Structural and Optical Properties of Lead Iodide Thin Films Prepared By Vacuum Evaporation Method

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Abstract

Structural and optical properties were studied as a function of films thickness for thermally evaporation PbI_2 films. X-ray diffraction analysis confirmed that PbI_2 films are polycrystalline having hexagonal structure. The optical absorption data indicate an allowed direct transmission with optical energy gap varies continuously from (2.15eV to 2.33eV) . The energy gap shows thickness dependence, which can be explained qualitatively by a thickness dependence of grain size through the decrease of the grain boundary barrier height with grain size. The low fluctuation in energy gap indicates that the grain size is quite small, which is finding in agreement with AFM results.

Keywords: PbI_2 thin film, The physical properties of PbI_2 thin film

الخصائص التركيبية والبصرية لاغشية يوديد الرصاص المحضرة بطريقة التبخير الحراري في الفراغ

الخلاصة

درست الخصائص البصرية والتركيبية كدالة لسمك اغشية يوديد الرصاص متعدد التبلور باستخدام طريقة التبخير الحراري وذلك بالترسيب على قواعد زجاجيه. اظهرت الاغشية المتوازنة كيمياويا تركيبا سداسي متعدد التبلور . بينت قيم الامتصاص البصري انتقالات مباشرة وبفجوة طاقة بصرية متغيرة ما بين (2.15eV- 2.33eV) ، في هذا البحث درس اثر تغيير السمك. اظهرت قيم فجوة الطاقة اعتمادا على السمك ، والذي يمكن تفسيره كميا باعتماد الحجم الحبيبي على السمك من خلال تناقص ارتفاع حاجز الجهد عند الحدود البلورية مع الحجم الحبيبي. التغير الطفيف في قيم فجوة الطاقة يبين ان الحجم الحبيبي صغير وهذا ما توافق مع نتائج مجهر القوى الذرية (AFM).

1-Introduction

Lead iodide PbI_2 is a wide band gap semiconductors Eg ~2.3 eV . Due to the high atomic number of its elements (Z_{Pb}=82, Z_I=53), it is a material with potential use as an ionizing radiation detector (X and γ rays)*[1,2,3]*. Lead iodide is an important and promising P- type semiconductor and crystallizes in an hexagonal structure and can be grown from solution, vapor and gels. *[4]*. The polytypism of PbI_2 seems to be a significant property of this material with no structure modification. Lead iodide is isostructural to CdI_2 and 20 polytypes have been reported. The poly types of PbI_2 are 2H ,4H, 6H, 8H, 12H, 12R, 14H, 18H, 18R, 20H, 20R, 36H ,42R, 48R. The most common type is 2H, which represents 95% polytypes described for PbI_2 structure *[5]*.

Recently many research was published on the development of the

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method of prepared thin films of PbI_2 from solutions, vapor, melts and gels. Simiraly to the recently published results reporting on the influence of rare earth (RE) elements on the quality of materials for radiation detectors*[6]*.

Electronic transport and optical measurements in polycrystalline PbI_2 by vacuum evaporation with different thickness and grain size up to 100 μm was studied *[7,8]*.

The aim of this work is to prepare a thin polycrystalline lead iodide films by vacuum evaporation method, and studying the optical and structural properties of this material to present preliminary results which in this approach could be a way to develop PbI_2 nuclear imaging devices beside the electrical properties .

2- Experimental details

Polycrystalline PbI_2 thin film samples were prepared on glass substrates using vacuum evaporation method . PbI_2 powder prepared in the laboratories without further purification as in *[9]* ,as checked by X-ray fluorescence the main residual impurity in the base material is Ag as is shown in figure (1).

The PbI_2 powder was preheated at temperature ~ 250 ^oC for several hours to remove occluded materials from it.

The prepared material was housed in a vacuum deposition chamber for the preparation of thin film. The E-glass substrate was kept in ambient at 200^oC to maintain stoichiometry. At first , a film has been prepared then by decreasing the substrate temperature at a rate ~ 1K per minute until we brought to room temperature. This process will reduce the defect and grain boundaries if any considerably. The color of the film appears to be pale yellow in nature.

