

## Optical and Structure properties of heavily Al-doped CdS Films

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### Abstract

Pure and heavy doped Cadmium sulfide thin films have been prepared using thermally evaporation on glass substrate at room temperature(R.T). CdS was doped by Al metal according to the weight ratio (CdS:Al=10:1,10:2). Crystalline structure of thin films that annealed at different temperature for 1h was zincblende (ZB) structure with lattice parameter about 5.84Å. The preferred orientation of pure and doped CdS (CdS:Al=10:1) is (111) plane. Most of these films have transparency over 80% in the visible spectrum. Aluminium doping into CdS films improved the optical transmittance in the visible region of light and increased the optical band gap from 2.38eV to 2.55eV.

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### 1.Introduction

The research on CdS thin films are important due to its applications in sensors, optoelectronic devices and, mainly, in solar cells(B.K.Maremadi et.al.1997, M.K. Kobayashi et.al.2000,J.Britt et.al.1993).

In the low-cost CdTe based solar cells, a transparent conducting CdS thin film is used as CdTe partner for formation of heterojunction(G.G.Rusu et.al.2005).

For solar cells applications,CdS films need to have a suitable conductivity ( $> 10^{16}$  carriers / cm<sup>3</sup>), and adequate

thickness to allow high transmission and good uniformity to avoid electrical short-circuit effects (J.Lee2005).

The deposition of CdS films has been explored by different techniques such as: thermal evaporation (A.Ashour et.al.1995, S.A.Mahmoud et.al. 2000), chemical bath deposition (CBD)(A.I.Oliva et.al.2001), molecular beam epitaxy (MBE) (Ph. Hoffmann et.al.1993) , spray pyrolysis (I.K.Battisha et.al.2002), electrodeposition (S.K.Das1993,T.Edamura et.al.1993) and laser ablation(N.M.Dushkina et.al.2000).

Cadmium sulfide is an n-type direct gap semiconductor at room temperature with band gap energy of 2.42eV and it's thin film solar cell has been considered for several years to be a promising alternative to the more widely used silicon devices(J.H.Lee et.al.2003).

Low resistivity CdS films are needed in heterojunction solar cells to lower the cell resistance, to confine the band bending to the narrow band gap material and to minimize the conduction band-Fermi level energy gap(W.J.Danaher et.al.1985).Efforts have been made to increase CdS film conductivity and the optical band gap by doping with indium and Boron(J.Lee et.al.2003 and F.Atay et.al.2003).

In the present study ,structured and optical properties of pure and Al-doped CdS thin films prepared by thermal evaporation method were studied.

## 2.Experimental

The pure and heavy doped CdS thin films (with a thickness of 4-6  $\mu m$ ) were prepared on glass substrate (2.5cm $\times$ 7.5cm) at room temperature by thermal vacuum evaporation method at  $10^{-5}$  torr .

CdS compound were mixed with Al metal according to the weight ratio (CdS:Al=10:1 and CdS:Al=10:2),the Aluminum powder mixed with cadmium sulfide in a gate mortar and grinding well. The pure and doped CdS compound (with above two weight ratio) evaporated on glass substrate at room Temperature to obtain thin films.

The obtained samples were annealed at different temperatures( $T_a$ ,373-573K) for 1h in a vacuum up to  $10^{-2}$  torr as illustrated in table(1) to improve the crystal structure .

The crystalline structure of the films was investigated by standard X-ray diffraction (XRD) technique, using  $Cu_{K\alpha}$  radiation ( $\lambda = 1.54\text{\AA}$ ).

For optical studies, Absorbance, A, and transmittance, T,in the vicinity of fundamental absorption edge were recorded using a (Helios  $\alpha$  thermo spectronic) spectrophotometer covering the range from(200-900)nm.

## 3.Results and discussion

### XRD measurements

The (XRD) patterns of pure CdS thin films which annealed at different temperature ( $T_a$ ) were shown in Fig.1 and we noticed

highly oriented peak corresponding to the (111) interplaner distance (d) of the cubic zincblende (ZB) crystalline phase (R.L.Morales et.al.2004, T.D.Dzhafarov et.al.1999, R.Traill et.al.1955).

Fig.2 shows the (XRD) patterns of heavy doped CdS film by Al according to the ratio CdS:Al=10:1, the major peak, (111) plane, could be attributed to CdS film (R.L.Morales et. al.2004, T.D.Dzhafarov et. al.1999 and R.Traill et. al.1955) with a small volume fraction of Cd-phase, but in the CdS films doped with Al by ratio CdS:Al=10:2, the structure was change from zincblende to amorphous even after the annealing on these samples, that is may be due to reaction of Al with CdS or the smallest grain size.

The inter-planer spacing ( $d_{hkl}$ ) was calculated for all planes using the Bragg's condition (C.Kittel, 1986):

$$2d_{hkl} \sin \theta = n\lambda \quad (1)$$

where  $\lambda$ : wavelength, d: lattice spacing, n: order number,  $\theta$ : Bragg's angle.

From the  $d_{hkl}$  values of each planes, lattice parameter (a) are calculated by using the relation (B.D.Cullity, 1967):

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (2)$$

where h, k, l are Miller indices.

The grain size (D) was calculated from Debye Scherrer's formula (B.D.Cullity, 1967):

$$D = \frac{0.9\lambda}{B \cos \theta} \quad (3)$$

where B is the full-width at half-maximum (FWHM) of the peaks.

