

## The Effect of Al Doping on Structural, Electrical and Optical Properties of CdSe Films

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### ABSTRACT

CdSe thin films were deposited on glass substrates by chemical bath deposition technique. The deposited CdSe thin films were annealed by thermal evaporation for (1h) at 250 °C. The samples were then coated with a different thicknesses of thin Al films (50, 100, 150, 200) Å by thermal evaporation method which then annealed at (1h,250°C). The structural, optical, and electrical properties of deposited and doped samples were studied. The X-ray diffraction analysis showed that the films have polycrystalline structure of hexagonal type. From optical properties, the band gap energy of undoped CdSe thin film was 2 eV and it is decreased by increasing of Al doping. Electrical resistivity of the doped films showed a decrease with the increase of the Al concentration. The doped and undoped samples revealed that the conductivity was n-type.

**Keywords:** CdSe thin film, Al doping, optical properties, semiconductor

### تأثير تطعيم Al على الخواص التركيبية، الكهربائية والبصرية لأغشية CdSe

#### المخلص

تم ترسيب أغشية CdSe الرقيقة على أرضية من الزجاج باستخدام تقنية الترسيب بالحمام الكيميائي Chemical Bath Deposition (CBD). أغشية CdSe الرقيقة المرسبة تم تلدينها بالتبخير الحراري لمدة ساعة عند 250 °C. العينات تم تطعيمها بغشاء من الألمنيوم الرقيق وبأسمك مختلفة (50, 100, 150, 200) Å بطريقة التبخير الحراري وبعدها تم تلدينها عند (1h, 250°C). تم دراسة الخواص التركيبية، البصرية والكهربائية للنماذج المرسبة والمطعمة. من تحليل حيود الأشعة السينية تبين بان الأغشية تمتلك تركيباً متعدد البلورات من النوع السداسي (Hexagonal). ومن الخواص البصرية، وجد أن فجوة الطاقة لأغشية CdSe غير المطعمة 2 eV وإنها تقل مع زيادة التطعيم بالألمنيوم. المقاومة الكهربائية للأغشية المطعمة تبين أنها تقل مع زيادة تركيز Al. النماذج المطعمة وغير المطعمة أظهرت توصيلية من النوع السالب (n-type).

**الكلمات الدالة:** أغشية CdSe الرقيقة، تطعيم Al، الخواص البصرية، أشباه الموصلات.

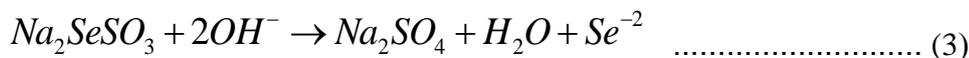
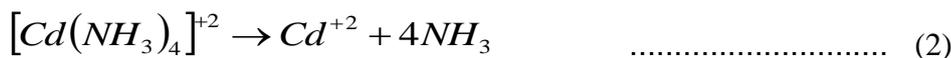
### INTRODUCTION

Cadmium Selenide is one of the II–VI semiconductor compounds. CdSe is an important material because of its optoelectronic properties in the visible range. It is used for the fabrication of solar cells, photo detectors, light emitting diodes, nanosensors, biomedical imaging devices and other photo electronic devices (Hendry *et al.*, 2006) (Schaller *et al.*, 2005). It has a direct band gap (2 eV) with high absorption coefficient near the band edge. CdSe thin films have been prepared by various film deposition techniques such as vacuum evaporation, sputtering, spray pyrolysis (Kalita *et al.*, 2003). Among them, chemical bath deposition (CBD) method (Nawfal *et al.*, 2014) is the most suitable one for thin film deposition because of its ability to deposit solid solutions without the aid of sophisticated instrumentation. CBC is also known as solution growth (Pathan *et al.*,