The evaporation was carried out in a conventional vacuum coating unit (INFICON V90) under a vacuum of order of $6X10^{-6}$ torr with deposition rate of ~ 4-7 nm sec^{-1}. A summary of the deposition conditions is shown in table (1). Film thickness was measured after evaporation by optical interferometer method, using He-Ne Laser λ =0.632 μm and the thickness were determined using the formula:

$$d = \frac{\Delta x}{x} . \frac{\lambda}{2} \qquad .....(1)$$

Where :d is the thickness of sample, x is fringe width, Δx is the distance between two fringes and λ is the wavelength of He-Ne laser light.

3- Results and discussion

X-ray diffraction analyses of all the films with different thickness show a high degree of crystallite orientation with the basal plane parallel to substrate and c-axis normal to the substrate plane indicated by the negligible relative intensity of (002), (003) and (004) reflection. X-ray diffraction (XRD) pattern of the films deposited on glass substrate in a "Shimadzu XRD 6000". Advance using Cu-Kα radiation of monochromatic wavelength (1.54 06 A^o) . For pure PbI_2 films recorded for a range of 2θ from 10^o to 60^o at 2^o glancing angle. Figure(2:A,B,C,D) shows a typical XRD of a thin film of lead iodide samples. The inter –planer distance d and (hkl) planes are shown in table (2) , which corresponds to XRD and standard ASTM data *[10]*, the main facts of all XRD patterns are the existence of the same peaks through different deposition conditions. A comparison between our results and those of the ASTM standard data is shown in table (2). It is clear that a strong peaks are observed at

(d= 3.486, 2.332 and 1.744 A^o) which corresponds to the reflection planes (002), (003) and (004) respectively.

These results are agree well with data achieved by others *[1,3]*. An accurate observation of each reflection peak for most samples reveals the presence of two less intense peaks very close to the main one (30-40^o). This is probably due to the presence of polytypes *[10,11]*.

As shown in figure (3A,B) an AFM(Atomic force micrograph) model (AA3000) scanning prop microscope was used in this search , the AFM results shows very smooth surfaces for both 1000nm and 2000nm thickness, with an average surface roughness of 23nm for 1000nm thickness and 19.1nm for 2000nm thickness. Also different in grains area with different thickness, in thickness 1000nm the grains area seems smaller than in the case of 2000nm thickness.

The X-ray diffraction data can also be used to determined residual stress or non uniform strain in the film due to structural defects like dislocation, stacking faults, which are quite common in the films grown by thermal evaporation. The in homogeneous stress in the film can be determined from the line broadening $\Delta_{(2\theta)}$, full width at half maximum (FWHM) (Where 2θ is the diffraction angel), which is also related to the variation in d spacing (where d is the distance between any two parallel crystal planes having the same Miller index (hkl) through a relation *[12]*.

$$\Delta_{(2\theta)} = 2 \tan\theta \ \Delta d/d \text{……..(2)}$$

The average grain size is determined from the full width at half maximum (FWHM) for the most intense peak using the Scherrers formula*[13]:*

Where G.S is the average grain size ,λ is the X–ray wavelength , $\Delta_{(2\theta)}$ is (FWHM), θ Bragg diffraction angle of XRD peak (degree). Figure (4) shows the variation in the average grain size with different thickness . Average grain size increases linearly with increasing thickness. The increasing tensile stress as it seen in figure (3) may be responsible for the flattening of grains. In the X-ray diffraction data, we have directly measured $\Delta_{(2\theta)}$ for major peaks of appreciable relative intensities we can calculate*[14]*:

$$\delta=[d_{ASTM}-d_{XRD}/d_{ASTM}]*100\% \quad .....(4)$$

Where δ is the residual stress. From the observed d_{hkl} with reference to d_{hkl} (ASTM) from corresponding powder data ASTM. All the analysis carried ,the residual stress $\Delta d/d$ was found to be tensile and increase linearly with film thickness as it shown in figure (5). The residual stress may increase with film thickness depending mainly on the depositing material and growth conditions *[13]*. Different materials show different behaviors. However, the linear dependence of $\Delta d/d$ on film thickness observed for PbI_2 films could be due to the orientation crystallite growth.*[15]* .

The optical transmission spectra of PbI_2 films deposited on the glass substrate at different thickness was recorded as a function of wavelength in the range of (380-900)nm at room temperature it shown in the figure(6) . The average transmission over the rang (380-900)nm exceeds 85% with a sharp fall near the fundamental absorption; whereas fall in transmission is gradual for other samples, these result is good agreement with the measurements results obtained by T.Ghosh et al *[16]* The absorption coefficient (α) was

calculated using Lambert law as follows*[14]:*

$$Ln(I_o/I) = 2.303A = \alpha d \ldots\ldots..(5)$$

Where I_o and I are the intensity of incident light and transmission light respectively, A is the optical absorbance and d the sample thickness.

