Structural and Optical Characterization of Nanocrystalline Pbs Thin Films Synthesized by CBD Method

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ABSTRACT

Nanocrystalline PbS thin films have been deposited on glass substrates by Chemical Bath Deposition (CBD) technique using lead acetate ,KoH, thiourea and T.E.A. The films were btained in a reaction bath at times of (15 ,30 ,45 ,60 and 90)min. Structure and surface morphology of thin films were characterized by X-ray diffraction and scanning electron microscopy (SEM). XRD indicates that the films have cubic structure. The crystallite size of the films were found to vary from (4.9 to 11.3 nm).The band gaps of the nanocrystalline PbS were determined from UV-Vis spectrophotometer and were found to be in the range(1.72 -2.4 eV).

Key words: Nano PbS, CBD method, XRD, SEM, Optical Properties.

الخصائص التركيبية والبصرية لاغشية كبريتيد الرصاص النانوية المحضرة بطريقة الحمام الكيمياوي

الخلاصة

تم ترسيب غشاء نانوي من كبريتيد الرصاص على قواعد زجاجية بتقنية الترسيب بالحمام الكيمياوي من خلال استخدام خلات الرصاص,هيدروكسيد البوتاسيوم,الثايوريا,وتراي ايثانول امين.تم الحصول على الاغشية بغمرها بالحمام بازمان مختلفة (15,30,45,60,90) دقيقة .كما وشخصت الخصائص التركيبية وتصوير السطح من خلال فحص حيود الاشعة السينية والمجهر الالكتروني الماسح .بين فحص حيود الاشعة السينية ان الاغشية لها تركيب بلوري مكعب وحجم بلوري قليل يتراوح ما بين (4.9-11.3) نانومتر.اما بالنسبة لفجوة الطاقة فتم حسابها من خلال جهاز المطياف للمنطقتين المرئية وفوق البنفسجية ووجد انها تتراوح ما بين (1.72-2.4) الكترون فولت.

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INTRODUCTION

Semiconductor nanomaterials are of current interest due to their unique optical and electronic properties which are different from that of the materials in bulk form [1]. Lead chalcogenides are important materials with wide variety of applications including spectrometer detector, IR detector, and pollution monitor [2] Although there are different methods for synthesizing nanocrystalline PbS, the(CBD) technique is relatively less expensive and suitable for large area deposits on substrates of different materials, size and shapes. PbS is well-known IV-VI semiconductor with a band gap of 0.41 eV. This band gap can be enhanced by decreasing the sizes of the crystallites [3].

This change in band gap in PbS can be obtained for comparatively larger crystallite size as its Bohr excitonic radiuses comparatively larger than other chalcogenides [4]. A major research goal of recent years is to understand the amount size dependent properties of nanocrystalline materials and considerable of work have so far been reported[5]. In the present study,results of structural characterization of nanocrystalline PbS synthesized by (CBD) method are reported .

Experimental Details

The samples studied here were thin Polycrystalline films of PbS layers prepared by (CBD) on glass slides. The substrates were washed with distilled water in ultrasonic bath and then immersed for 24hr in chromic acid (1gm of CrO_3 in 20 ml of distilled water) and finally wished again with distilled water. The aqueous solution of the deposition bath was prepared by the sequential addition of 5 ml of 0.25 M lead acetate, 5 ml of 1M KOH ,6ml of 0.5 M thiourea and 1ml of 0.1M T.E.A in 100 ml beaker . The total volume was completed to 100 ml with distilled water.

The glass substrate immersed in the solution vertically. The reaction process in considered as follows [6]:

$$Pb(CH_3COO)_2.3H_2O \longrightarrow Pb^{2+}+2CHCOO^{-}+3H_2O\ldots \quad \ldots\ldots(1)$$

$$Pb^{2+} +4NH_3 \longrightarrow Pb(NH_3)_4^{2+} \quad \ldots\ldots(2)$$

$$SC(NH_2)_2 +2OH^{-} \longrightarrow S^{2-} +CH_2N_2 +2H_2O \quad \ldots\ldots(3)$$

$$PbS+4NH_3+SC(NH_2)_2+2OH^{-} \longrightarrow PbS+4NH_3+CH_2N_2+2H_2O \quad ..(4)$$

After deposition of the films , substrates were taken out and thoroughly washed in doubly distilled water and then dried in air .Thickness measurement were made by optical method ,using He-Ne laser λ=0.632μm. Structural characteristics of the films were determined by X-ray diffraction system (Philips – PW1840) at room

temperature with Cuká radiation and 0.15405 nm wavelength . The morphological properties of the films determined by SEM type VEGA TE SCAN,with an accelerating voltage of 30kV and magnification of 10000x . Optical absorption spectra of the samples were taken with help of UV-Vis spectrophotometer in the wavelength range (375 -1100 nm) .

