Correlation between Thickness, Grain Size and Optical Band Gap of CdI_2 Film

Modaffer A. Mohammed*

Received on:18/3/2008
Accepted on:22/1/2009

Abstract

Structural and optical property was studied as a function of film thickness for thermally evaporated CdI_2 films. Stoichiometric films (up to 250 nm thickness) showing hexagonal structure, and good c-axis alignment normal to glass substrate plane. The optical absorption data indicate an allowed direct inter – band transition near the absorption edge with optical energy gap varies continuously from 2.9 eV to 3.6 eV.Part of the optical data was fitted to an indirect type transition to determine the indirect optical energy gap which also varies continuously from 2.2 eV to 3.1 eV . Both energy gaps show thickness dependences, which can be explained qualitatively by a thickness dependence of the grain size through the decreasing of the grain boundary barrier height with grain size.

Keywords: CdI_2 thin films, Optical Band-Gap

الترابط بين السمك والحجم الحبيبي مع فجوة الطاقة البصرية لأغشية يوديد الكادميوم

الخلاصة

درست الخصائص البصرية والتركيبية كدالة لسمك أغشية يوديد الكادميوم المحضرة بالتبخير الحراري.أظهرت الأغشية المتوازنة كيماويا(لحد سمك250nm) تركيبا سداسيا وترصيف جيد في المحور(c-axis) العمودي على القواعد الزجاجية.بينت قيم الامتصاص البصري انتقالات مباشرة مسموحة بين الحزم قرب حافة الامتصاص وبفجوة طاقة بصرية متغيرة ما بين (2.9eV to 3.6eV). جزء من القيم البصرية كانت مطابقة للانتقالات غير المباشرة وبها حددت فجوة طاقة بصرية غير مباشرة متغيرة أيضا مابين(2.2eV to 3.1eV).أظهرت كلا فجوتي الطاقة اعتمادا على السمك,والذي يمكن تفسيره كميا بأعتماد الحجم الحبيبي على السمك من خلال تناقص ارتفاع حاجز الجهد عند الحدود البلورية مع الحجم الحبيبي.

1- Introduction

CdI_2 is an important compound having a layered structure with a hexagonal unit cell held with neighbring layers by Van derWaals forces, in which each hexagonal sheet of Cd atoms sandwich between two similar sheets of I atoms, the Cd atoms being octahedrally coordinated [1]. As many as 200 polytypes of CdI_2 material are recorded [2]. Recent studies have revived interest in cadmium iodide films [3-5].The optical absorption data fit best to direct band to band transition indicating a direct band gap, a smaller indirect band gap can also be near the absorption edge. The optical absorption measurement carried out on CdI_2 single crystal samples were fitted to an indirect energy gap of 3.2 eV while the reflectivity spectra reveal a direct transition at 3.8 eV.The band structure calculation show the presence of both direct and indirect band gaps, the difference between the two is only about 0.3-0.6 eV [6-11].

Material modification such as grain size, morphology etc, can be achieved by bombarding CdI_2 single crystals and thin films with laser radiation or highly kinetic ions (plasma), where CdI_2 crystals showed a linear variation of energy gap with intensity of laser radiation (0 to 125 mW) and decreasing in the energy gap value from (3.28 to 3.11 eV). The effect of plasma irra-

* Applied Sciences Department, University of Technology / Baghdad

diation on poly type (002) oriented CdI_2 stoichiometric film was found to change the orientation to (110), decre- ase in grain size and residual stress. The iodine - iodine distance in the unit cell could be responsible for the change in Eg with stress [12, 13]. The report on the structure of CdI_2 films show that thinner films (<100 nm) are amorphous and thicker films tend to crystallize[2-5], it is also known that CdI_2 films grown at substrate temperature less than 300 k are amorphous and these either grown or annealed above 300 k polycrystalline[14].

In this paper we tried to correlate the variation in the band gap of evaporated films with different thickness with the optical properties.