Table (2) illustrates the lattice parameter and grain size of pure and doped CdS films, while fig.(3) shows the grain size as function of annealing temperature for pure and Al doped CdS films, in general, the grain size for doped films are greater than that for pure one. This behavior can only be related to the incorporation of Al into the lattice. The smaller ionic radius of  $Al^{3+}$  ( $0.51 \text{ \AA}$ ) as compared with that of  $Cd^{2+}$  ( $1.02 \text{ \AA}$ ), can be the cause for the decreasing of the grain size, this can only happen if Al-ions enter substitutionally in Cd sites which occur in some other cation-doping-CdS cases (J.A.Davila 2006). The change of structure from (ZB) structures to a morphous, in this case the Al may be enter in both substitutionally and interstitially or it is probable the Al impurities originate a lot of disorder in the CdS lattice in such a way that the lattice could be shrunken (J.A.Davila 2006).

The grain size of pure and Al-doped CdS films with a weight ratio (CdS:Al=10:2)

is increasing as the annealing temperature increases as it is shown in fig.(3),except the CdS film which is annealed at 473K and Al-doped film that annealed at 373K ,where the grain size is lesser than the other films ,that is due to the smallest of these thickness ( $2\mu m$ ) comparison with other films ( $4\mu m$ ) (S.J.Ikhmayies et al.2008).

The lattice parameter values,5.75-5.84Å, agree on a qualitative level with that obtained by (J.Vazquez et al.1999 and J.Conde et al.2003).

### Optical properties

The optical transmission spectrum as a function of wavelength for CdS,CdS:Al=10:1 and 10:2 films annealed at different temperature are shown in fig.(4),fig.(5) and fig.(6) respectively.

The direct band gap ( $E_g$ ) for pure and doped CdS films was determined by analyzing the optical absorbance ( $\alpha$ ) and the photon energy ( $h\nu$ ) using the relation(A.Ashour,2003):

$$\alpha = \alpha_0 (h\nu - E_g)^{1/2} / h\nu \quad (4)$$

where  $\alpha_0$  is a constant depended on the probability of transition.

Fig.7,fig.8 and fig.9 are a sketch of an absorption coefficient ( $\alpha$ ) with ( $h\nu$ ),it can

be seen the absorption coefficient of all samples (pure and doped CdS) are multiply by ( $10^4$ ),so the optical band gap is direct before and after doping by Al-metal.

As we shown in fig.10,fig.11 and fig.12 the plot of  $(\alpha h\nu)^2$  versus ( $h\nu$ ) was analyzed by using equation 4,the intercept of the extrapolated straight linear portion with energy axis yields the direct band gap value.

It is clearly seen from this spectra, generally, that the absorption edge shifts towards the longer wavelength with increase in the doping concentration. This shift towards the longer wavelength indicates that the decrease of optical band gap ,the value of the optical band gap,  $E_g$ , is estimated by plotting  $(\alpha h\nu)^2$  as a function of ( $h\nu$ ), which decreases from 2.4eV for undoped film to 2.3eV for Al doped CdS by ratio (CdS:Al=10:2) at (R.T),slightly less than the energy band gap calculated for CdS:In thin films(2.4eV)(J.A.Davila 2006),table(3).

The sample C4 has energy band gap about 2.55eV,that indicates the improved optical properties,the tendency of  $E_g$  as a function of doping ratio is, in general ,a decreasing function, which is indicating the effects on the optical band gap of defects that occur by the introduction of Al in the CdS volume.

Generally, it was investigated that all films have direct band transition by plotting  $(\alpha h\nu)^2$  vs.  $(h\nu)$ , these properties make them very desirable window layers for photovoltaic thin film solar cell applications.

the energy band gap ( $E_g$ ) is increased with the increasing of annealing temperature as we shown in table(3). This range of energy band gap value is in a good agreement with the reported value by (J.Lee,2005).

#### 4. Conclusion

The effect of heavily Al-doped on the structure and optical properties of the CdS

thin films evaporated onto unheated substrates was investigated. Generally we have note a decreasing of energy band gap with the increase of Al ratio. The maximum value of energy band gap is (2.55eV) obtained for CdS:Al film doped by the ratio (10:2) and annealed at (573K). The change of structure from simple cubic for pure CdS to semi-amorphous when increase the doped ratio, so we concluded the crystallinities of CdS effected by the ratio of doping and all concentration of doping has a strong influence on structures and optical band gap.

**Table (1):CdS films grown under different conditions.**

Sample code	CdS:Al ratio	$T_a$ (K),1h
A1	Pure CdS	as deposited
A2		373
A3		473
A4		573
B1	10:1	as deposited
B2		373
B3		473
B4		573

