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EFFECT OF GRAIN SIZE ON THE ELECTRICAL CONDUCTION MECHANISM FOR ALUMINUM DOPED CdS THIN FILMS

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ABSTRACT
Aluminum-doped CdS thin films have been deposited onto heated glass substrates by spray pyrolysis technique. Films were polycrystalline in nature and oriented preferentially in the 002 direction. Electrical properties have been investigated by resistivity and Hall effect measurements in order to understand the role of Al in the electrical transport mechanism. It was observed that 9% and 12% Al concentrations are the optimal doping amount in order to achieve the maximum conductivity, results have been analyzed according to the grain-boundary scattering mechanism. Increase in the electrical conductivity σ on the incorporation of Aluminum can be attributed to the reduction in grain boundary scattering, which leads to a decrease of the height of barriers (modulation of mobility μ) and to injection free carriers (modulation of carrier concentration N), the decrease of σ with a further increase of Aluminum may be occured because Al^{+3} introduce additional charged scattering centers at the grain boundaries which restrict carriers transport. Carrier concentrations and hall mobility of the films are dependent on the grain size, the film with a smaller grain size has a lower carrier concentration and lower mobility.The electrical conductivity is related to the grain size and shows a maximum for the film with grain size of about 43.469 nm, activation energy studies support this increase in the conductivity due to improvement in crystallinity of the films.
Key Words: Doped CdS thin films, Spray Pyrolysis, Grain size, Electrical Conductivity.

I. INTRODUCTION

Cadmium sulphide (CdS) is an important material which can be used to make n-type materials for thin film hetero junction solar cells; low resistivity CdS films are needed in hetero junction solar cells to lower the cell series resistance. CdS has attracted technological interest because the energy gap can be tuned and the lattice parameters can be varied [1,2].It is well known that the electrical and optical properties of semiconducting materials depend strongly on defect density created by external doping as well as their preparation and growth conditions. The addition of trace amount of transition metal ion into CdS plays an important role in modifying the structural, optical and electrical transport properties of the binary alloy material also doping of group III elements has been found to increase the conductivity of CdS thin films [3], the efficiency of CdS semiconductor film was improved by changing its optical and/or electrical properties by doping with some foreign elements such as Gallium, Copper and Aluminum [4, 5]. Al doped CdS thin film has emerged as an important material due to its applications in photovoltaic cell as window layers and as transparent conducting semiconductor for optoelectronic devices ,conductivity of CdS thin films increase after doping with Al, Al^{+3} ions tend to replace Cd^{+2} ions in the lattice substitutionally, however Al^{+3} ions tend to enter the lattice substitutionally at low concentration, and interstitially at high concentration,interstitial Al^{3+} ions will act as recombination centers decreasing N and increasing the resistivity [6]. Doped CdS films can be deposited by several methods such as Thermal Evaporation, Chemical bath Deposition and Spray Pyrolysis [7, 8], among all technique spray pyrolysis has been used extensively being large area deposition and chemically viable technique, we have shown that spray pyrolsis is a suitable technique for Aluminum doping of CdS. Concentration of the starting material (solution) highly affects the nature of the film mainly its grain size, growth of the film [9]. Many researchers [10,11] have studied the structural, optical and electrical properties of doped CdS thin films, but the mechanism of conductivity of Aluminum doped CdS thin films has not been reported so far, hence we have carried out systematic investigations on structural and electrical conductivity of CdS thin films doped with Aluminum to improve the properties of the films for device applications. The objective of this work is mainly to study the role of Aluminum as dopant in the electrical conductivity of CdS thin films and to correlate it to the grain size of the prepared films.