2002). The CBD is a slow process that works on the principle of ion by ion condensation in a solution state similar to the atom by atom deposition in a vacuum process (More *et al.*, 2003). The deposition parameters such as pH, temperature, concentration of the solution and deposition time influence the formation of thin films and crystallite size which in turn engineer the band gap of the material (Rai *et al.*, 1997). The optical and electronic properties of semiconductors are strongly influenced by the doping process, which provides the basis for tailoring desired carrier concentration and consequently, absorption, emission and transport properties (Haufe *et al.*, 1988). Doping is an efficient approach to monitor the electrical properties of semiconductors e. g. CdSe doped with various elements to obtain p-type CdSe or high carrier concentration of n-type CdSe such as CdSe: Sb (Masumdar *et al.*, 2002), CdSe doping with Er<sup>3+</sup> (Flores *et al.*, 2006), CdSe doping with indium (Perez Gonzalez and Arreola, 2009) and doping with Ni (Pawar *et al.*, 2012). In the present work CdSe thin films have been deposited on glass substrates by chemical bath method and then we demonstrated the effect of Al doping on the optical and electrical properties of CdSe films.

### EXPERIMENTAL

The substrate cleaning is very important in the deposition of thin films. Commercially available glass slides with a size of (7.5cm × 1 cm) were washed using soap solution and subsequently kept in hot chromic acid for 10 min. and then cleaned with distilled water to be rinsed neat acetone. For the deposition of CdSe thin films, Cadmium Chloride and Sodium selenosulphite were used as sources of Cd<sup>2+</sup> and Se<sup>2-</sup> ions respectively, while ammonia is used as a complex agent in the synthesis of CdSe thin films. For the preparation of Sodium seleno-sulphite (Na<sub>2</sub>SeSO<sub>3</sub>), mixture of 0.5 M of Na<sub>2</sub>SO<sub>3</sub> and 0.5 M of Se metal was added in 10 ml distilled water then heated in (2-4 h). Cadmium Chloride was dissolved in 10 ml distilled water and then added in 1 ml ammonia solution. After that glass substrates were kept in reaction mixture for 24 h at room temperature. Cadmium Selenide films were found to be homogenous with thickness of 0.6 μm, well adherent to the glass substrate and orange red in color. The deposition process is based on slow release of Cd<sup>2+</sup> and Se<sup>2-</sup> ions in the solution, which then condense ion by ion on the surface of the substrate. The deposition of CdSe occurs when the product of Cd<sup>2+</sup> and Se<sup>2-</sup> exceeds the solubility of CdSe. The preparation process is done according to the following reactions (Eya, 2006):



The deposited CdSe thin films were annealed in vacuum (10<sup>-6</sup> torr) for 1 h at 250 °C. After that the samples of CdSe are doped with Al layer with various thicknesses (50, 100, 150, 200 Å). The doped samples have also annealed in 1 h at 250 °C. The optical properties of the doped CdSe films and undoped were measured by using UV-VIS-NIR spectrophotometer in the range (320-1000 nm). The electrical resistivity of the doped and undoped CdSe thin films were also measured by four probe method. The type of charge carriers were known by using the Hall effect with magnetic field 600 G.

## RESULTS AND DISCUSSION

### Structural properties

#### X-ray diffraction:

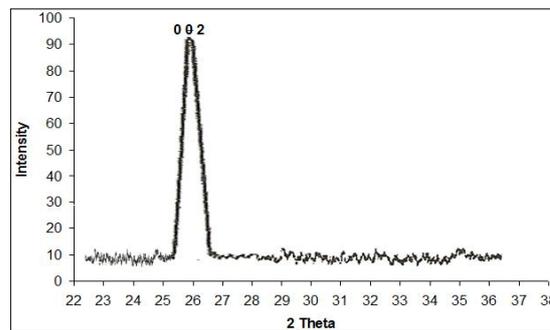
The structure of the deposited CdSe thin films was confirmed by ray diffractometer using CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) within the  $2\theta$  range  $22\text{--}38^\circ$ . The CdSe thin films were crystallized in wurtzite (hexagonal) structure at (002) plane with diffraction angle ( $2\theta=25.9^\circ$ ) and a preferential orientation [002]. The lattice plane distance  $d_{hkl}$  can be determined by XRD, using the Bragg's equation  $2d \sin \theta = n\lambda$ , where  $n$  is the diffraction order ( $n= 1$  in our case). In the hexagonal phase,  $d_{hkl}$  can be expressed as (Angerer *et al.*, 1997):