2- Experimental:

The CdI_2 films were grown on glass substrates at room temperature by th- ermal evaporation at a pressure better than 10^{-6} Torr (BALZERS BAE 080) using a molybdenum boat .The start- ing material was analar grade powder 99.999% pure stoichiometric material, which was pelletized for evaporation. Film thickness was measured after evaporation by optical interfero- meter method, using He-Ne Laser λ= 0.632 μm and the thickness were determined using the formula:

$$d = \frac{\Delta X}{X}\frac{l}{2} \qquad ....(1)$$

Where: x is fringe width, Δx is the distance between two fringes and λ is the wavelength of the laser light. Films up to 100 nm were completely transparent and become translucent for higher thicknesses .The films of thickness below 50 nm were nonuniform, and above 600 nm peel off from the substrate. To determine the nature of the growth and the structural characteristics of CdI_2 film, x-ray diffraction measurement has been done and compared with the ASTM cards, using (Philips PW-1840 X-ray diffractometer of λ= 1.54 Å from Cu-Kα). Optical transmission measured using a double beam spectrophotometer (Cecile CE 7200 spectrophotometer, by Aquarius Company).

3 Results and discussion

3-1 Structural Investigation:

The structural properties of the CdI_2 films were studied using XRD irrespective of the films thickness. The XRD result shows that the films are polycrystalline. Figure (1) shows diffraction spectrum scan over a rang of $10^o \leq 2\Theta \leq 50^o$,from which it is clear that our X-ray diffraction data is in agr- eement with ASTM No.(12-574).Table (1) summarize the calculated parameter- rs for XRD. The total absence of (001), (101),or(111) reflection, the high deg- ree of orientation with the basal plane parallel to substrate and c-axis normal to the substrate plan can be seen as indication of a good agreement with earlier study[15].However, another less intensity reflection plane(110) have been observed with 250 nm thick films.

This indicates a slight misalignment among the grains .We have determined the average grain size from the full width at half maximum (FWHM) of the most intense peak using the Scherre formula [16]:

$$GS = \frac{A\ l}{\Delta\ q\ \cos\ q} \qquad .... (2)$$

Where ΔΘ is the full width at half ma- ximum (FWHM) of XRD peak appear- ing at the diffraction angle Θ, A the shape factor depends on the crystalline shape, and generally it is 1. Fig. (2) shows the average grain size as a function of films thickness, from this curve we could conclude the following points:

a- For thickness less than 250 nm the thickness have no influence on grain size.

b- For thickness greater than 250 nm the grain size increased with a ratio of 0.13.

By comparing this result with these of Fig. (1) if is clear that such variation with grain size is due to the prwdomin- ated orientations. At thickness<250 nm both planes (002),(004) are in compot- ation and by increasing deposition time

(increasing thickness) the plane (002) become faster growth rate and become longer where as slower growth rate (004) are conserved.

3-2 Optical Properties

Optical transmition and absorption spectra of various thickness films were obtained and analyzed in wavelength from 350-900 nm at room temperature Fig.3 and Fig. 4. The absorption coefficient α was calculated by [17]:

$$a = 2.303 \frac{A}{t} \quad .....(3)$$

Where A is the absorbance and t the film thickness. The samples show a high absorption coefficient ($\alpha > 10^5$ cm^{-1} for $\lambda <$ 400 nm, 10^4 cm^{-1} for $\lambda > 400$ nm).

The dependence of α on hν near the band edge is shown in Fig.5. It is clear that the value of α increases with increasing photon energy. In a crystalline or Polycrystalline material both direct or indirect optical transition is possible depending on the band structure of the material.In general absorption coefficient is related to the photon energy by following equation [17]:

$$a hn = A(hn - E_g)^n \quad ..... (4)$$

Where A is constant depending on transition probability Eg is the band gap of the material and n has different values depending on the nature of the absorption process.

The usual method of determining energy gap is to plot a graph between $(\alpha h \nu)^{1/n}$ and hν and look for that value of n which gives best linear curve in the absorption edge region. Plotting $(\alpha h \nu)^{1/n}$ versus h ν for CdI_2 films of various thickness shows that the best fit was obtained for n =1/2, indicating a direct type of allowed transition as shown in Fig.6.The part of the optical absorption data near the tail of the direct absorption edge have to be replotted as $(\alpha h\nu)^{1/2}$ vs hν to determine indirect gap as shown in Fig.7.Table (2) summarizes the optical direct and indirect band gap, average grain size for CdI_2 films with different thickness. Our value of Eg(direct) of 3.6 eV determined for thicknesses ≤150nm agrees well with the predicted value of 3.8 eV from band structure calculation [9]. However, both type of band gaps showed thickness dependence as shown in table (2) which gives also the grain size.