C1	10:2	as deposited
C2		373
C3		473
C4		573

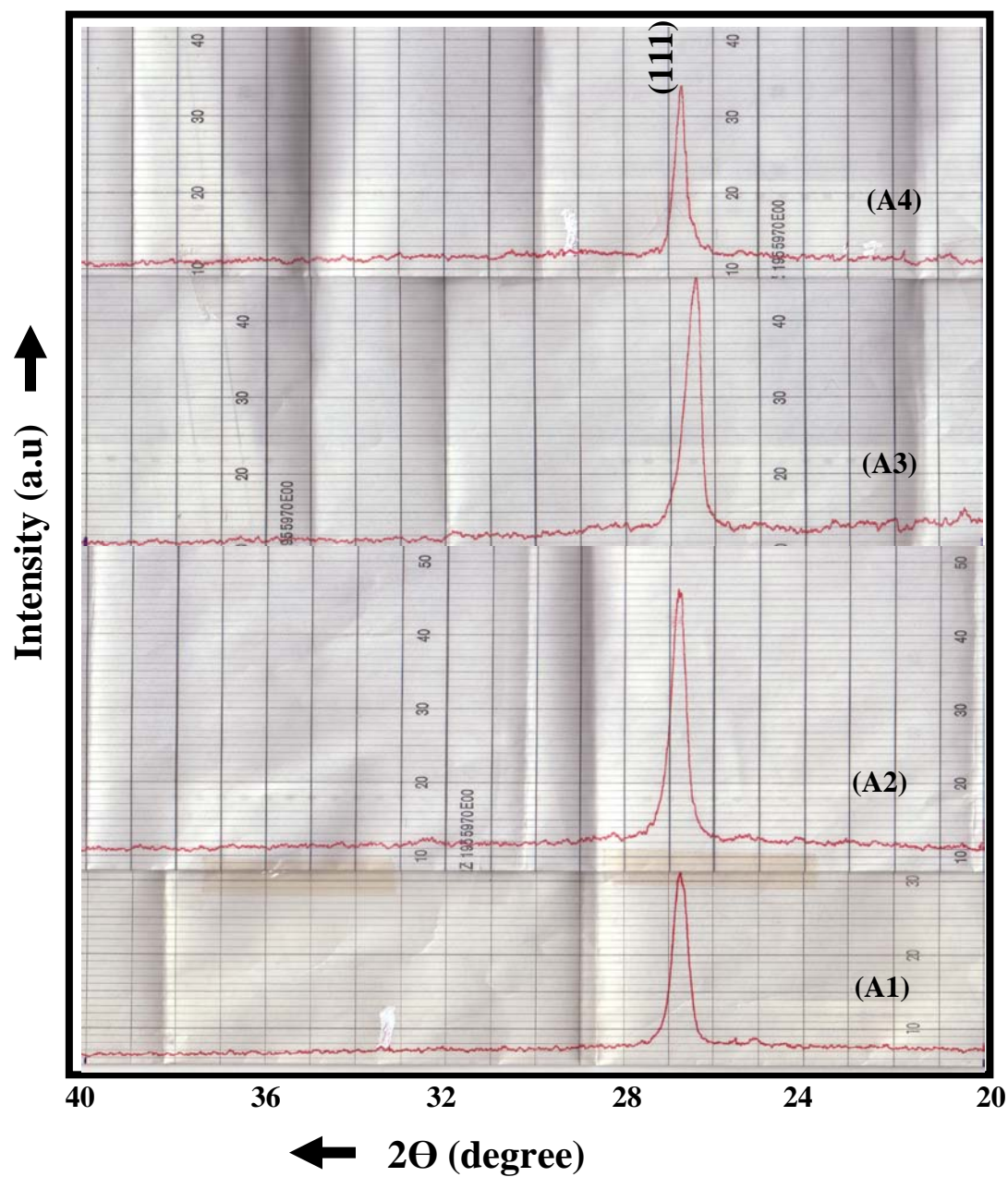
**Table (2):**lattice parameter and grain size of pure and doped CdS films.

<i>Sample code</i>	<i>a (Å)</i>	<i>D (Å)</i>	<i>Ref.</i>
<i>A1</i>	<i>5.75</i>	<i>386.49</i>	<i>Present work</i>
<i>A2</i>	<i>5.75</i>	<i>441.66</i>	<i>= =</i>
<i>A3</i>	<i>5.84</i>	<i>257.76</i>	<i>= =</i>
<i>A4</i>	<i>5.77</i>	<i>515.27</i>	<i>= =</i>
<i>B1</i>	<i>5.79</i>	<i>257.71</i>	<i>= =</i>
<i>B2</i>	<i>5.77</i>	<i>237.89</i>	<i>= =</i>
<i>B3</i>	<i>5.75</i>	<i>343.48</i>	<i>= =</i>
<i>B4</i>	<i>5.77</i>	<i>441.66</i>	<i>= =</i>
<i>C1</i>	-	-	<i>= =</i>
<i>C2</i>	-	-	<i>= =</i>
<i>C3</i>	-	-	<i>= =</i>
<i>C4</i>	-	-	<i>= =</i>
<i>CdS thin film</i>	<i>5.82</i>	<i>380</i>	<i>(J.G.Vazquez et.al.1999)</i>
<i>CdS:In thin film</i>	-	<i>364</i>	<i>(F.Atay et.al.2003)</i>