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \cdot \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \dots\dots\dots(5)$$

where  $hkl$  are the Miller indices of the lattice planes,  $a$  and  $c$  are the lattice parameters for the hexagonal structure. The obtained values  $a=4.316\text{\AA}$  and  $c=6.889\text{\AA}$  for CdSe, which coincide well with JCPDS data ( $a = 4.299 \text{ \AA}$ ,  $c = 7.010 \text{ \AA}$ ) are given in Table 1. Fig.1 shows the XRD pattern of as-deposited CdSe thin films on glass substrates by chemical bath deposition technique without annealing and without doping. It is clear from this fig. that there is no any further peak that indicates the presence of Cd or Se separated atoms in the deposited films.

**Table 1: XRD results of CdSe films and the parameters in JCPDS card**

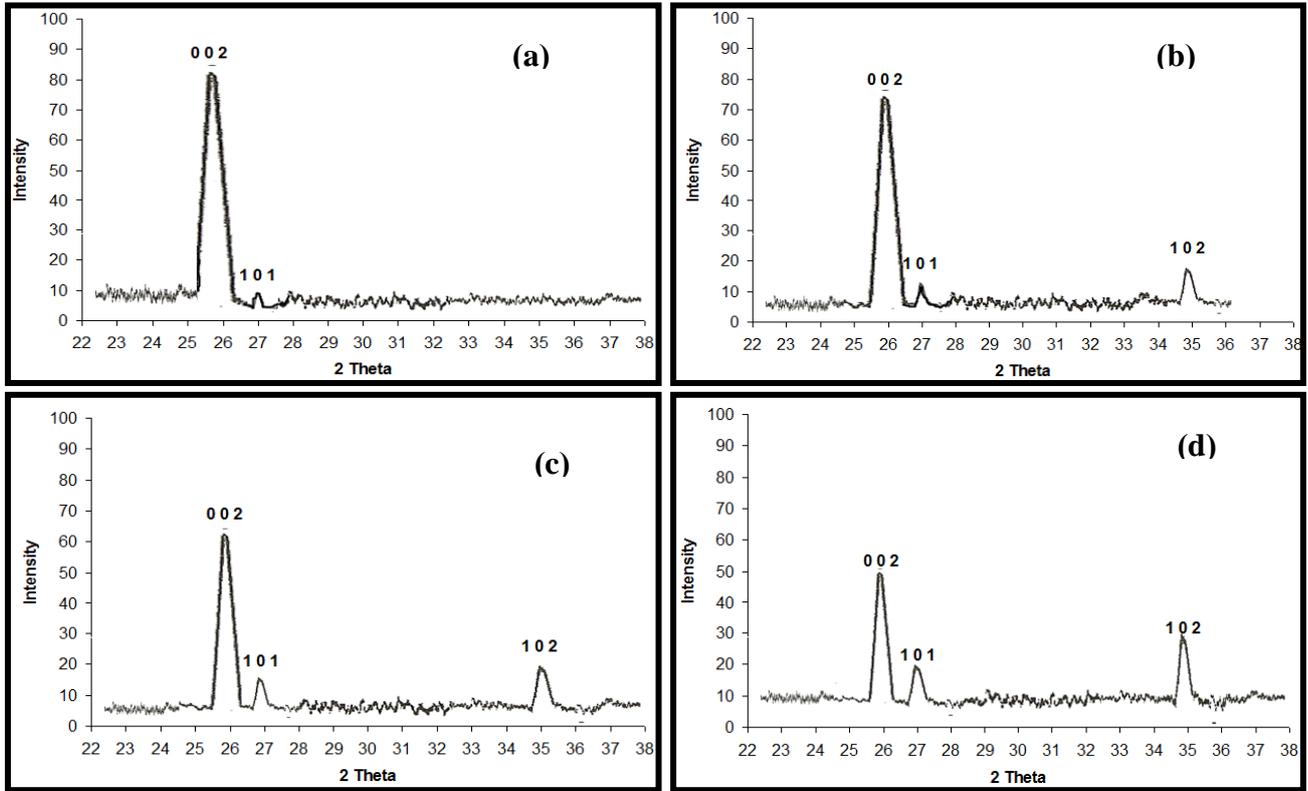
(1)&( 2) Data from fig $a = 4.316 \text{ \AA}$ $c = 6.889 \text{ \AA}$						Data from Jcpds card $a = 4.299 \text{ \AA}$ $c = 7.010 \text{ \AA}$
$t_{Al} (\text{\AA})$	Peak no.	$2\theta$ (deg.)	$d (\text{\AA})$	Hkl	D (nm)	$d (\text{\AA})$
0	1	25.9	3.44	(002)	28.4	3.51
50	1	25.7	3.46	(002)	31.6	3.51
	2	27.0	3.29	(101)	71.2	3.290
100,150,200	1	25.9	3.44	(002)	35.5, 40.6, 47.4	3.51
	2	27.0	3.29	(101)	95.0, 71.2, 57.0	3.290
	3	34.9	2.56	(102)	72.6, 48.4, 58.1	2.554



