

**Nanocrystalline Lead Sulphide Thin Films Deposited by Chemical Bath Deposition Technique**

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**Abstract**

In the present paper, nanocrystalline lead sulphide (PbS) thin films were prepared by a chemical bath deposition (CBD) technique onto glass substrates using the mixed aqueous solutions of lead acetate, thiourea and ammonia. The structure of the films was studied by X-ray diffraction. XRD studies show that the preferential orientation is (200). The optical properties were carried out from spectroscopy measurements in the wavelength range 300-1100 nm. The optical band gap of the prepared films was found to be higher as compared with respect to the bulk value (0.4 eV) due to quantum size effect with shift toward shorter wavelengths.

**Keyword:** Nanocrystalline thin films, Structural properties, Optical properties, CBD technique, lead sulphide.

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### أغشية كبريتيد الرصاص النانوية التركيب المحضرة بتقنية الحوض الكيميائي

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#### الخلاصة

في هذا البحث، تم تحضير أغشية كبريتيد الرصاص البلورية النانوية بتقنية الحوض الكيميائي على أرضيات زجاجية، وباستخدام مزيج سائل من خلات الرصاص، الثايوريا والأمونيا. الخصائص التركيبية للأغشية المحضرة تم دراستها من خلال فحوصات حيود الأشعة السينية. حيث اوضحت القياسات ان الاتجاه السائد للأغشية المحضرة هو (200). الخصائص البصرية تم دراستها باستخدام جهاز دراسة الطيف البصري للمنطقة الطيفية المرئية وفوق البنفسجية حيث وجد ان فجوة الطاقة البصرية للأغشية المحضرة ذات قيمة اعلى من قيمة فجوة الطاقة البصرية للأغشية عندما تكون في الحالة المحسوسة (Bulk) نتيجة التقيد الكمي مع ازاحة تجاه الاطوال الموجية القصيرة.

**الكلمات المفتاحية:** الاغشية نانوية التركيب، الخصائص التركيبية، الخصائص البصرية، تقنية الترسيب بالحوض الكيميائي، كبريتيد الرصاص.

#### Introduction

Recent studies on nanocrystalline semiconductors have attracted much interest in their synthesis, characterization and fabrication of possible devices [1]. Most studied nanocrystalline semiconductors belong to the II-VI and IV-VI groups as they are relatively easy to synthesize and are generally prepared as particles or in thin film form [2]. When the dimensions of the films are comparable with some characteristic length such as the electron mean free path or the de Broglie wavelength of the electron, the physical properties start to become functions of the film size [3]. The electronic and optical properties of semiconductor materials can be changed by changing their size and shapes [4]. Nanocrystalline materials exhibit increased strength, hardness, enhanced diffusivity, improved quality, roughness, reduced elastic modulus, higher

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thermal expansion coefficient, lower thermal conductivity and superior soft magnetic properties to the conventional bulk materials [5]. Lead sulphide (PbS) is an important direct narrow gap semiconductor material with an approximate energy band gap of 0.4 eV at 300K [6-8]. This band gap is very suitable for infrared detection applications and can be enhanced by decreasing the size of the crystallites [9,10]. Such a significant widening of the band gap is associated with small effective mass of electrons and holes ( $m_e=m_h=0.09 m_0$ ) as well as with a relatively large exciton Bohr radius (20 nm) of PbS [11]. PbS thin films can be obtained by several methods such as electrodeposition, spray pyrolysis, photoaccelerated chemical deposition, microwave heating and chemical bath deposition (CBD). Among these methods, chemical bath deposition is just one of the more utilized due to its low cost, the quality of the films and convenience for large area deposition [4]. By CBD method, the dimensions of the crystallites can be controlled by varying the deposition parameters: reaction time, temperature, pH, and presence of impurities in the solution [3,12]. In this paper, the effect of temperature and deposition time on structural properties and optical properties of nanocrystalline PbS films using CBD method has been reported.