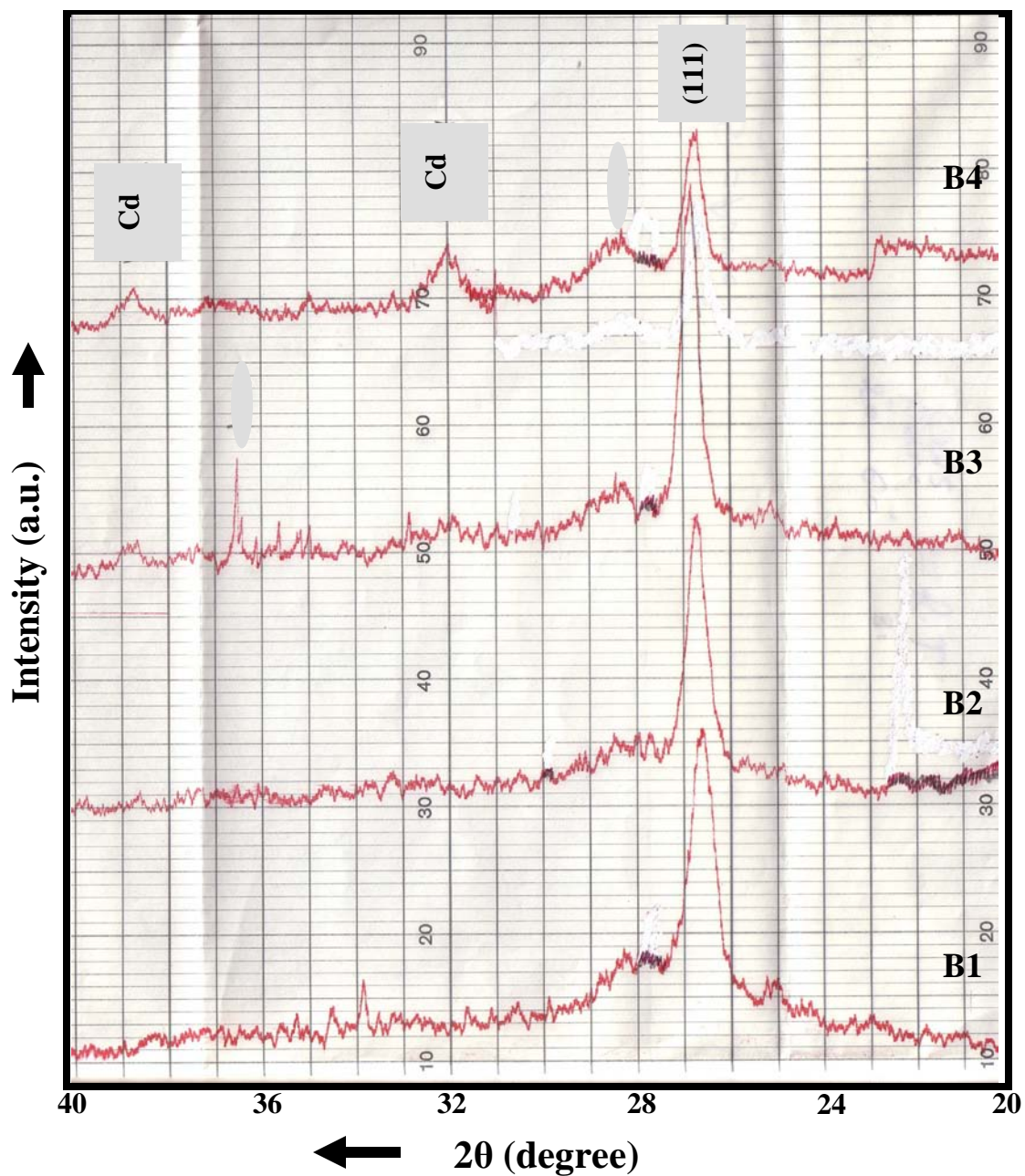
**Table (3):**Energy band gap of pure and doped CdS films.

<i>Sample code</i>	<i>E<sub>g</sub> (eV)</i>	<i>Ref.</i>
<i>A1</i>	<i>2.4</i>	<i>Present work</i>
<i>A2</i>	<i>2.38</i>	<i>= =</i>
<i>A3</i>	<i>2.4</i>	<i>= =</i>

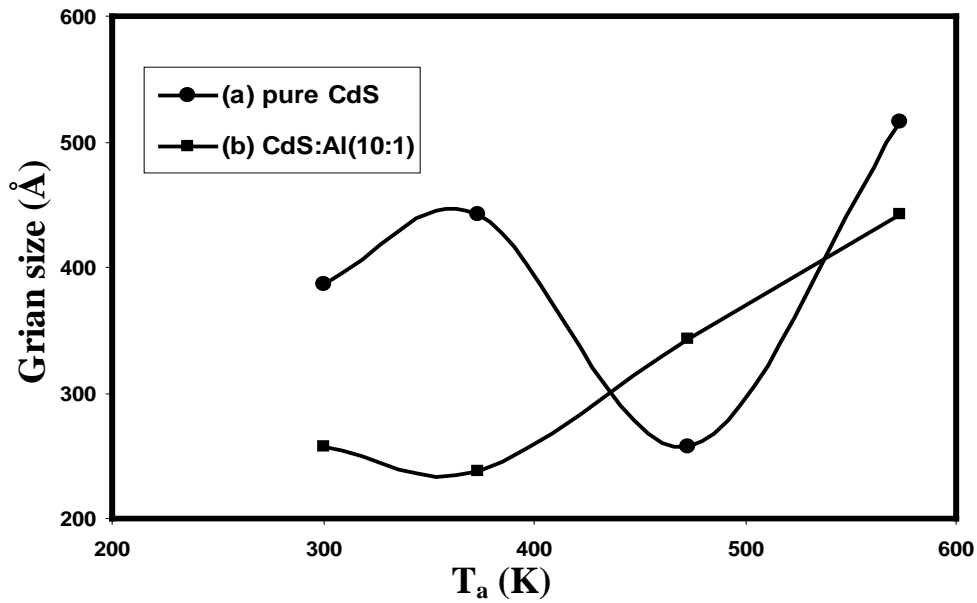
<b>A4</b>	<b>2.42</b>	<b>= =</b>
<b>B1</b>	<b>2.5</b>	<b>= =</b>
<b>B2</b>	<b>2.5</b>	<b>= =</b>
<b>B3</b>	<b>2.42</b>	<b>= =</b>
<b>B4</b>	<b>2.42</b>	<b>= =</b>
<b>C1</b>	<b>2.5</b>	<b>= =</b>
<b>C2</b>	<b>2.5</b>	<b>= =</b>
<b>C3</b>	<b>2.5</b>	<b>= =</b>
<b>C4</b>	<b>2.55</b>	<b>= =</b>
<b>CdS thin film</b>	<b>2.61</b>	<b>(R.Devi et.al.2007)</b>
<b>CdS thin film</b>	<b>2.53</b>	<b>(J.G.Vazquez et.al.1999)</b>
<b>CdS Thin film</b>	<b>2.45</b>	<b>(J.Lee,2005)</b>
<b>CdS:In Thin film</b>	<b>2.4</b>	<b>(J.A.Davila2006)</b>