RESULTS AND DISCUSSION

Thickness Measurements

The films thickness (d) is calculated using equation [7]:

$$d = \frac{\Delta x}{x} . \frac{\lambda}{2} \qquad \text{... (5)}$$

Where Δx is the width of dark fringes and x is the width of light fringes.

The variation of deposited films thickness with deposition time is shown in Figure (1).For short deposition time (<30 min) thickness increases and reaching a value of (129nm). Subsequently, a quasi saturation stage start, where the deposition rate decreases in the time range (60-90min), resulting in a terminal thickness. The higher rate of deposition in the initial stages of growth is due to the higher concentration of Pb^{2+} and S^{2} ions. As more and more PbS is formed, the solution becomes depleted of ions, resulting in a lower rate of deposition. The deposition rate becomes zero (resulting in a terminal thickness), when the concentration of Pb^{2+} and S^{2-} ions decreases to a values such that S <1. This results in good agreement with results of Yu. Jang and Shengshui Hu et al [8].

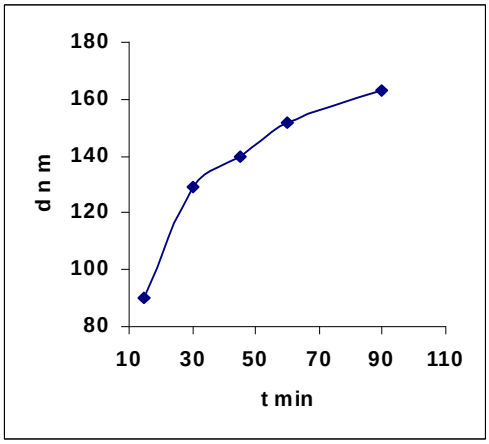

Figure (1) Thickness of Nano PbS Films as a Function of Deposition Time at T=30ºC, pH=11.6, MPb=0.25M and MSc=0.5M)).

XRD Studies

Figure (2) shows the XRD patterns of the PbS films deposited at different time keeping other parameters fixed(T= 30ºC , pH =11.6 , MPb = 0.25M and MSc = 0.5M).

The patterns display five diffraction peaks at 2è values of approximately(25º, 26º,29º,35º,30º, 43º ,51º and 53º) which correspond to the diffraction plans C (111),C(200) ,C(220) ,C(113) ,C(311) and C(211) crystalline planes of the PbS cubic phase (galena), respectively. It is clear that the four diffraction shows a preferred orientation growth along the C(200) direction and the intensity of the peaks increases with the time deposition of the films. This effect can be related to the increase of both, thickness and grain size of the PbS films with time. The grain size of the films were determined from the (200)
plane by using the Scherrer formula [9]:

$$G.S=K\lambda/\Delta\theta\cos\theta \quad \text{... (6)}$$

Where k is a constant taken to be 0.94, λ is the wavelength of X-ray used which is Cuká radiation, and $\Delta\boldsymbol{\theta}$ is Full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane . The value of the crystallite size G.S Table(1) varies with in the range (4.9 to 11.3) nm. The value of G.S, as determined by Scherrer s formula which gives the size of the crystallites in a direction perpendicular to the respective planes, FWHM of whose diffraction profile is taken for calculation of G.S, is found to be different in different directions for all the crystallites the size is small in a direction perpendicular to (200) plane. These results are in good agreement with data achieved by N. Choudhury and B. K. Sarma [10].