**Fig. 1: XRD pattern of as-deposited CdSe thin films by CBD technique without annealing and doping**

Fig. (2.a,b,c,d) shows the XRD pattern of CdSe thin films with various thicknesses (50,100,150,200  $\text{\AA}$ ). The X-ray diffractograms indicate the polycrystalline nature of the films. In all figs. the prominent peaks corresponding to (002) reflection of CdSe was observed at  $2\theta=25.9$  and was also observed a difference in the relative intensity of all peaks which indicate that the crystal

growth of grains is effected by the doping quantity in which the preferential orientation is also [002]. From the XRD pattern of doped film at 50Å ,we noticed that it has a high intensity at (002) plane and appears with low intensity at (101) plane. A depression in plane intensity (002) and height in two plane intensity (101) and (102) with increasing of doping quantity was also observed.

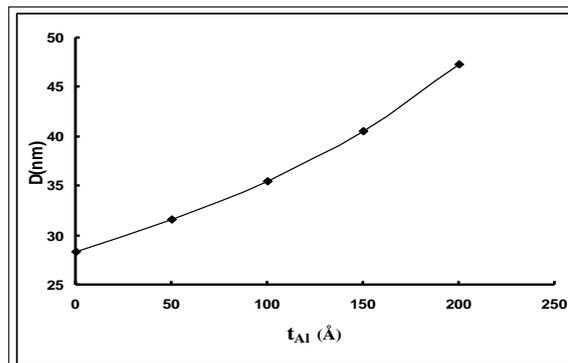


**Fig. 2: XRD pattern of CdSe thin films doped with thicknesses a =50 Å, b= 100 Å, c= 150 Å and d = 200 Å**

Fig. 3 shows that the variation of grain size with increasing of Al doping quantity at (002) plane; it can be deduced that the doping with Al layer causes a broadening of the (002) CdSe peak and, consequently, a decrease of the FWHM; therefore, the average grain size D of the doping CdSe films is increased in the direction (002) which was expected due to fill the vacancies by Al atoms which in turn due to Cd and also decreasing the dislocation defects. This leads to the increase of the grains size. The grain size was evaluated using Scherer formula (Zahug, 1996):