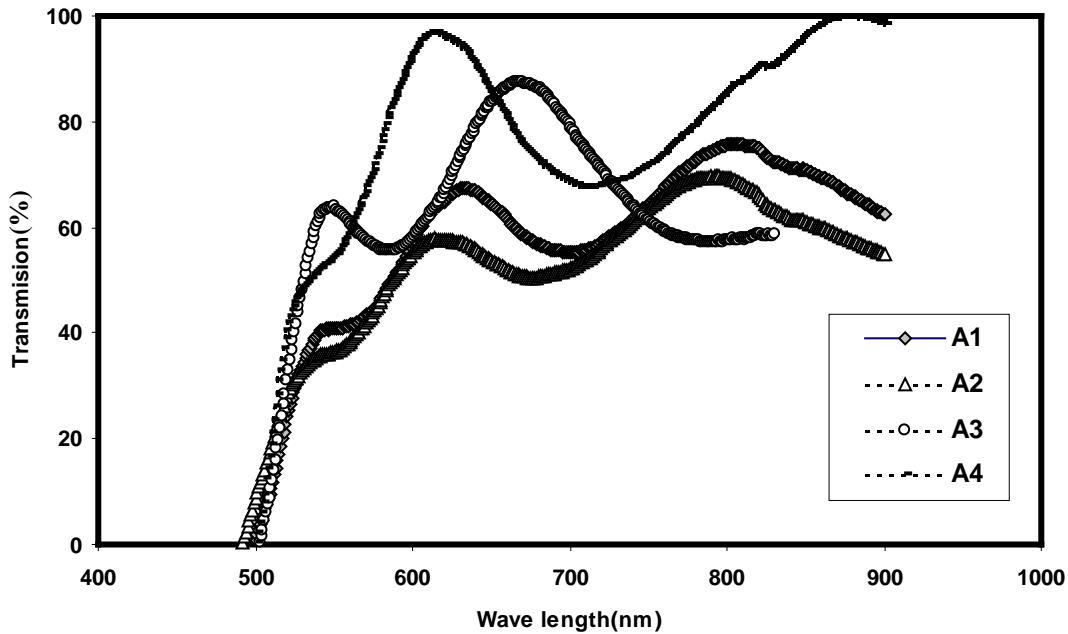
Figure(1):XRD pattern for pure CdS thin films annealed at different temperature for (1h),A1:as deposited, A2:373K, A3:473K, A4:573K.



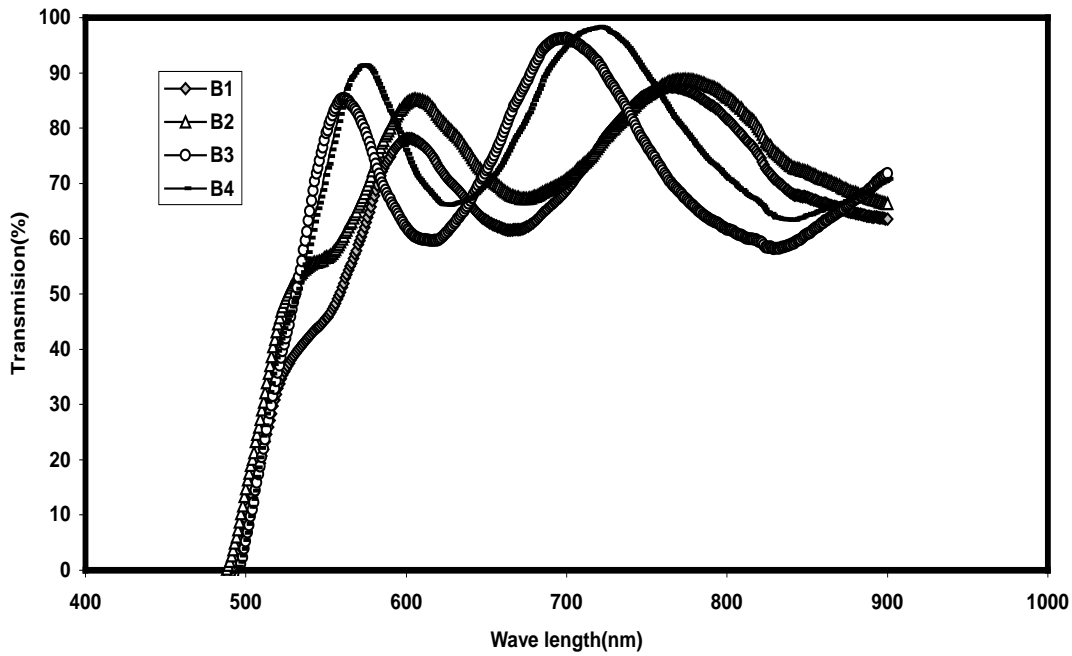
Figure(2):XRD pattern for CdS:Al (10:1) thin films annealed at different temperature for (1h),B1:as deposited, B2:373K, B3:473K, B4:573K.