II. EXPERIMENTS

The spray pyrolysis technique is a simple technology in which an ionic solution-containing the constituent elements of a compound is sprayed onto over heated substrates using a stream of dry air, the detailed description of the spray technique is given elsewhere [12]. The CdS thin films were prepared by spraying an aqueous solution of cadmium chloride ($CdCl_2$) and thiourea [$(NH_2)_2CS$] on glass substrate kept at 400°C, the substrate temperature was plays an important role in the film formation, if the substrate temperature is below 200°C the spray falling on the substrate will undergo in complete thermal decomposition giving foggy film whose electrical conductivity will be very poor. Al doped CdS films were deposited by adding Al_2Cl_3 as a dopant source to the solution, the atomic percentage of Aluminum in the solution were 3%, 9%,12% and 15% .Thickness was determined by the optical interference method, all of the CdS films had a thickness of approximately 400nm and showed good reproducibility. X-ray diffraction has been used to study the structure of the films, for resistivity measurements the circuit which consist of LCR meter and oven was used to measure the resistance in the temperature range 300-420K, hall mobility and carrier concentration were evaluated by Hall effect measurements in a Van der Pauw four-point probe configuration using set up consist of Kethley electrometer (616) and magnetic induction of 0.215T.

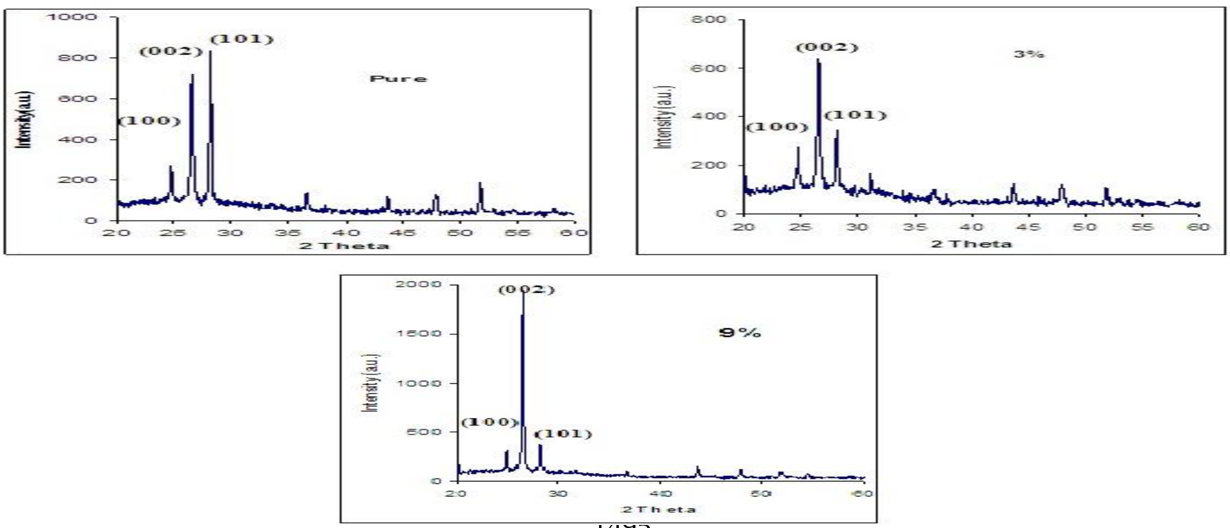
III. RESULTS AND DISCUSSION

III. 1. Structure of the films

A typical XRD pattern for pure and Aluminum doped CdS films on glass substrate is shown in fig.(1). The patterns indicate that all the films are polycrystalline hexagonal, and no crystalline Al phase is recognizable, Al is present in the CdS matrix mainly as donor state, with increasing Al content the diffraction peaks become large and sharp indicating more grains growing up, the highest (002) orientation seems to be happening at about 9% and 12.% Al concentrations, the average crystallite sizes estimated from the Debye-Scherrers [13].

$$D=0.9\lambda/B\cos\theta \qquad (1)$$

where θ is the diffraction angle, λ is the wavelength of the X-ray source and B is measured in radian as full-width at half maximum of the diffraction line, the grain size of CdS thin films were found to be around 37.459±5 nm as listed in table 1, apparently grain size becomes larger as increasing Al content up to 12%, because the scattering of electron at grain boundaries is decreased due to growth of grains, this result is in a good agreement with that reported by other-workers[14].