### Experimental Detail

#### Synthesis

For preparation of nanocrystalline PbS thin films, aqueous solutions of lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and thiourea ( $\text{CS}(\text{NH}_2)_2$ ) were used as sources of ( $\text{Pb}^{2+}$ ) cation and ( $\text{S}^{2-}$ ) anion respectively. In the beginning, 20 ml of lead acetate was taken in a beaker, ammonia solution ( $\text{NH}_4\text{OH}$ ) was used to provide an alkaline medium needed for maximum growth.  $\text{NH}_4\text{OH}$  was added drop by drop in solution under vigorous stirring to maintain the pH value of the solution at 10. Then under continuous stirring, 20 ml of thiourea solution was added. The clean glass substrates were immersed vertically into the solution. The beaker with the reactive solution was immersed in water bath. As soon as the product of the free  $\text{Pb}^{2+}$  and  $\text{S}^{2-}$  ion concentrations exceed the solubility product of PbS, the precipitation of PbS takes place. After

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the deposition, the PbS thin films were washed with distilled water ultrasonically to remove the loosely adhered PbS particles on the film and finally dried in air placed into desiccators. The resultant thin films were homogeneous and good adhered to the substrate. The experimental details are summarized in Table 1. The chemical reaction for the deposition of PbS films can be written as follows [1]:

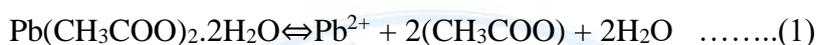


Table1: Experimental details for prepared PbS thin films

Temperature effect	Deposition Temperature (°C)	Deposition Time ( min. )	Bath conditions
Sample 1	30	40	Vol. of (Pb(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O) = 20 ml of (0.1 M) Vol. of CS(NH <sub>2</sub> ) <sub>2</sub> = 20 ml of (0.1 M) PH=10
Sample 2	40	40	
Sample 3	50	40	
<b>Time effect</b>			
Sample 1	50	20	
Sample 2	50	30	
Sample 3	50	40	

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### Characterization techniques.

The films were structurally characterized by X-ray diffraction (XRD) using a SHMADZU XRD-7000 (X-ray diffractometer) in the range  $10^\circ$  to  $60^\circ$  with  $\text{CuK}\alpha$  radiation  $\lambda = 1.54059 \text{ \AA}$ , operated at 40 kV and 30 mA. Optical properties of lead sulphide films were measured at room temperature with UV-VIS spectrophotometer (Jenway 6800) to measure the absorbance and transmittance of the films in the range of wavelengths 300-1100 nm.

### Results and Discussion

#### Structural characteristics of the films:

Figure 1 shows XRD patterns of films deposited at various bath temperatures (30, 40 and 50  $^\circ\text{C}$ ) for constant pH=10 and deposition time =40 minute. Diffraction peaks existed at  $2\theta = 25.98^\circ$ ,  $30.13^\circ$ ,  $42.96^\circ$  and  $50.66^\circ$ , which correspond to the diffraction lines produced by the (111), (200), (220) and (311) crystalline planes of the PbS cubic phase respectively. All the peaks in the diffraction patterns correspond to the structure of lead sulphide, which were found to be in good agreement with the standard data from JCPDS card No. 78-1901. The average crystallite size was calculated by measuring the full-width at half-maximum of the preferred orientation growth along the (111) peak using Scherrer's formula [13]:

$$D = K\lambda/(\beta\cos\theta) \quad \dots\dots\dots(5)$$

Where K is a constant taken to be 0.94,  $\lambda$  is the wavelength of X-ray used,  $\theta$  is a Bragg's diffraction angle in degrees and  $\beta$  is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular set of crystal planes. The crystallite sizes is found to increase with deposition time and deposition temperature of the solutions. With the increase of deposition time or bath temperature of the solutions larger number of  $\text{Pb}^{2+}$  and  $\text{S}^{2-}$  ions are reacting to form the deposit resulting in the increase of crystallite size. The peak broadening suggested that the deposited films on the substrates are of nano-size and the prominent peak of any one of each pattern confirm that the synthesized particles have crystalline structure with

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random crystal orientation. This result is in agreement with Valenzuela [10]. The results of XRD are summarized in Table (2).