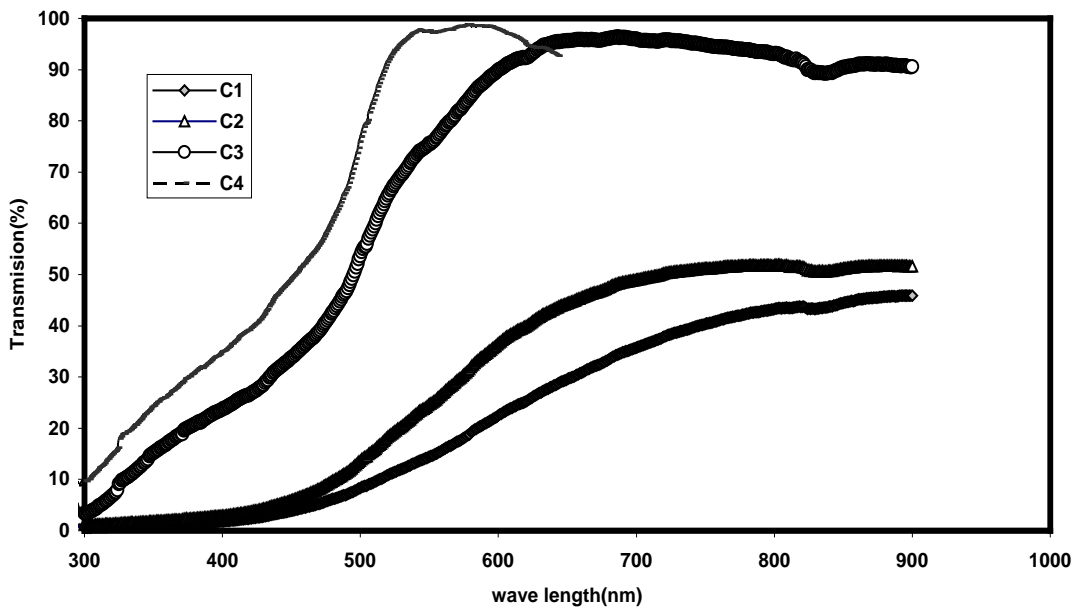
Figure(3):Grain size of (a) pure CdS (b)CdS:Al(10:1) thin films as a function of annealing temperature.



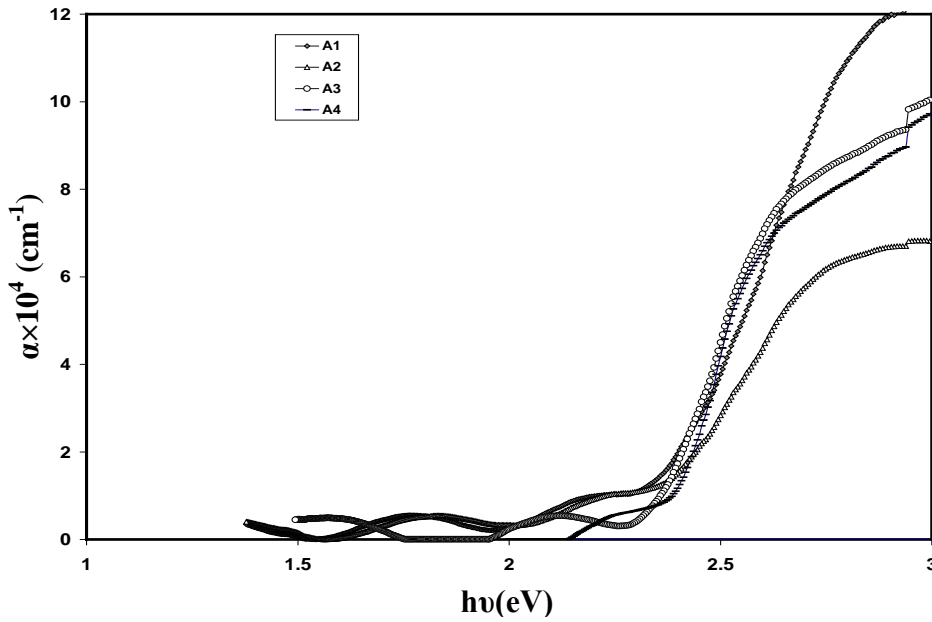
Figure(4):Transmission vs.wavelength for pure CdS films annealed at different temperature for 1h,A1:as deposited, A2:373K, A3:473K, A4:573K.



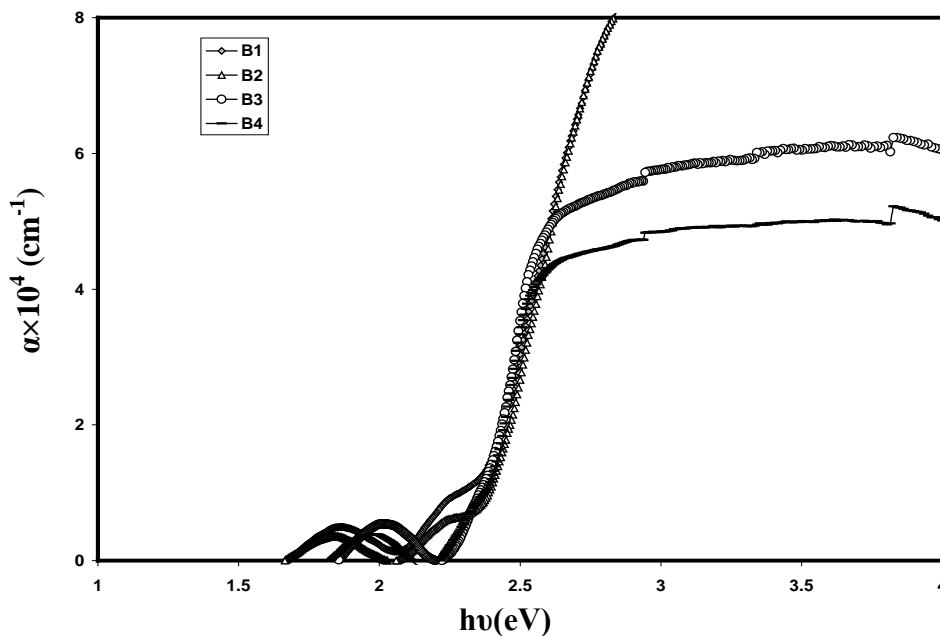
Figure(5):Transmission vs.wavelength for CdS:Al=10:1 films annealed at different temperature for 1h,B1:as deposited,B2:373K,B3:473K, B4:573K.