The absorption coefficient (α) was found to follow the relation:

$$\alpha = [G(h\upsilon - E_g)^{1/2}] / h\upsilon \ldots\ldots\ldots(6)$$

Where G is a constant and E_g the optical energy gap , figure (7) shows the relation between absorption coefficient and photon energy. Plots of $(\alpha h\upsilon)^2$ versus the photon energy (hυ) in the absorption region near the fundamental absorption edge indicate direct allowed transmission in the film material, as shown in figure (8). The optical energy gap was estimated from the extrapolation of the linear portion of the graph to the photon energy axis*[17]*. It is observed that E_g degreases with increasing thickness as it shown in figure(9).The interface between the substrate and films is an important junction where free energy supplied and minimizing it by a slow process shall reduce the chance of formation of decades , and the grain size*[5]*. In general, thickness dependence of optical band gap can a rise due to one or combined effect of the change in barrier height due to change in grain size in polycrystalline films*[18]*.

Conclusions

The X- ray diffraction analysis confirm that PbI_2 films are polycrystalline, having hexagonal structure. The inception of the data for pure thin film of lead iodide indicates that the observed (d) values closely matched with the existing standard values for hexagonal structure. The low fluctuation in the value of structure parameters are due to the fluctuation in lattice parameters which is attributed to the stress (positive) which is accompanies with the increase in grain size. The values of band gap varing from (2.15eV- 2.33eV). The low fluctuation in energy gap with samples thickness indicates that the drain size is quite small. The results are in agreement with the existing works adopting different techniques for film preparation. The reproducibility in making thin films of PbI_2 is very good by present method.

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Table (1) summary of deposition conditions.(Substrates, cleaned with tri-chloro-ethylene, acetone and alcohol .To avoid unwanted deposited , a shutter puts between source and substrate .By conducting ion cleaning the ultimate vacuum improve prior to deposition *[5]*.

Coating Unit	**INFICON V90**
Materials	Lead iodide (PbI_2) powder
Substrates	glass slides
Vacuum	~ $6x10^{-6}$ torr
Substrate to film gap	15 cm
Deposition rate	~ 4-7 nm sec^{-1}

Table (2) Structural values of PbI_2 thin films at different thickness with ASTM

Thickness nm	2θ	d (A^o) Observed	d (Ao) ASTM	hkl	δ	FWHM (deg.)	Average G.S(nm)
300	25.5126	3.4886	3.4890	002	0.011	0.2455	36.7303
	38.6567	2.3260	2.3270	003	0.043	0.2777	
	52.362	1.7458	1.74490	004	0.114	0.3401	
1000	25.5221	3.48733	3.4890	002	0.057	0.24110	39.4976
	38.6581	2.32520	2.3270	003	0.077	0.25760	
	52.3631	52.3631	1.74490	004	0.16	0.34820	
1400	25.5476	3.48390	3.4890	002	0.171	0.21590	43.6354
	38.7002	2.3250	2.3270	003	0.086	0.2323	
	52.4105	1.74439	1.74490	004	0.057	0.2538	
2000	25.4951	3.4909	3.4890	002	0.054	0.2527	46.4670
	38.6434	2.32469	2.3270	003	0.103	0.21797	
	52.348	1.74632	1.74490	004	0.172	0.3795	