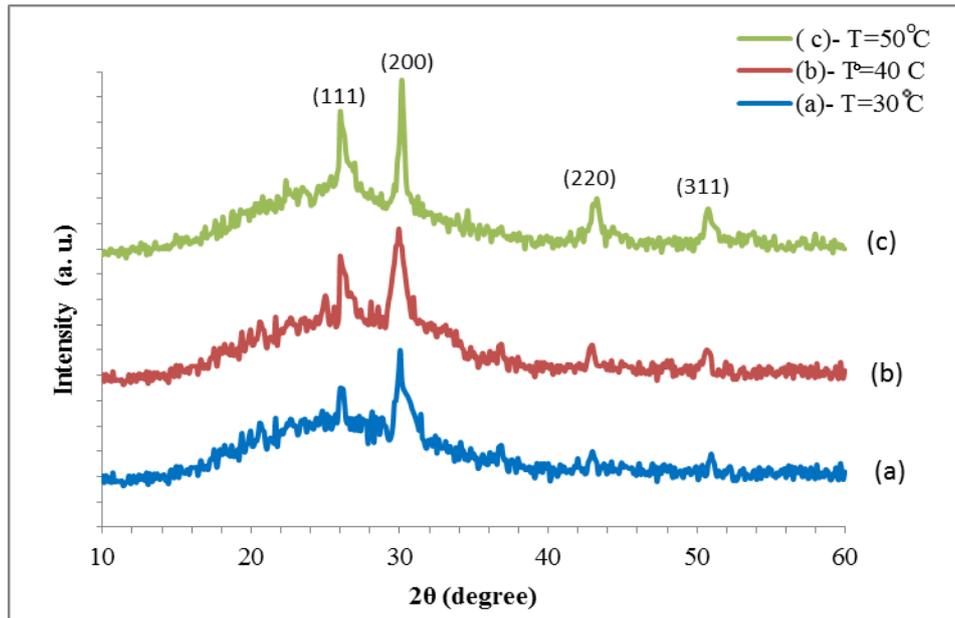


Figure 1: X-ray diffraction patterns of PbS thin films prepared at different deposition temperatures: (a) 30, (b) 40, and (c) 50 °C.

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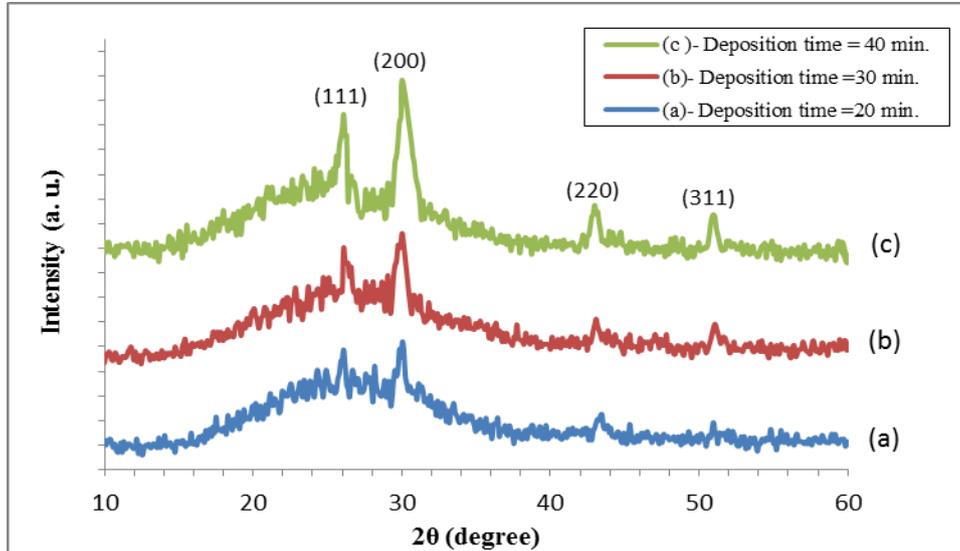


Figure 2: X-ray diffraction patterns of PbS thin films prepared at different deposition times: (a) 20, (b) 30, and (c) 40 minute.

Table 2: The obtained results of the XRD for nanocrystalline PbS thin films.

Deposition Condition		2θ (degree)	hkl	d (nm) XRD	FWHM (deg.)	Crystallite size (nm)
Temperature effect (t=40 min.)	30°C	30.10	200	2.9660	2.489	4
	40°C	30.02	200	2.9735	1.558	6
	50°C	30.14	200	2.9632	0.590	15
Time effect (T=50°C)	20 min.	30.02	200	2.9735	2.696	3
	30 min.	30.02	200	2.9735	1.448	6
	40 min.	30.02	200	2.9735	1.031	9

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### Optical properties

#### 1. Transmittance

The optical properties of PbS nanocrystalline thin films are determined from absorbance measurements in the range of 300-1100 nm at normal incidence. Figure (3) shows the transmittance spectra of nanocrystalline PbS thin films deposited at different temperatures (30, 40 and 50 °C).