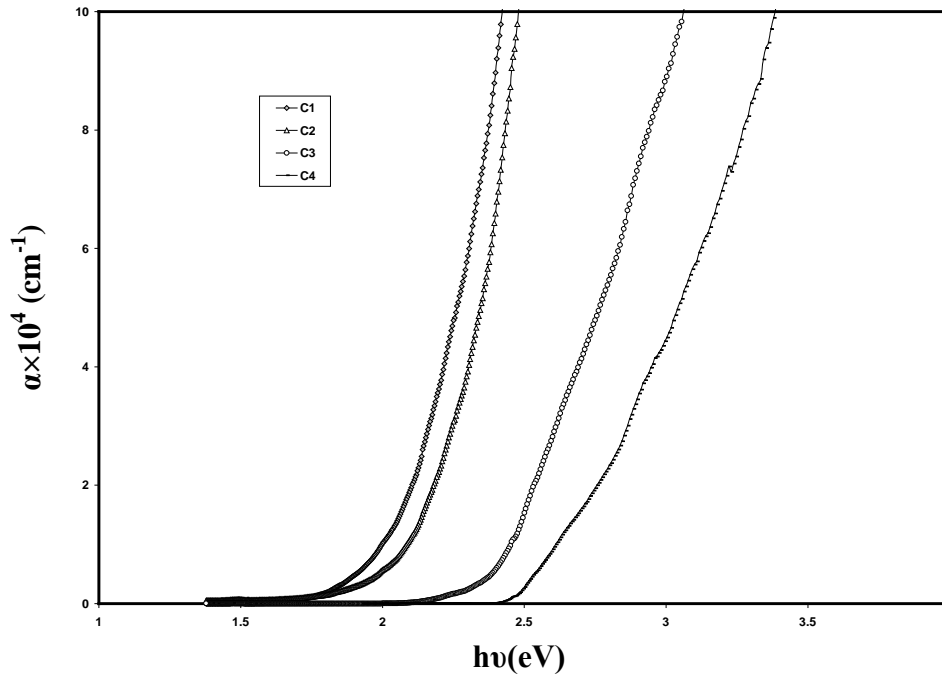
Figure(6):Transmission vs.wavelength for CdS:Al=10:2 films annealed at different temperature for 1h,C1:as deposited,C2:373K,C3:473K, C4:573K.



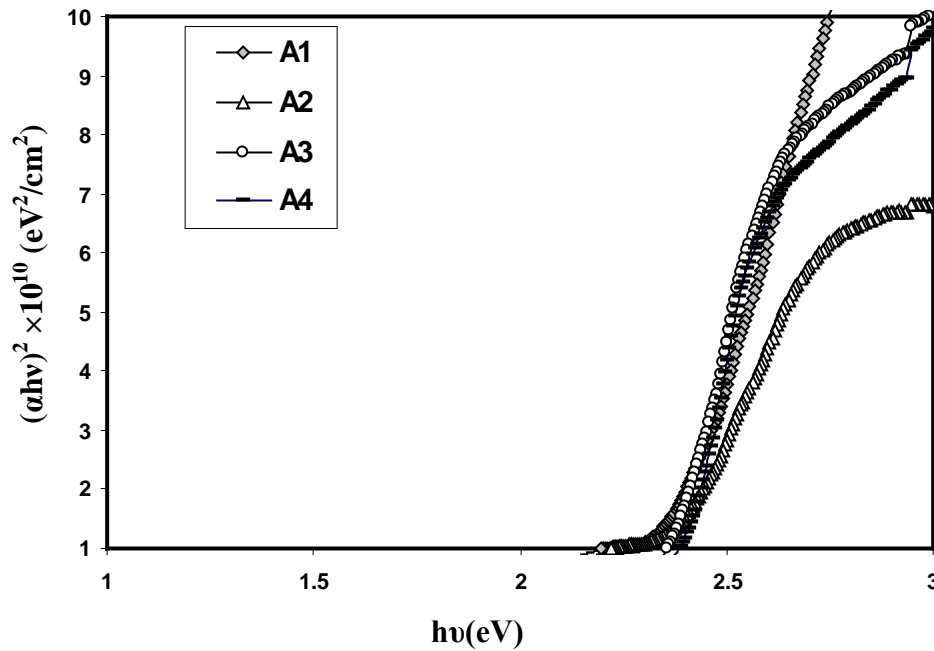
Figure(7):Variation of absorption coefficient( $\alpha$ ) with photon energy ( $h\nu$ ) for pure CdS films annealed at different temperature for 1h,A1:as deposited, A2:373K, A3:473K,A4:573K.