Table (3) Values of band gap for different thickness of PbI_2

Thickness (nm)	Band gap (eV)
300	2.33
1000	2.3
1400	2.24
2000	2.15

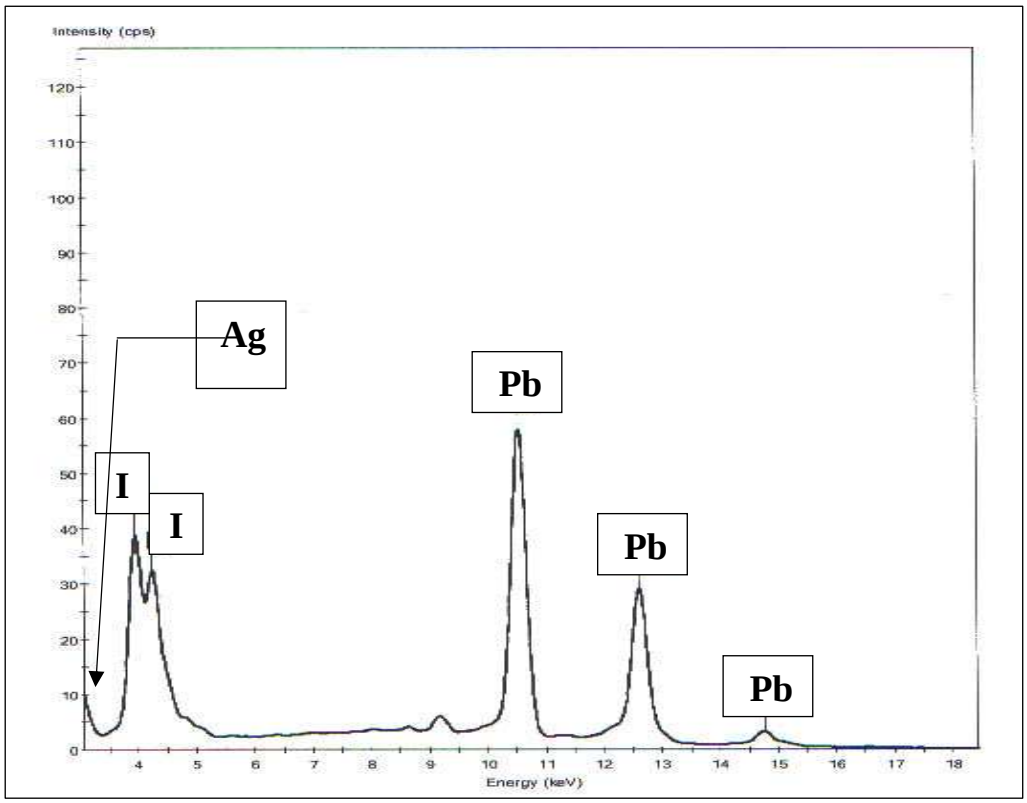
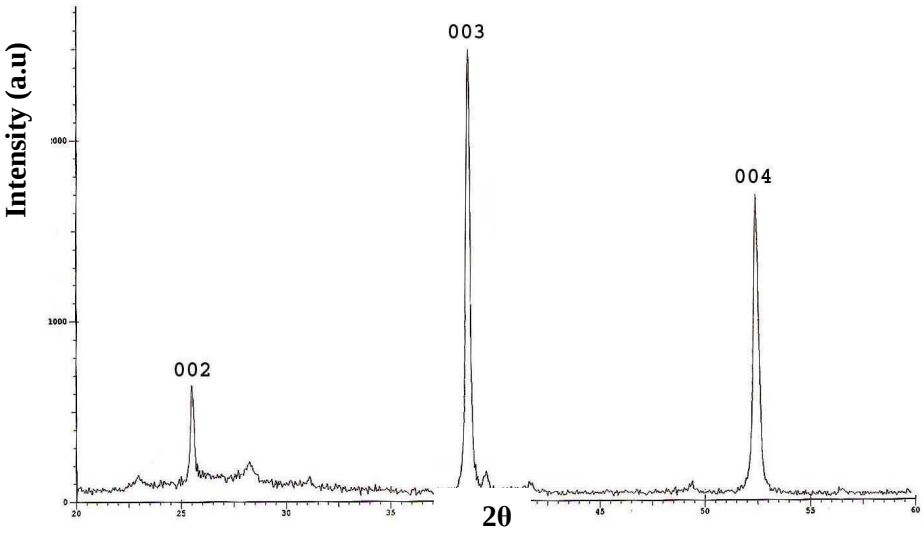
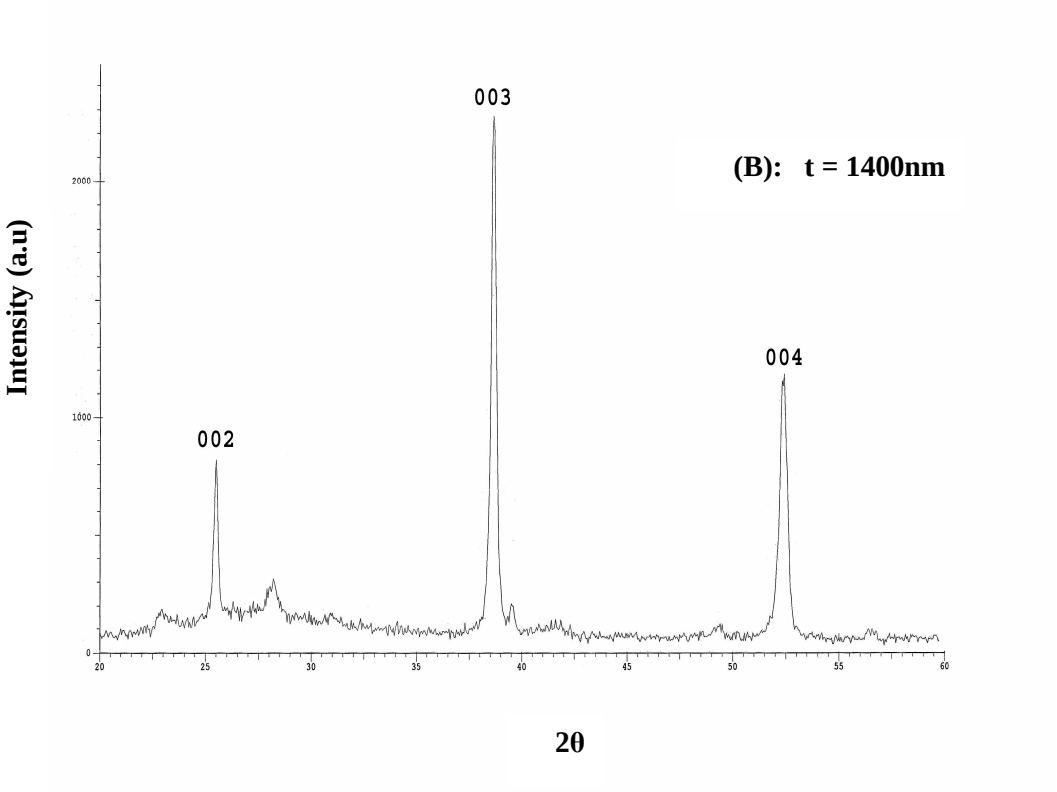
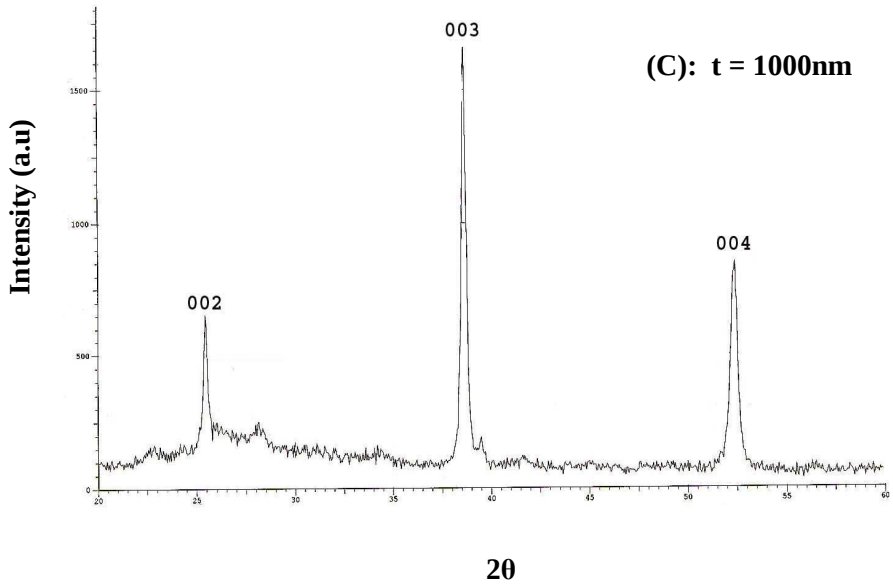