$$D = \frac{0.9\lambda}{\beta \cos \theta} \dots\dots\dots(6)$$

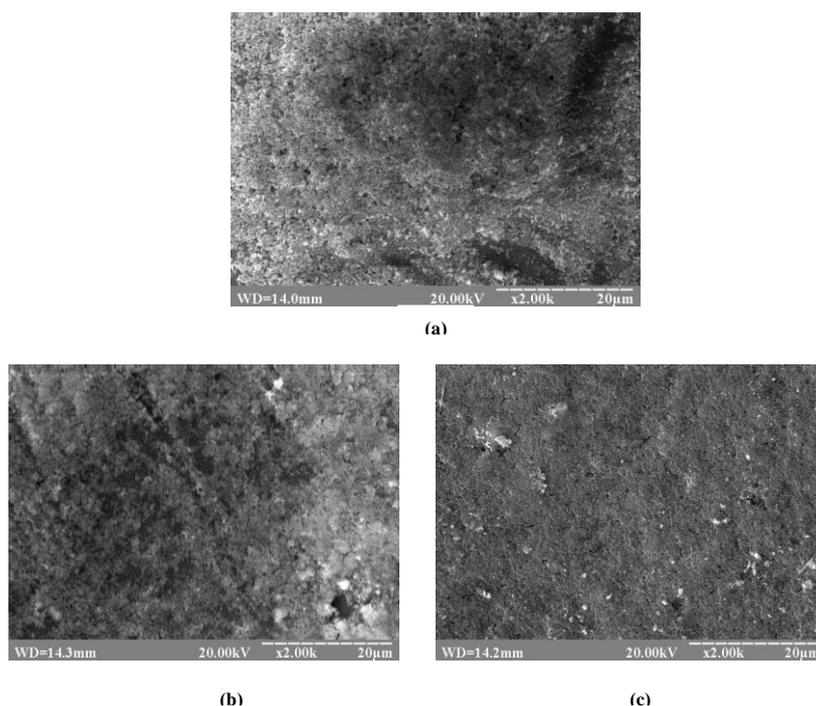
where  $\lambda$  is the wavelength of X-ray used (Å ),  $\beta$  is the angular peak width at half maximum in radian and  $\theta$  is the Bragg’s diffraction angle.



**Fig. 3: Variation of grain size with Al doping at (002) plane**

Similar type of conclusion can be drawn from the study of scanning electron micrographs, shown in Fig.4. Fig.(4a) shows CdSe film without annealing and doping which shows that the presence of non homogeneous grains that are densely packed and having different sizes. In Fig. (4 b, c) we observed the doped sample at 50 Å that shows better homogeneous structure more than that from Fig.(4a) and the presence of peaks due to the surface waves (because the surface is being rough). In the case of the doped sample at 200 Å, the film shows more crystalline behavior and without voids on the sample surface.

**Scanning Electron Microscope:**



**Fig. 4: SEM of (a) as-deposited (b) Al doped CdSe films 50 Å 200 Å (c) Al doped CdSe films 200 Å).**

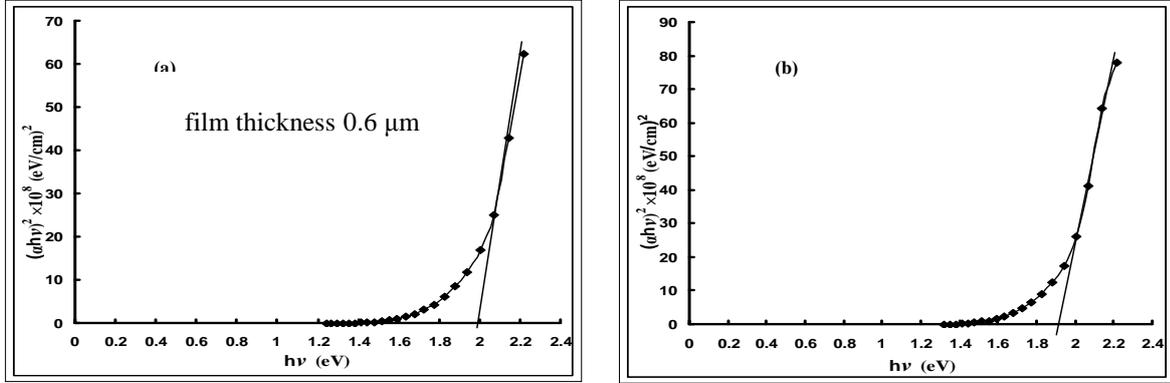
**Optical properties:**

The optical absorption measurement was made by using UV–VIS–NIR spectrophotometer in the wavelength range from 320 to 1000 nm. The absorption spectra was used to calculate absorption coefficient, optical band gap and type of transition. The simplest form of equations obeyed near and above absorption edge is (Grah, 1999):