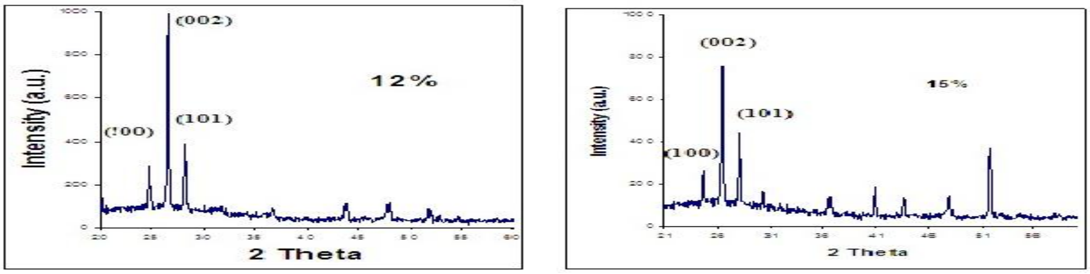


Fig.1: X-ray patterns for non doped and Al doped CdS films.

III. 2. Electrical properties

The electrical conductivity σ of all samples have been determined using the formula[15]:

$$\sigma = AR/L \quad (2)$$

where R is the film resistance, L is the distance between the electrodes and A is the cross-sectional area of the films, the temperature dependence of conductivity follows the relation:

$$\sigma = \sigma_o \exp(-Ea/k_B T) \quad (3)$$

where σ is conductivity at temperature T, σ_o is the conductivity at 0K ,k_B is the Boltzmann constant and Ea is the activation energy required for conduction, fig.(2) shows the temperature dependence of conductivity for Al doped CdS films with different Al concentration, the electrical conduction in the temperature range 300-420k is thermally activated by thermionic emission between grains ,it can be noticed that the conductivity at 15%Al overlap with that of 9 and 12%Al then decreased with increasing Al concentration.

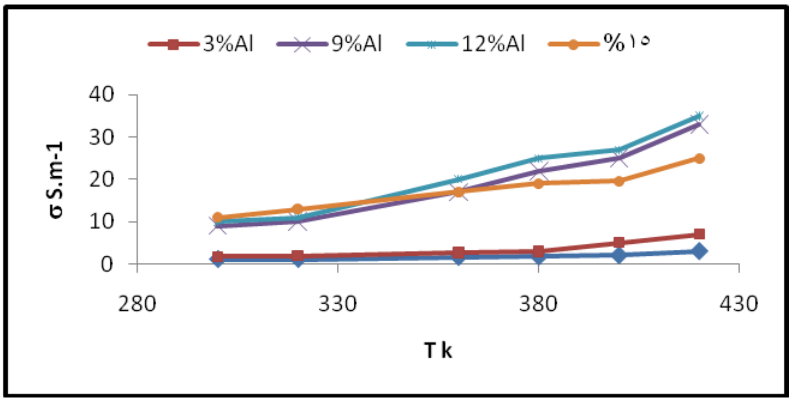


Fig.2: Relation of conductivity with temperature at different Al concentrations

The behavior of σ can be explained as follows, the incorporation of Al^{3+} ions as well as sulfur deficiency in Al-doped films gives rise to donor levels in the band gap of CdS , as the Al concentration increases up to 15%, the donor levels become degenerate and merge in the conduction band of CdS, causing the conduction band to extend into the band gap which reduces the band gap, in the room temperature the conductivity is increased from 0.54 $S.cm^{-1}$ for pure CdS film to around 12.409 $S.cm^{-1}$ at 9% and 12%Al concentration. Activation energy Ea of the films was determined using data from the Arrhenius plot, fig. (3) shows the Arrhenius plot of (logσ) with reciprocal of temperature (1/*T*), it can be observed that Ea decreased with increasing Al concentration which can be attributed to an increase the charge carrier mobility and decrease in defect levels with increase in the Al content, the values of Ea are given in table 1.