In general, thickness dependence of band gap can a rise due to one or combined effect of (1) the change in barrier height due to change in grain size in polycrystalline films. (2) A large density of dislocation for thickness > 150 nm.

The decreasing of energy gaps with grain size for CdI_2 as shown in Fig.8. However, both energy gaps show thickness dependence as shown in Fig.9.

4. Conclusion

1. The optical absorption data indicate a direct type of inter-band transition near the absorption edge yielding a direct optical energy gap varies continuously from 2.9 eV to 3.6 eV.

2. Part of the optical data was fitted to an indirect type of transition to determine the indirect optical energy gap varies continuously from 2 eV to 3.1 eV.

3. The direct and indirect band gap of CdI_2 films decreasing with film thickness can be attributed to grain size dependent grain boundary barrier height, at least for film thickness > 150 nm.

4. The lattice parameter c of hexagonal structured CdI_2 films shows a wavy dependence on film thickness in the rang 150 – 600 nm, the films show c-axis alignment normal to substrate plan for film thickness up to about 250 nm.

References

[1]. Hulliger F, Levy F and Reidel D 1976 in structural chemistry of layer – type phases (Dordrecht, Holland: Ed. Publishing Company) pp 31 -34 and 275

[2]. G. C. Trigunayat; Solid State Ion. 48 (1991) 3.

[3]. P. Tyagi, A. G. Vedeshwar, N. C. Mehra, Physica B 304 (2001)166.

[4]. P.Tyagi, A. G. Vedeshwar; Bull. Mater. Sci. 24 (2001) 297.

[5]. P. Tyagi, A. G. Vedeshwar; Eur. Phys. J. AP 19 (2002) 3.

[6]. I. Pollini, J. Thomas, R. Coehoorn, C. Haas; Phys. Rev. B 33 (1986) 5747.

[7]. J. Bordas, J. Robertson, A. Jakobsson; J. Phys. C: Solid State Phys. 11 (1978) 2607.

[8]. J. Robertson; J. Phys. C: Solid State Phys. 12 (1979) 4753.

[9]. J. V. McCanny , R. H. Williams , R. B. Murray , P. C. Kemeny ; J. Phys. C : Solid State Phys. 10 (1977) 4255.

[10]. H. Nakagawa, T. Yamada, H. Matsumoto, T. Hayashi; J. of the Phys. Soc. of Jap. 56 (1987) 1185.

[11]. S. Kondo, H. Matsumoto; J. of the Phys. Soc. of Jap. 50 (1981) 3047.

[12]. A. Nayak , G. L. Bahlla , B. Kumar , G. C. Trignnyat ; Phys. Stat. Sol. (b) 213 (1999) 487 .

[13]. K. Sreelatha, C. Venugopal, S. K. Chaudhary, N. V. Unnikrishnan; Cryst Res. Technol. 34(1999) 897.

[14]. S. Konda, T. Suzuki, T. Saito; J. Phys. D 31(1998) 2733.

[15]. R. D. Bringans, W. Y. Liang; J. Phys. C 14(1981) 1065.

[16]. B .D. Cullity and S. R. Stock," Elements of X-ray Diffraction",Third edition Prentice-Hall in the United States of America, 2001.

[17]. N. F. Mott, E. A. Davis 1979 Electronic Processes in Noncrystalline materials (Oxford:Claren- don Press) P. 27.

