC (Washington, D.C., 1996) p. 751.
[4] I. Kaur, D.K. Pandya, K.L. Chopra, J. Electrochem. Soc. 127 (1980) 943.
[5] I.O. Oladeji, L. Chow, C. Ferekides, V. Viswanathan, Z. Zhao, Energy Mater. Sol. Cells. 61 (2000) 203.
[6] O. Vigil-Galan, J. Ximello-Quiebras, J. Aguilar-Hernandez, G. Contreras-Puenta, A. Cruz Orea, J. Mendoza-Alverez, J. Gardona-Bedoya, C. Ruiz, V. Bermudez, Semicond. Sci. Technol. 21 (2006) 76.
[7] A. Ashour, H.H. Afify, S.A. Mahmoud, Thin Solid Films 248 (1994)253.
[8] B. Thangaraju, Thin Solid Films 71 (2002) 402.
[9] B.N. Patil, D.B. Naik, V.S. Shrivastava, Chalcogenide letters 8(2) (2011) 117.
[10] J. Santos Cruz, R. Castanedo Pérez, G. Torres Delgado, O. Zelaya Angel, Thin Solid Films 518 (2010) 1791.
[11] Ulrich, B., Tomm, J.W., Dushkina, N.M., Tomm, Y.,Sakai, H. and Segawa, Y., Solid State Communications, 116, pp 33-35 (2000).
[12] 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)
[13] 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
[14] R. D. Shannon, Acta Cryst. A32, 751 (1976).
[15] S Tewari and A Bhattacharjee, Pramana – J. Phys. 76, 153 (2011)
[16]. 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)
[17] Muhammad Nafees, Wasim Liaqut, Salamat Ali, Muhammad Ahsan Shafique Appl Nanosci (2013) 3:49–55