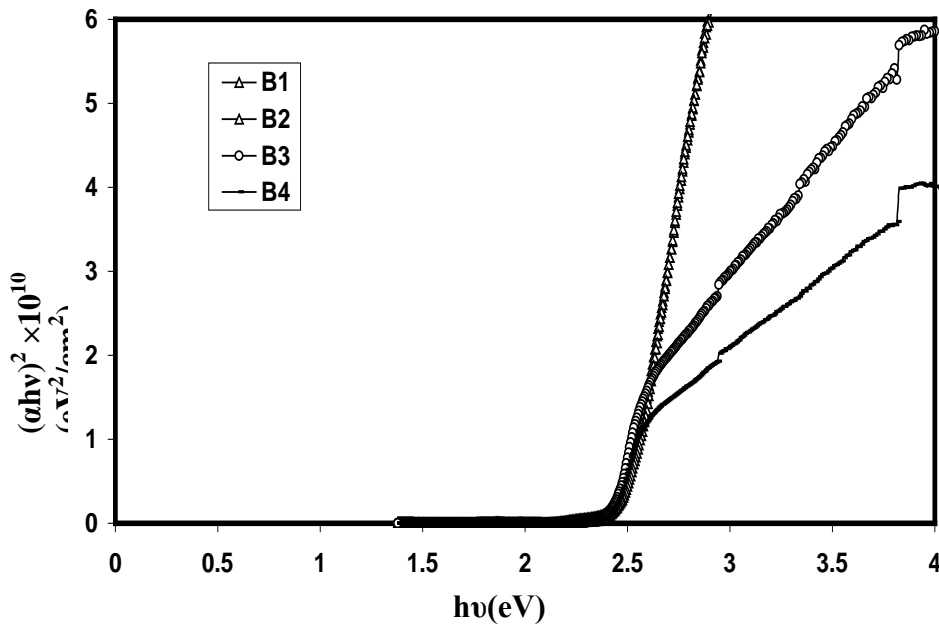
Figure(8):Variation of absorption coefficient ( $\alpha$ ) with photon energy ( $h\nu$ ) for Al-doped CdS films (10:1) annealed at different temperature for 1h,B1:as deposited, B2:373K, B3:473K,B4:573K.



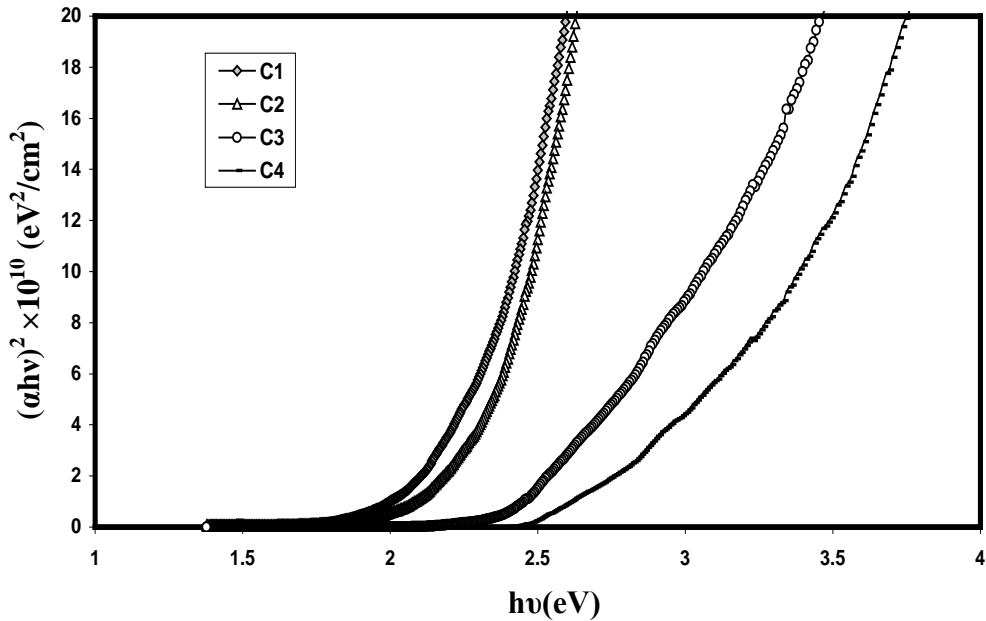
Figure(9):Variation of absorption coefficient( $\alpha$ ) with photon energy ( $h\nu$ ) for Al-doped CdS thin films (10:2) annealed at different temperature for 1h,C1:as deposited, C2:373K, C3:473K,C4:573K.



Figure(10):Variation of  $(\alpha h\nu)^2$  with photon energy ( $h\nu$ ) for pure CdS thin films annealed at different temperature for 1h,A1:as deposited, A2:373K, A3:473K,A4:573K.



Figure(11):Variation of  $(\alpha h\nu)^2$  with photon energy ( $h\nu$ ) for Al-doped CdS thin films (10:1) annealed at different temperature for 1h,B1:as deposited, B2:373K, B3:473K,B4:573K.



Figure(12):Variation of  $(\alpha h\nu)^2$  with photon energy ( $h\nu$ ) for Al-doped CdS thin films (10:2) annealed at different temperature for 1h,C1:as deposited, C2:373K, C3:473K,C4:573K.

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### المستخلص

حضرت اغشية رقيقة من المركب الثنائي CdS النقي والمشوبة بالالمنيوم بطريقة التبخير الحراري في الفراغ على قواعد من الزجاج في درجة حرارة الغرفة (R.T) وكانت النسبة الوزنية للتشويب هي (CdS:Al=10:1, 10:2). ان التركيب البلوري ل اغشية الرقيقة المحضرة من المركب CdS النقي والمشوب بالنسبة الوزنية (CdS:Al=10:1) والتي عوملت بدرجات حرارية مختلفة لمدة (1h) كانت على شكل مكعب zincblende (ZB)، يمتلك ثابت شبكية ( $a=5.84\text{\AA}$ ) وان الاتجاه المفضل للنمو هو للمستوي (111). ان معظم الاغشية تمتلك نفاذية اعلى من 80% في مدى الضوء المرئي وان تشويب المركب CdS بالالمنيوم قد حسن الخواص الضوئية للاغشية حيث ازدادت قيمة فجوة الطاقة من 2.38eV الى 2.55eV.