Table (1) analysis of the XRD study of CdI_2 films

Thickness (nm)	d(Å) Observed	d (Å) ASTM	2θ degree	(hkl)	Average G.S.(nm)
150	6.77 3.46 2.30	6.84 3.42 2.28	13 25.7 39.2	(002) (004) (006)	110
250	6.75 3.475 2.30	6.84 3.42 2.28	13.1 25.6 39.1	(002) (004) (006)	113
450	6.828 3.42 3.233 2.284 2.119 2.024	6.84 3.42 3.24 2.28 2.122 2.024	12.95 25.97 27.55 39.4 42.6 44.7	(002) (004) (102) (006) (110) (112)	144
600	6.828 3.42 3.233 2.284 2.119	6.84 3.42 3.24 2.28 2.122	12.95 25.97 27.55 39.4 24.6	(002) (004) (102) (006) (110)	180

Table (2) direct and indirect optical band gap, average grain size of CdI_2 films of different thickness

Thickness (nm)	Eg(eV) direct	Eg(eV) indirect	Average G.S.(nm)
150	3.6	3.1	110
250	3.3	2.93	113
450	3.18	2.7	144
600	2.9	2.2	180

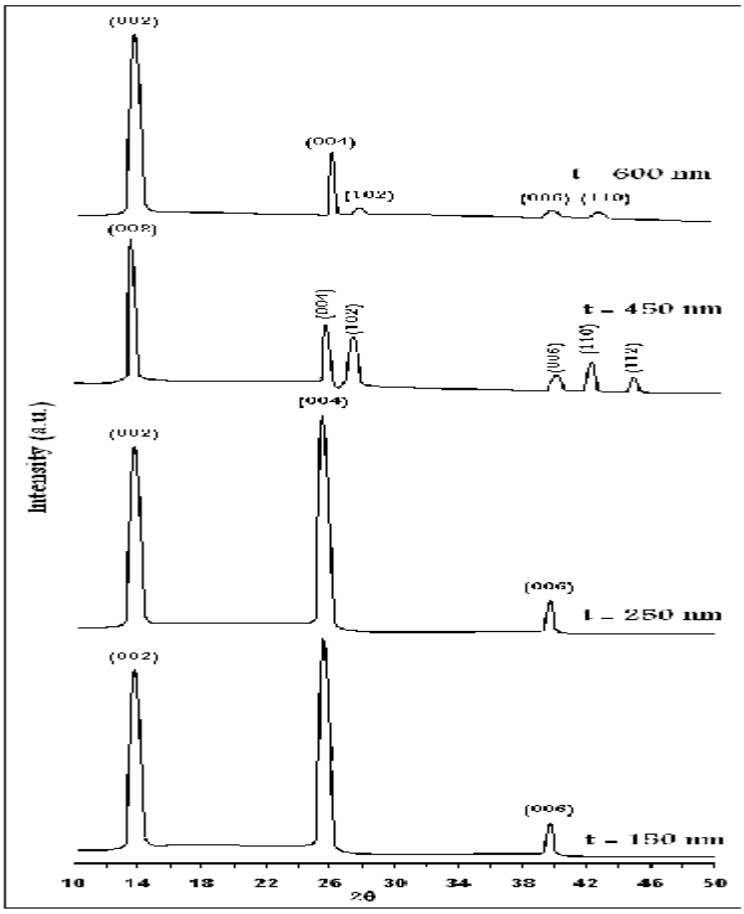

Figure 1: X-ray diffraction patterns and Miller indices of CdI_2 films prepared with different thickness.