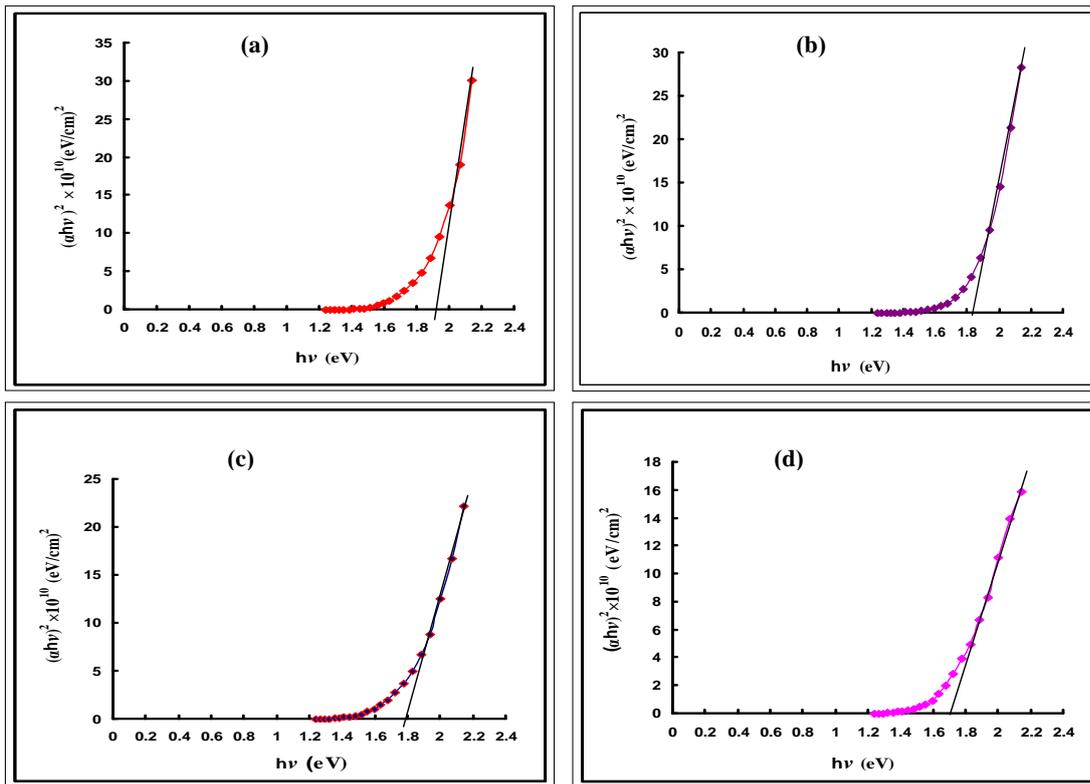
$$\alpha h\nu = A (h\nu - E_g)^n \dots\dots\dots(7)$$

The plot of  $(\alpha h\nu)^2$  versus  $h\nu$  should be a straight line whose intercept to the x-axis gives the optical band gap. The plot of  $(\alpha h\nu)^2$  versus  $h\nu$  is shown in Fig.5. The linear nature of plot shows the existence of direct transition. It is observed that the band gap decreases after annealing as shown in Fig. (5.b) due to the increase in grain size and decrease in crystalline defects. The absorption spectra of representative Al doped films are shown in Fig. 6. For all the compositions, the value of absorption coefficient is high. However, for higher level doping, a continuous decrease of gap occurs. The decrease can be, in general, correlated with the creation of new donor levels in

forbidden zone near to the conduction band. The value of band gap for sample with 200 Å of Al was found to be 1.7 eV as shown in Fig. (6.a,b,c,d).



**Fig. 5:  $(\alpha hv)^2$  versus  $h\nu$  of CdSe ( $0.6 \mu\text{m}$ )**  
**(a) as-deposited (b) annealing (1h,  $250^\circ\text{C}$ )**



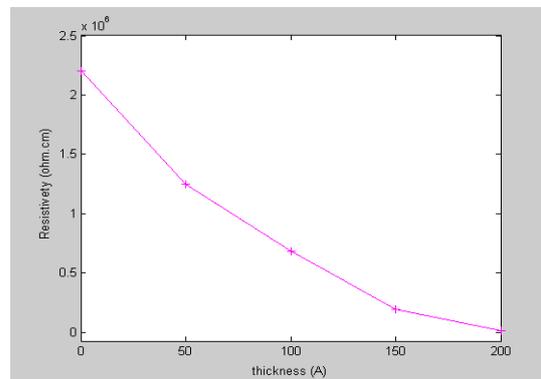
**Fig. 6: Absorption coefficient vs. photon energy of representative thin films with different thickness of Al (a) 50 Å, (b) 100 Å, (c) 150 Å and (d) 200 Å.**