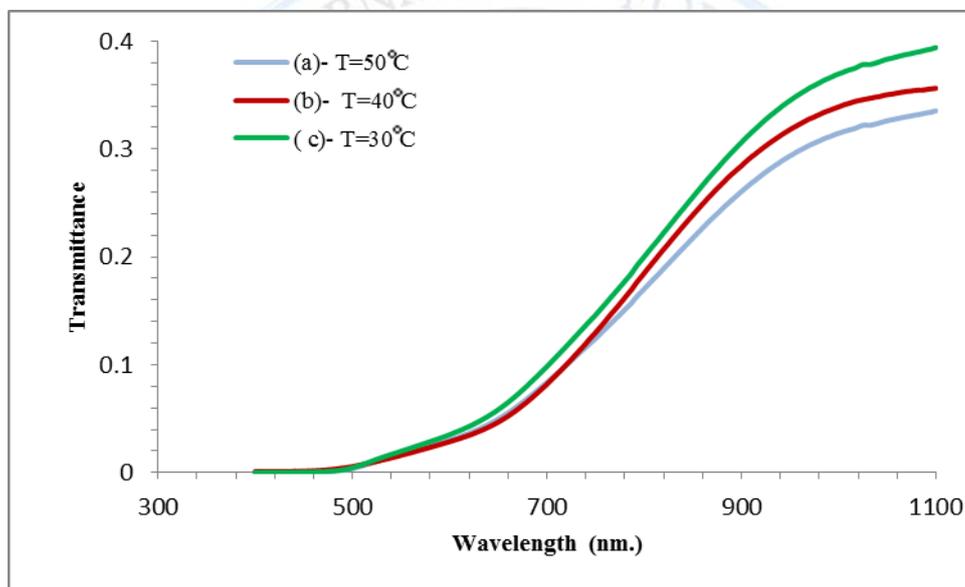


Figure 3: Transmittance spectra of nanocrystalline PbS thin films versus wavelength deposited at different temperatures (30, 40 and 50 °C).

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The increase in temperature from (30 to 50 °C) results in an increase in PbS thickness, which is directly observed from the decreasing of optical transmission spectra. The transmittance of the films in the visible region was low. Also, we observe steep optical absorption feature, which indicates a relatively better crystallinity and lower defects density near the band edge. This feature makes these films a good material for optoelectronic devices such P-type for solar cells application.

### 2. Absorption coefficient and optical band gap

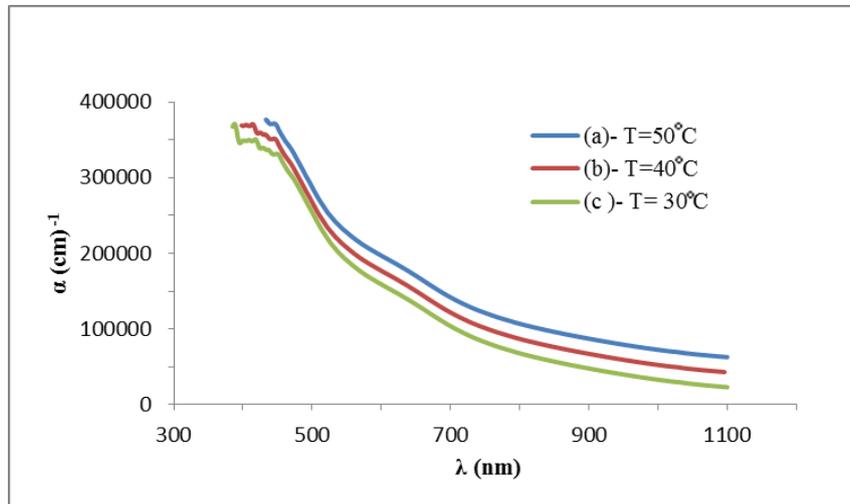
The study of optical absorption is important in understanding the behavior of semiconductor nanocrystals. Absorption coefficient associated with the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using the relation [14]:

$$\alpha = 2.3026 A/t \dots\dots\dots(6)$$

Figure (4) shows variation of the absorption coefficient ( $\alpha$ ) with wavelength for PbS nanocrystalline thin films with different temperatures (30, 40 and 50 °C). As the deposition temperature increases, the film thickness increases which leads to increasing of the absorption coefficient of the prepared samples. Also, we observed gradual shift of absorption edge towards longer wavelengths as the deposition temperature increases. This result can be interpreted as absorption coefficient of the films increased with the bath temperature which shows that thicker films have more atoms present hence more states are available for the photon energy to be absorbed. It can be conclude that PbS has the high absorbing nature [3].