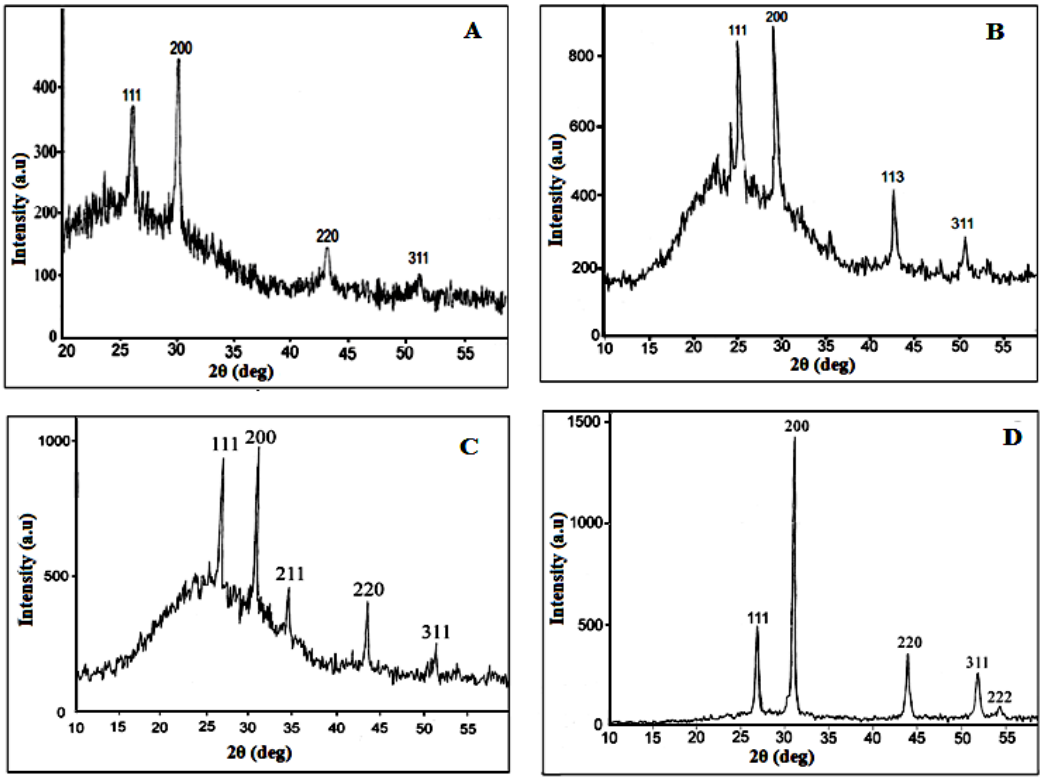

Figure (2)X-ray Patterns of Nano PbS Thin Films for Different Time : (A)15min (B)30min (C)45min (D)60min.

Table (1) Structural and Optical Parameters of Nano PbS Thin Films for Different Time.

t(min)	d(nm)	Hkl	a $_{XRD}$ nm	%ä	G.S nm	E_g eV
15	90	200	0.5952	0.0572	4.9	2.4
30	129	200	0.5937	0.0930	6.4	2.3
45	140	200	0.5922	0.1549	9.2	2.1
60	152	200	0.5778	0.2661	11.3	1.98
90	163	.....	.....	.....	.....	1.72

Figure (3) shows variation of grain size from (4.9 to 11.3) nm with thickness, which shows that the crystallinity of PbS increases with thickness.

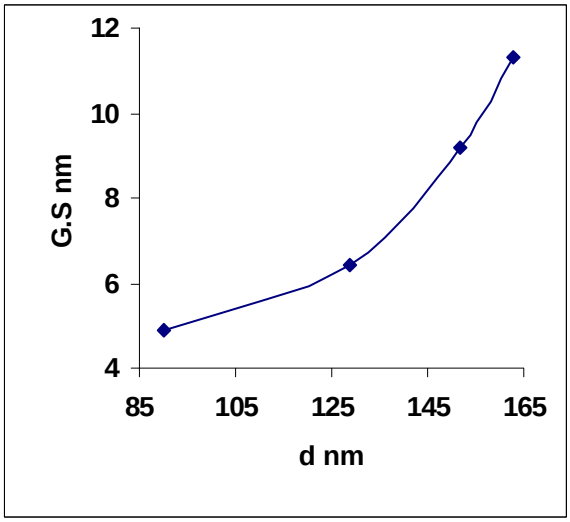

Figure (3) Variation of Grain Size with Film Thickness of Nano PbS.

The residual stress δ developed in the layer is calculated from X-ray diffraction data employing the relation (11):-

$$\delta = [|a_{ASTM} - a_{XRD}| / a_{ASTM}] * 100\% \quad \ldots \quad \ldots (7)$$

The residual stress(Δa /a) was found to be tensile and compression and decrease with film thickness as shown in Figure (4).The residual stress may decrease with film thickness depending mainly on the depositing material and growth condition. Different material show different behaviors. However, the linear dependence of(Δa/a) on film thickness observed for PbS films could be due to the orientation crystallite growth. The average value of stress assessed from the measurement of a– spacing or d– spacing depends on the grain size, which determines the extent of penetration of the stress into the grain interior.