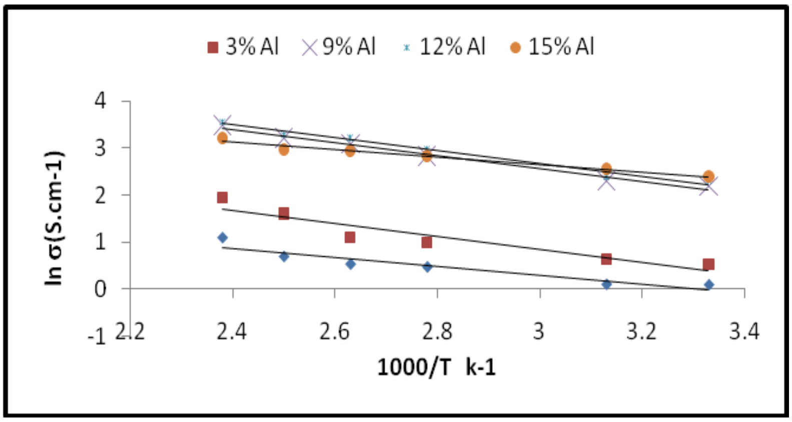


Fig. 3: Arrhenius plot of (logσ) S.cm with (1000/T K^{-1})

Table 1: Values of grain size, activation energy and σ

Al- ratio	Grain size(nm)	Ea(eV)±0.002	σ(Scm^{-1})
0%	30.865	- 0.026	1.002
3%at.	36.121	0.022	1.61
9%at.	40.456	0.019	12.321
12%at.	43.467	0.017	12.525
15%at.	30.675	0.0173	9.708

III. 3. Mechanism of Conduction

The conduction process can be explained by the grain boundary barrier effect ,it is known that a polycrystalline film contains a large number of microcrystal's separated by grain boundaries, the grain boundary consists of a couple of atomic layers of disordered atoms that produce large number of defects ,these defects impede the transit of carriers from one grain to the other acting as potential barriers, the height of the barrier is a function of the grain size hence grain size and grain boundary density in polycrystalline film influence the electrical conductivity mainly due to carriers being scattered by the disordered atom layers. The presence of grain boundaries leads to inter grain depletion layers $e\Phi_b$ and to Schottky energy barriers $e\Phi_s$, modulation of the depletion layer width and the energy barrier height at each grain depend on Al-Cd interaction processes that cause a change in the resistance of the film [16,17].

III. 4. Hall effect measurements

Measurements are fundamental tool in order to get information about the electrical transport properties of thin films, since both the carrier mobility μ and concentration N can control the conductivity σ by these measurements one can distinguish if σ is mainly controlled by inter-grain depletion barriers $e\Phi_b$ (modulation of μ) or by carrier depletion in the grains $e\Phi_s$ (modulation of N) or by a combination of the two effects, generally the grain-boundary mobility μ, and the carrier concentration N terms can be written as [18]:

$$\mu=\mu_o \exp (E_\mu /kT) \qquad (4)$$

$$N=N_o \exp (E_N /kT) \qquad (5)$$

where μ_o and N_o are constants, and $E\mu=e\Phi_b$, $E_N=e\Phi s$ are the activation energy of μ and N respectively at room temperature the values of activation energy are $E\mu=0.03$ev and $E_N=0.002\pm0.001$eV, moreover the condition $Ea \cong E\mu+ E_N$ is verified at the Al level under study. The grain boundary barriers can act as an energy filter to eliminate the lower energy carriers, one can deduct that the film with the smaller grain size will have a higher barrier [19].

Fig.(4) shows the conductivity σ, carrier concentration N and the hall mobility μ of the films as a function of Al concentration, all the films show n-type conductivity, the initial increase in the electrical conductivity on the incorporation of Aluminum can be attributed to the reduction in grain boundary scattering, which leads to an increase of σ by a decrease of the height of barriers (modulation of μ) and by an injection of free carriers (modulation of N), the decrease of σ with a further Al increase may be occurs because Al^{+3} introduce additional charged scattering centers at the grain boundaries which trap and scatter the conduction electrons and increases the height of the Schottky barriers ,so restrict carriers transport, it can be also observed that N initially increases as Al increase up to 12% due to electron released by Al ,and it decreases due to the increased disorder causing an increase in the activation energy of donors. The dependence of mobility as a function of the Al concentration is analogous to that of N, thus the combination of N and μ may change the conduction regime from fully depleted grains to partially depleted ones, in addition .It is clearly shown that σ,N and μ values systematically increase with increasing the grain sizes, similar behavior has been observed in the films of other materials [19,20]