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**Figure 4: Absorption coefficient of nanocrystalline PbS thin films versus wavelength deposited at different temperatures (30, 40 and 50 °C).**

The fundamental absorption, which corresponds to the transition from valence band to conduction band, can be used to determine the band gap of the material. The relation between  $(\alpha)$  and the incident photon energy ( $h\nu$ ) can be written as [15]

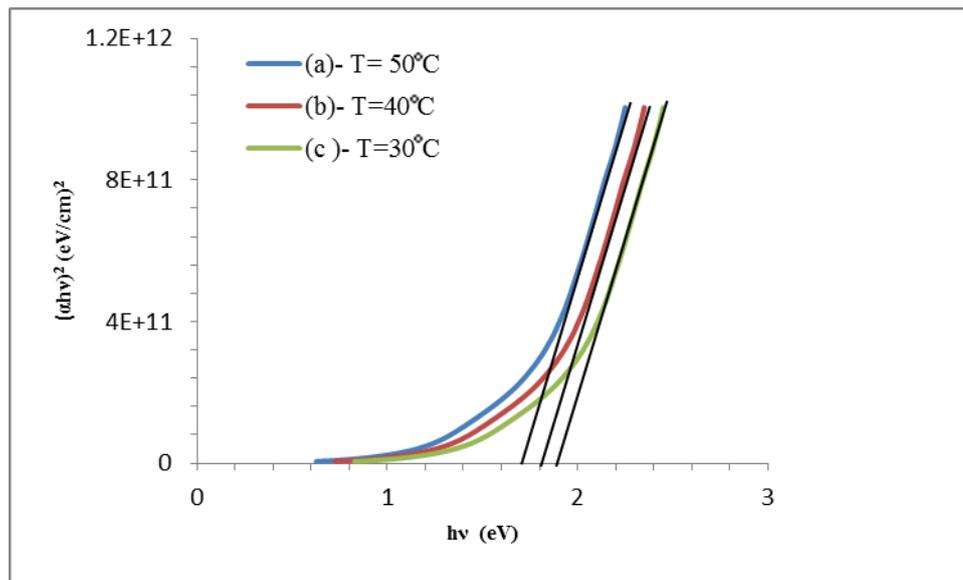
$$(\alpha h\nu) = k (h\nu - E_g)^n \quad \dots\dots\dots (7)$$

Where  $k$  is a constant and  $n$  is the number which characterizes the optical processes  $n=1/2$  for a direct allowed transition (such as PbS), 2 for the indirect allowed transition, 3/2 for a forbidden direct transition and 3 for a forbidden indirect transition. The best linear fit was obtained for  $n=1/2$ . Figure (5) shows the variation of the optical band gap of nanocrystalline PbS thin films versus photon energy at different temperature (30, 40 and 50 °C). The band gap energy was found to depend on the deposition temperature. The band gap decreased as the deposition temperature increased. The results of variation of optical band gap with deposition temperature are summarized in Table (3). The optical band gap obtained using the absorption spectra are greater than the bulk band gap and this indicates the formation of nanoparticles. As the size of

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the semiconductor particle decreases to the nanoscale, the band gap of the semiconductor increases causing a blue shift in the UV-Vis absorption spectra as compared with bulk [16].



**Figure 5: Optical energy gap of nanocrystalline PbS thin films deposited at different temperatures (30, 40 and 50 °C).**

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**Table 3: Variation optical energy band gap with different temperatures.**

Experiment number	pH	Temperature (°C)	Concentration of $(\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})$ and $\text{CS}(\text{NH}_2)_2$ (Molar)	Deposition time (min.)	Eg (eV)
Sample 1	10	30	0.1	40	1.9
Sample 2		40			1.8
Sample 3		50			1.7

### Conclusion

Nanocrystalline PbS thin film was successfully deposited onto glass substrates by chemical bath deposition technique at different temperatures (30, 40 and 50 °C). The X-ray diffraction pattern show that nanocrystalline PbS thin film is polycrystalline with a cubic structure. The deposited films have good adherent to the substrates with various crystallite sizes. The band gap energy was decreased as the deposition temperature increases. The obtain nanocrystalline PbS thin films may be used in optoelectronic device such as absorber layer in solar cells.

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