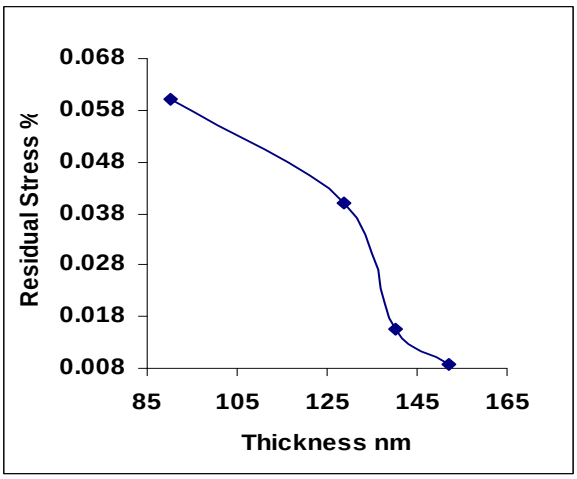

Figure (4) Residual Stress with Film Thickness of Nano PbS.

SEM Studies

The morphology of nano PbS films for different time deposition on glass substrate were examined by scanning electron microscopy SEM Figure (5). From the micrograph it is observed that grain sizes are uniform. Figure (5A) the sample deposited at 15min, this figure showed a discontinuous nano-crystalline film consisting of spherical particles with typical size of 10.5nm. Increasing deposition time to 30min Figure (5B) resulted in a well adherent, dense compact layer which covers the entire substrate surface. In addition, an increase in partical size to 21nm was observed. Further increase of the deposition time to 45min Figure (5C) shows the first signs of change in particle shape. There are still round particles with typical lateral size of 32nm, but this film have a sponge nature of elongated fibers. This abrupt transition in crystal size and morphology occurs with increasing film thickness. Further increase in deposition time to 60min Figure (5D) the film have more sponge nature with typical size of 40nm. We observed that the average grain sizes determined by SEM are comparatively larger than measured by XRD. This larger value of grain sizes may be due to the agglomeration of grains. The surface of the films is smooth and covers to the glass substrate well and with brown color. Conversely K.K. Nanda and F.E. Kruis attributes similar results to the either the decrease in grain size and to the strong quantum confinement [12].