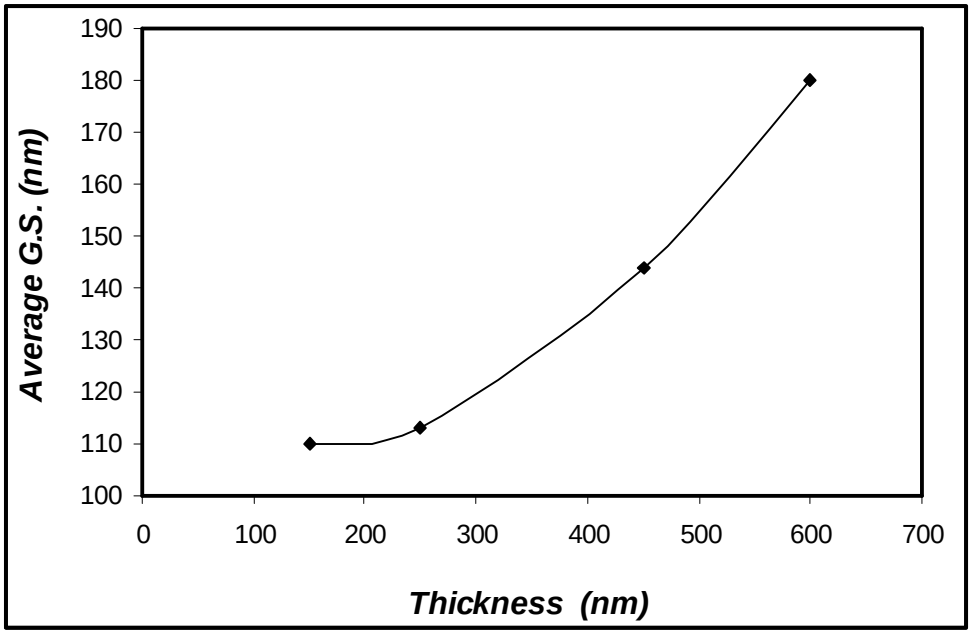

Figure 2: Variation of grain size with thickness of CdI_2 films.

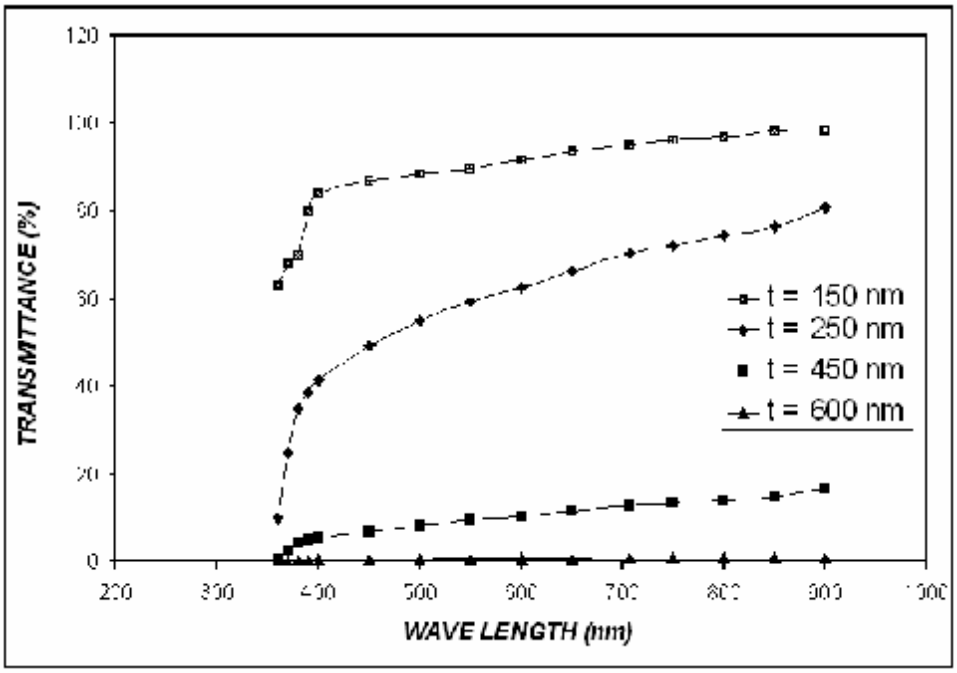

Figure 3: The optical transmission spectra for different thicknesses of CdI_2 films.