**Electrical Properties:**

The measurements of electrical resistivity and conductivity of the same samples were conducted using a standard four-point probe method. The electrical resistivity,  $\rho$ , is determined by loading a direct current,  $I$ , through the outer pair of probes and measuring the voltage drop,  $V$ , between the inner pair of probes which are positioned at a distance of  $s = 2 \text{ mm}$ , using the following equation (Smits, 1958):

$$\rho_m = 2\pi s \frac{V}{I} \dots\dots\dots(8)$$

The electrical resistivity of the thin films is  $2.24 \times 10^6 \Omega \cdot \text{cm}$  at room temperature. The high value of the room temperature resistivity can be attributed to the small thickness of the films, crystallite boundary discontinuities and presence of surface states which agree with other studies (Kale and Lokhande, 2004). Fig. 7 shows that the resistivity of the samples decreases to  $0.96 \times 10^4 \Omega \cdot \text{cm}$  with the increase in Al doping, which is the indication of typical semiconductor characteristics. This may due to the increase in the charge carrier concentration as shown in Fig. 8 and table 3, similar observation has been made by (Santhosh *et al.*, 2017). And due to the increase in crystallite size of the samples and the presence of other growth orientation as shown from XRD measurements. This behavior may also be attributed to Al atoms filling the voids in the crystal structure of CdSe films at growth, This result is in good agreement with (Perna *et al.*, 2003). The results are shown in table 2.

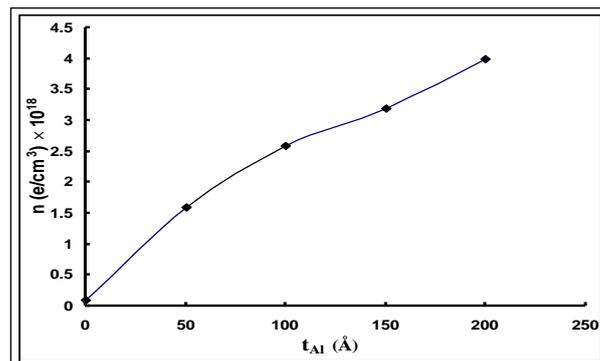


**Fig. 7 : Variation of electrical resistivity with thickness of CdSe films**

**Table 2: Electrical measurements results of CdSe films**

$t_{Al}$ (Å)	Resistivity $\rho_m$ ( $\Omega \cdot \text{cm}$ )
0	$2.24 \times 10^6$
50	$1.25 \times 10^6$
100	$6.80 \times 10^5$
150	$1.90 \times 10^5$
200	$0.96 \times 10^4$

By using the Hall effect, results indicated that the doped and undoped CdSe films have n-type conductivity. This means that the charge carriers are electrons. Fig. 8 shows that the variation of electrons concentration with thickness of CdSe films and the results shown in Table 3.



**Fig. 8: Variation of electrons concentration with thickness of CdSe films.****Table 3: Hall effect results of CdSe thin films.**

$t_{Al}$ (Å)	Electrons concentration (n) $e/cm^3$
0	$1.1 \times 10^{17}$
50	$1.6 \times 10^{18}$
100	$2.6 \times 10^{18}$
150	$3.2 \times 10^{18}$
200	$4.0 \times 10^{18}$

### CONCLUSION

In this work, it is concluded that the CdSe thin films are deposited by using chemical bath deposition method. The films grow highly oriented in the hexagonal phase and the growth preferential orientation is [002]. The grain size of (002) plane was found to increase when the Al concentration is increased. The absorption study shows the presence of direct band gap. The band gap decreases from 2 to 1.7 eV as the doping concentration increases. The electrical resistivity at room temperature for all the films was found to be in the order of  $10^6 \Omega \cdot cm$  which decreases with increasing Al concentration. All the films exhibited n-type conductivity by using the hall effect.

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