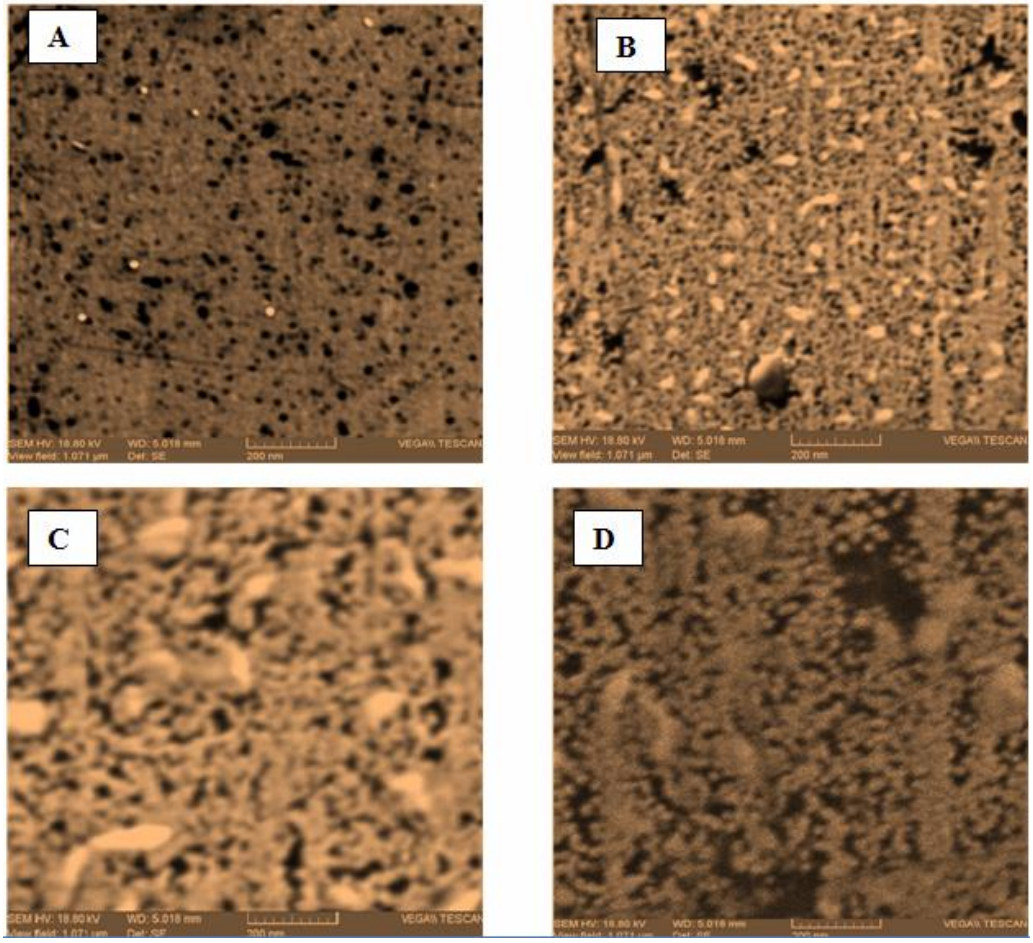

Figure (5) SEM Micrographs of Nano PbS Thin Film for Four Different Time :(A)15min (B)30min (C)45min (D)60min.

Optical Absorption Studies

The absorption coefficient α is defined as the ability of material to absorb the light of a given wavelength, its unit of measurement is the reciprocal of distance. The optical absorption of PbS thin films were studied in the wavelength range (375-1100 nm). It is calculated by using the equation [13]:

$$\alpha = C(h\upsilon - E_g)^{1/2} \qquad \text{for } h\upsilon > E_g \qquad ...(8)$$

Where α is absorption coefficient, C a constant , hυ incident photon energy and E_g the band gap. Figure (6) shows the optical absorption spectra recorded for the PbS films for different deposition time. The absorption coefficient increases with increases

the deposition time. It is clear that the films have high absorption coefficient at short wave length range (375 500 nm), then decrease at different rates dependence on the films structure to reach constant values at long wave lengths (>750 nm), where the films become transparence at this wave lengths. For different deposition conditions absorption coefficient á change between (104 -$10^5$$cm^{1-}$).

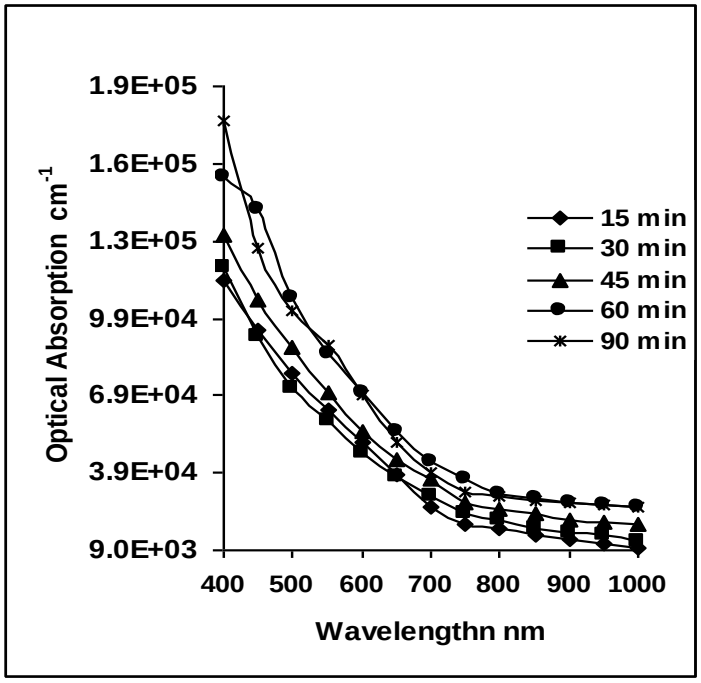

Figure (6) Plot of Optical Absorption vs. Wavelength for Nano PbS Films with Different Deposition Time.