Figure (1) X- ray florescence pattern of PbI_2



(A): t = 2000nm


(B): t = 1400nm
Intensity (a.u)
003
004
002
2θ


(C): t = 1000nm
Intensity (a.u)
003
004
002
2θ

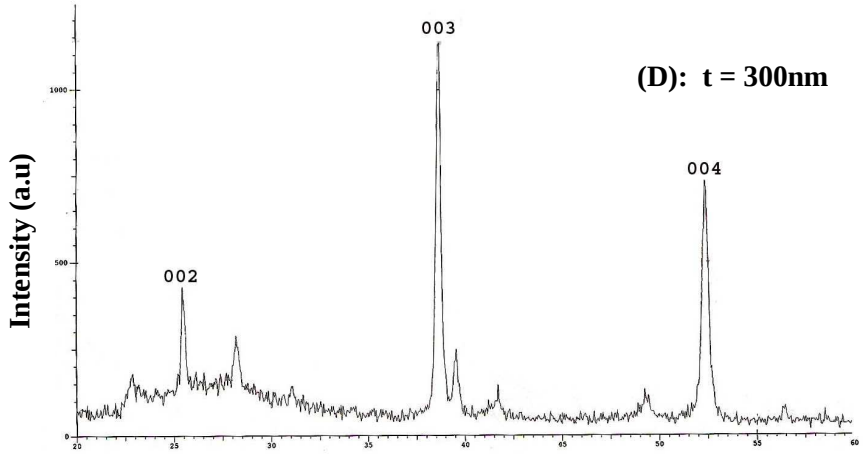


Figure (2:A,B,C,D) X-Ray diffraction pattern and miller indices of PbI_2 films prepared with different thickness