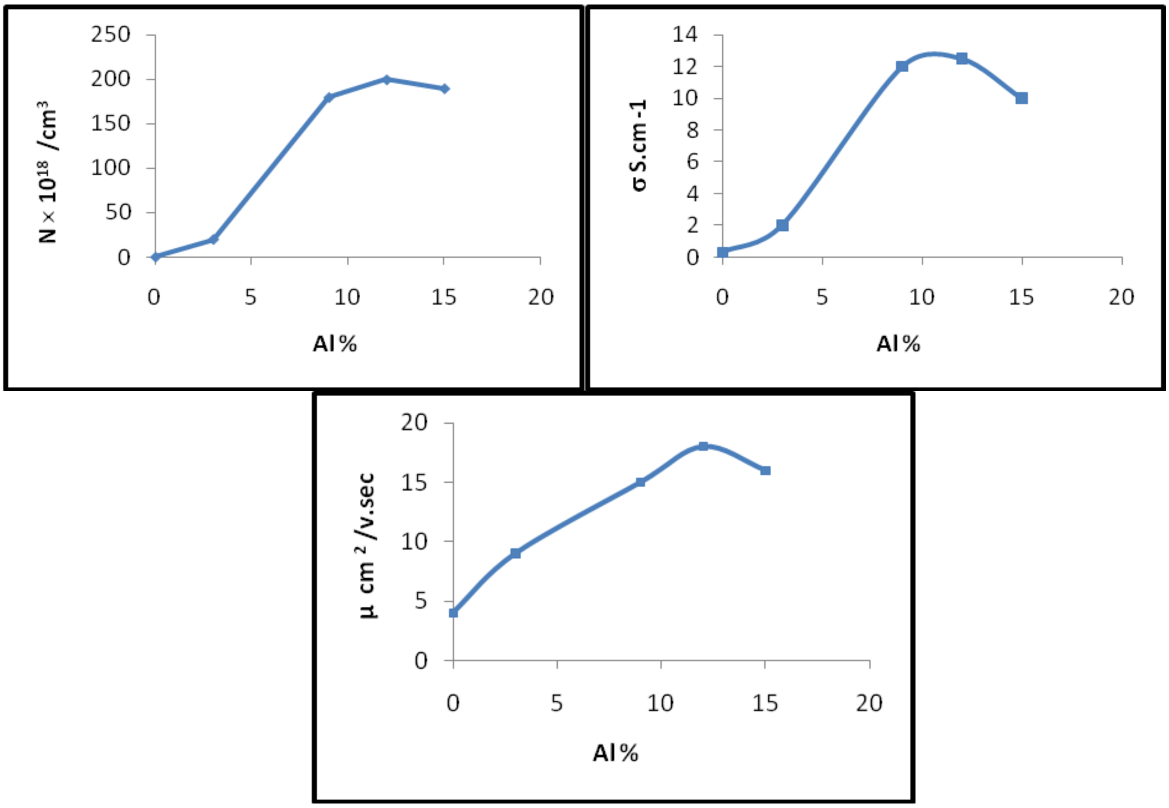


Fig.4: Carrier concentration N, conductivity σ and hall mobility μ as a function of Al concentration.

IV. CONCLUSIONS

From the obtained results following conclusions can be drawn:

1. The XRD results showed that the crystallinity of CdS thin films was improved with Al content and nanocrystalline films with about 43.467nm in diameter grain size obtained.
2. The structural and electrical properties of CdS are found to be doped dependent.
3. The conductivity of CdS films was highly increased by Al doping and showed a maximum values at 9% and 12%Al concentration, and it is noted that the conductivity is enhanced for the large scale of the grains of the thin films.
4. Activation energy studies support the increase in the conductivity due to improvement in crystallinity of the films which would increase the charge carrier mobility and decrease in defect levels with increase in the Al content.

Conductivity type and the resistivity values of the films meet the requirements for application in electro-optic devices such as photoconducting cells.

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