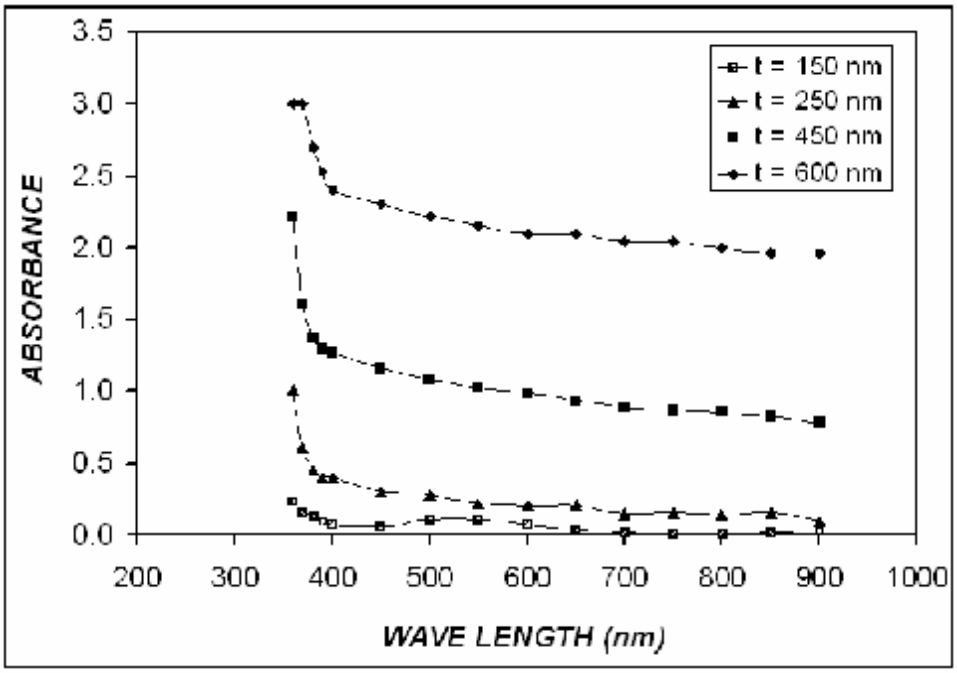

Figure 4: The optical absorption spectra of CdI_2 films of different thickness.

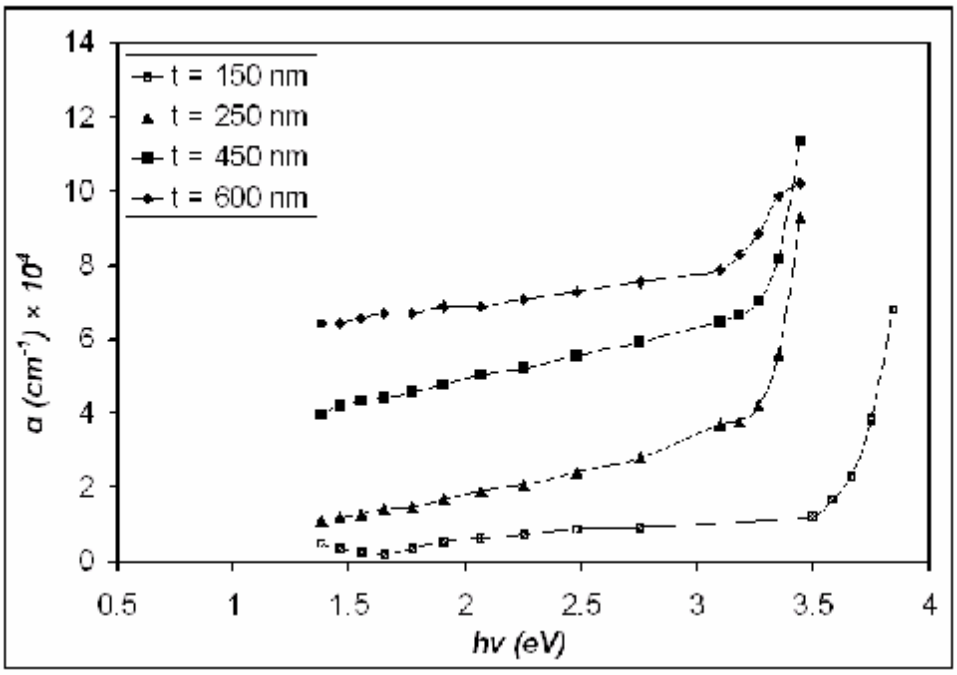

Figure 5: The absorption coefficient α as a function of hν for CdI_2 films with different thickness.