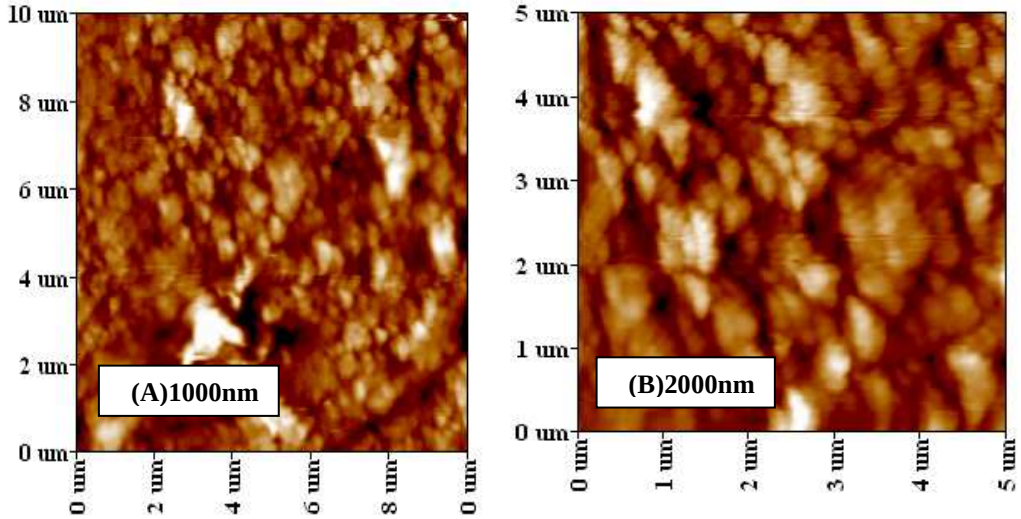


Figure (3) AFM photograph of PbI_2 films at thickness (A) 1000nm and (B) 2000 nm

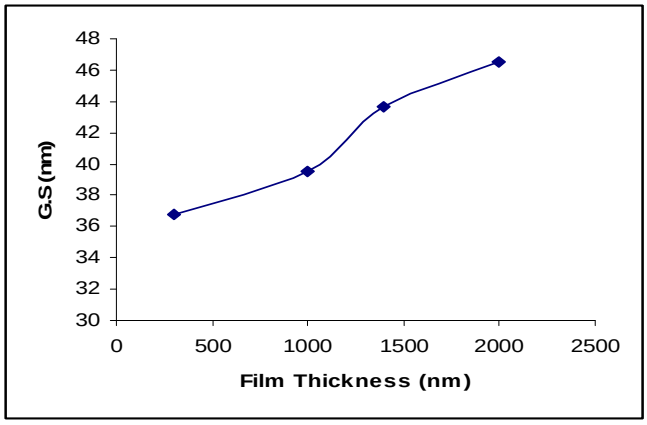


Figure (4) Grain size with film thickness of PbI_2

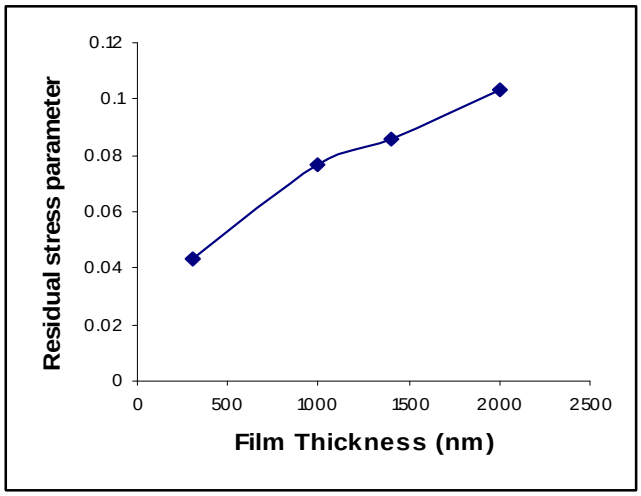


Figure (5) Residual stress with film thickness of PbI_2 films

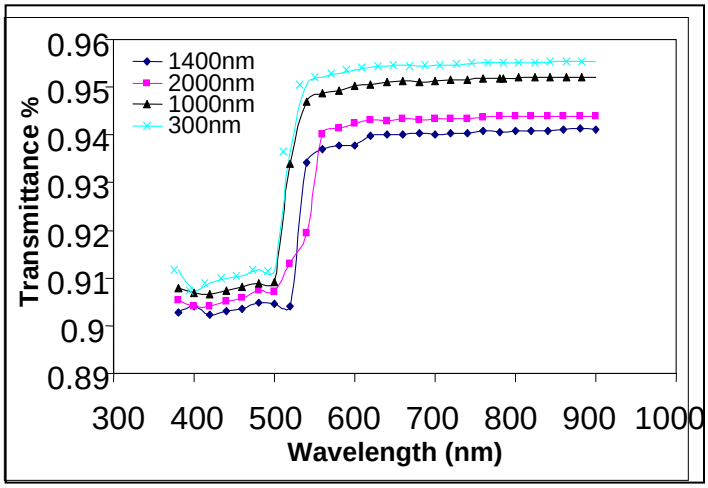


Figure (6) Optical transmittance spectra for different thickness of PbI_2 films

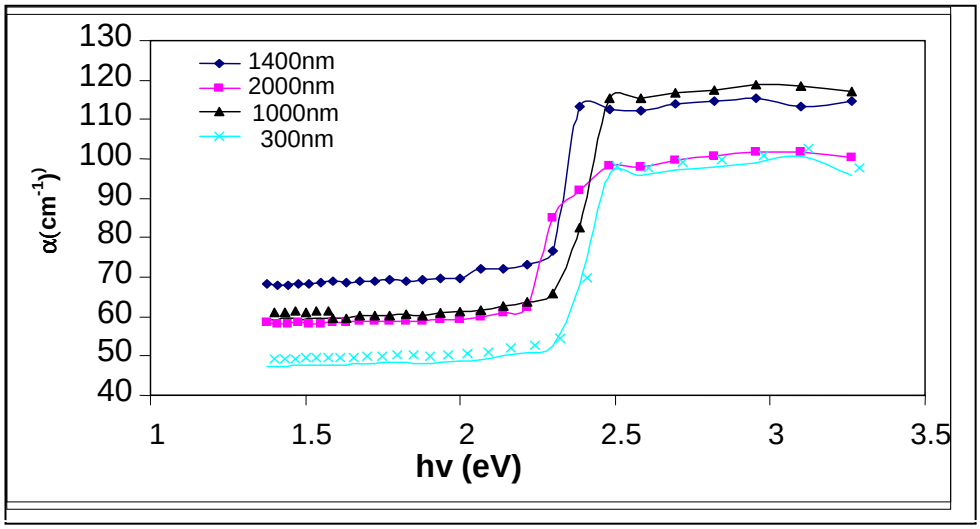


Figure (7) Absorption coefficient α as a function of hν for PbI_2 films with different thickness