The energy gap values depends in general on the films crystal structure, the arrangement and distribution of atoms in the crystal lattice, also it is affected by crystal regularity [14]. Energy gap Eg value calculated by extrapolation of the straight line of the plot of $(\alpha h\upsilon)^2$ versus photon energy for different deposition parameters as shown in Figure (7). The linear dependence of $(\alpha h\upsilon)^2$ with $(h\upsilon)$ indicates direct band gap. The band gap decreasing with increasing deposition time, this could be attributed to the enhancement of the degree of crystallity and also due to the increasing in films thickness. This decrease of band gap is consistent with theoretically shown band gap dependence on crystallite size. These results are consistent with other published results such as results of R.N.Mulik and S.G.Pawar et al [15]. Figure (8) shows variation in E_g from (1.72 -2.4 eV) with crystallite size G.S.

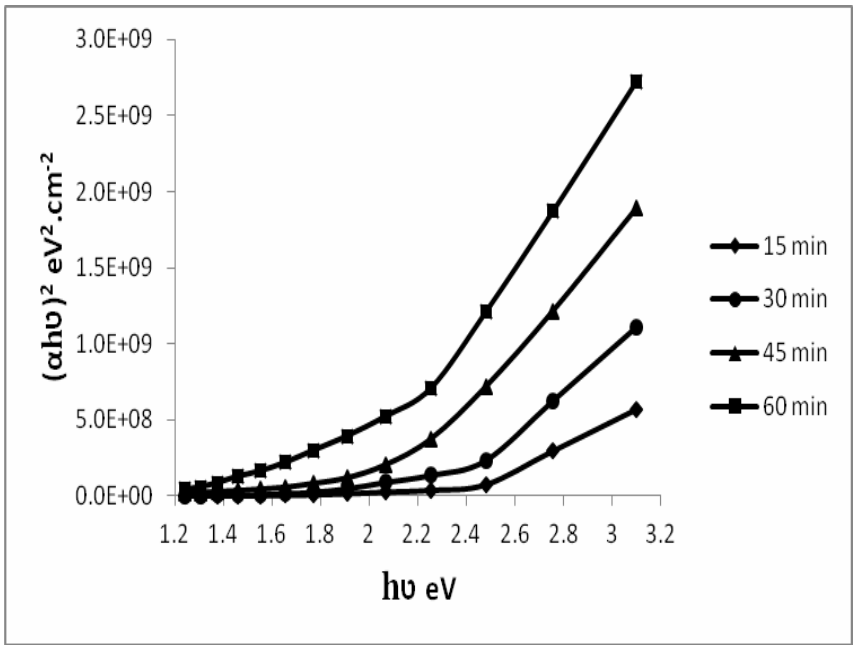

Figure (7) Plot of $(\alpha h\upsilon)^2$ vs.hυ for Nano PbS with Different Deposition Time.

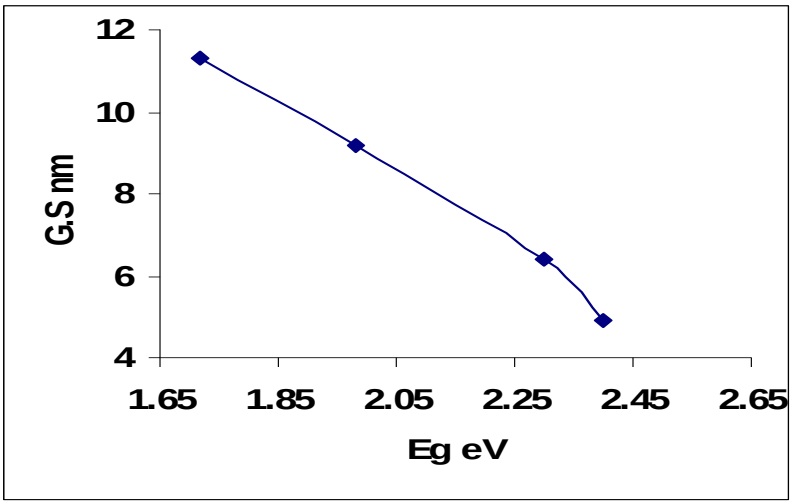

Figure (8) Variation of Grain Size with Energy Band Gap of Nano PbS.

CONCLUSIONS

Nanostructured PbS thin films at different time were prepared by a simple Chemical Bath Deposition method. The results of XRD and SEM show that the deposited PbS film consists of nano sized grains and the grain size increases with increasing film thickness. An XRD study shows nanocrystalline structure with cubic phase (galena). The Optical absorption study reveals that PbS thin films have allowed direct transitions. The optical band gap energy varies from 1.72 to 2.4 eV with thickness.

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