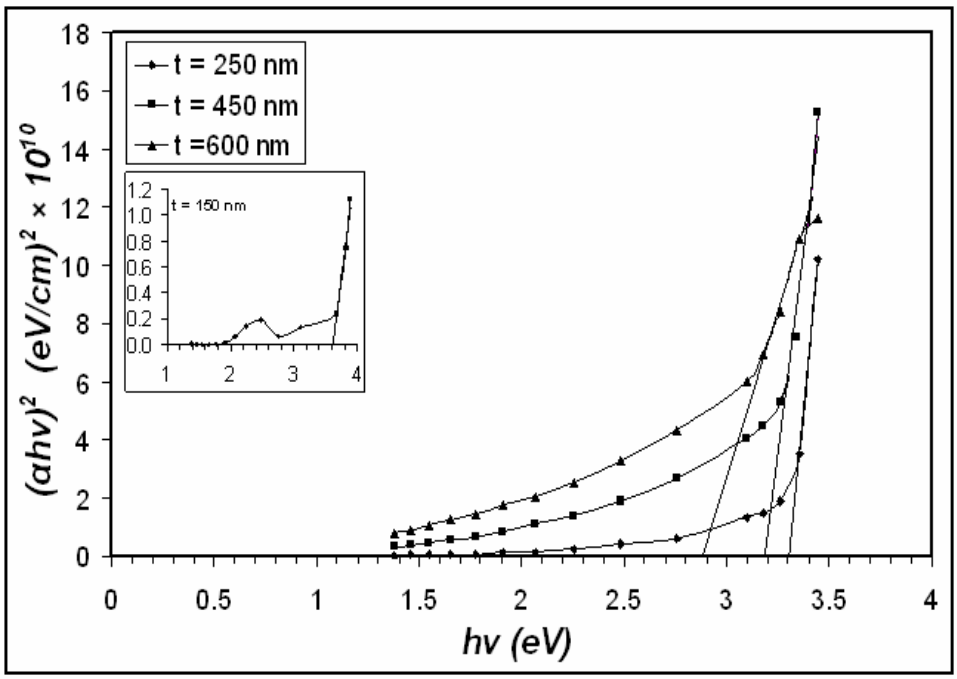

Figure 6: Photon energy dependences of the absorption coefficient squared for CdI_2 films with different thickness to determination of Eg (direct).

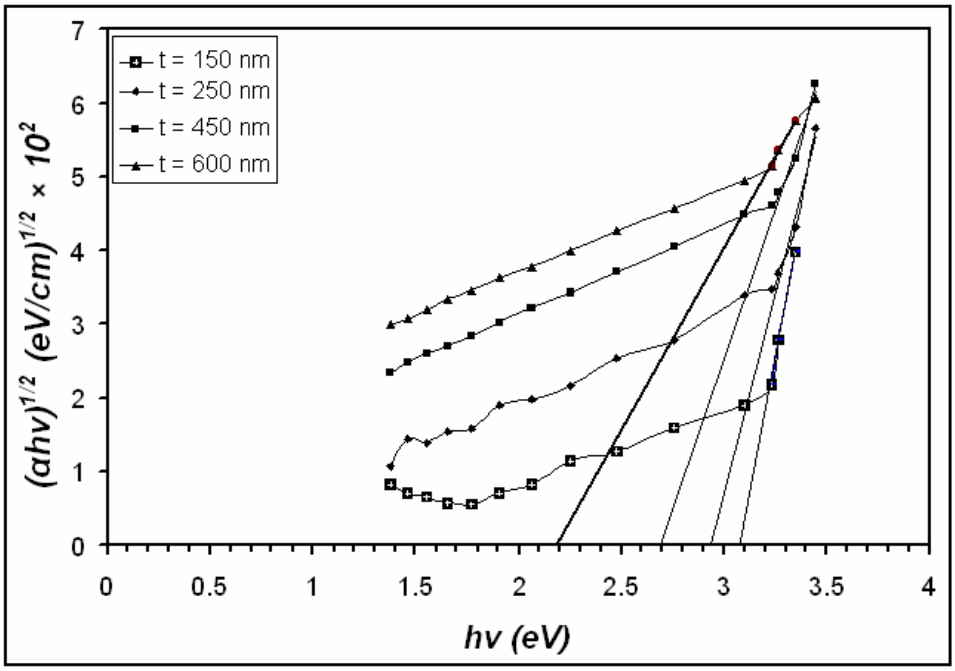

Figure 7: Shows (α h ν) $^{1/2}$ versus hν plot for the determination of Eg (indirect)