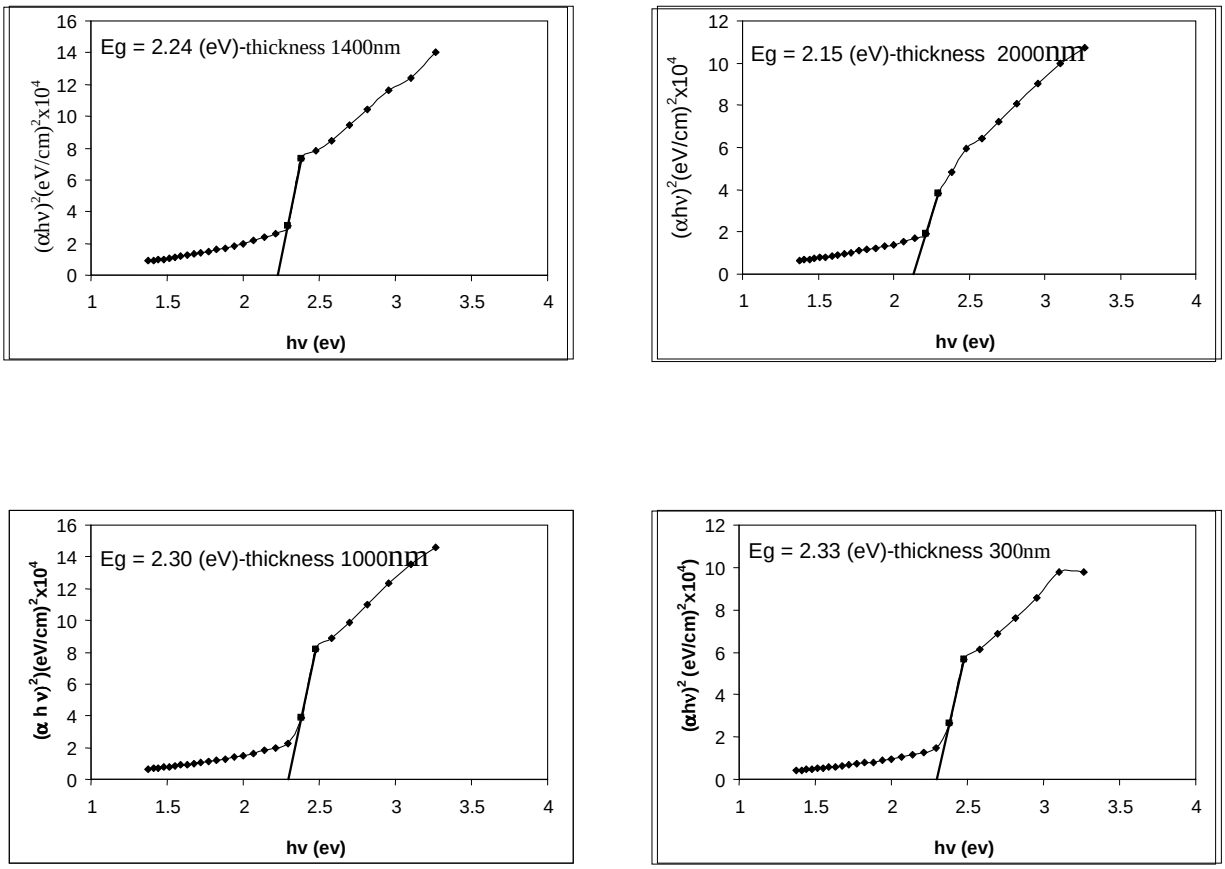


Figure (8) Photon energy dependences of the absorption coefficient squared for PbI_2 films with different thickness to determined of Eg

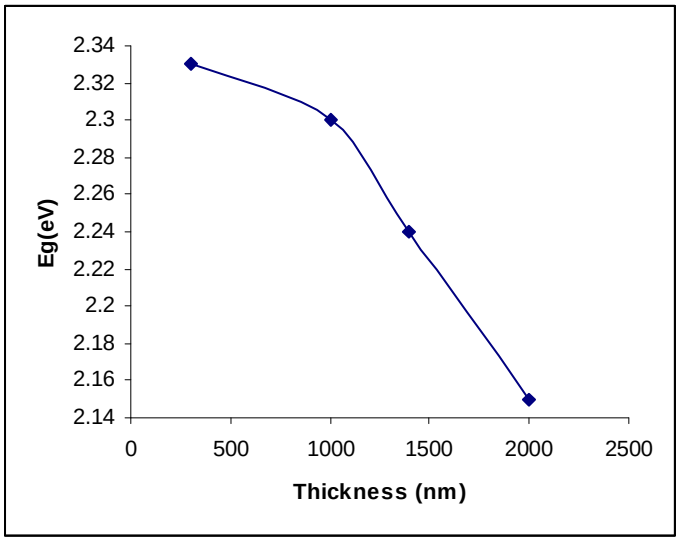


Figure (9) Film thickness dependence on direct optical energy gap for PbI_2 films