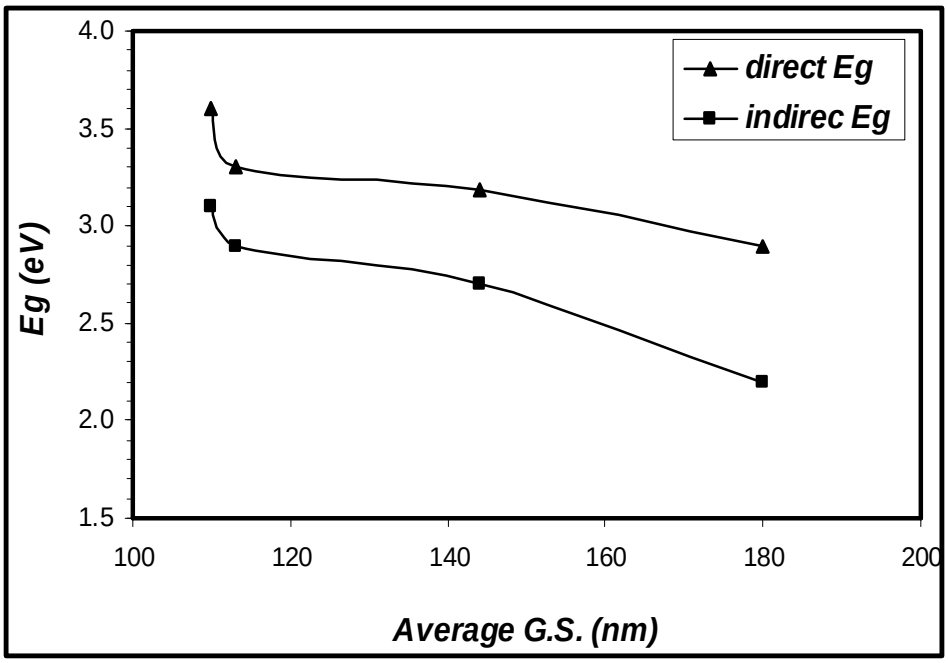

Figure 8: The grain size dependence of Eg for CdI_2 films.

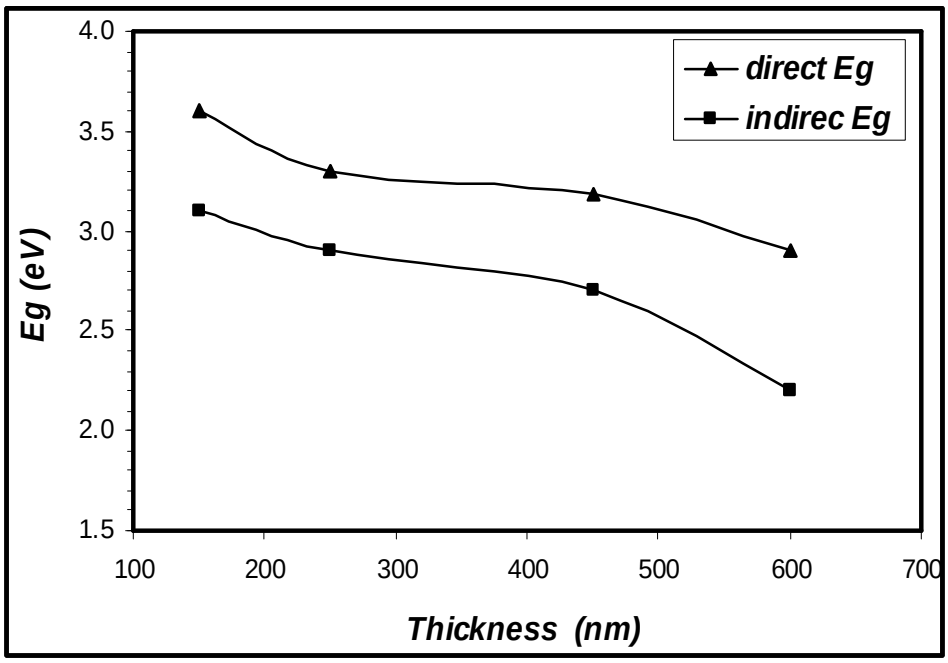

Figure 9: Thickness dependence of Eg for CdI_2 films.