Mugla Journal of Science and Technology

CHEMICAL BATH DEPOSITION OF PbS THIN FILMS

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Received: 18.08.2020, Accepted: 17.11.2020
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Research Article
DOI: 10.22531/muglajsci.782229

Abstract

In the current study, thin films of PbS were fabricated at 35 ºC bath temperature via chemical bath deposition (CBD) method. During the experiment, 0.1460 M NaOH and 0.0085 M Pb $(NO_3)_2$ were dissolved in 100 ml of deionized water and 0.510 M thiourea was inserted. Thiourea, which is used as the ligand source, was inserted to the solution at zero, one point five, three, six and nine minutes intervals, in 10 parts, unlike conventional production methods. When the first sample was produced, thiourea was inserted to the solution at one time and compared with other samples. XRD patterns were used in determining the structural features of the produced films. XRD patterns show that peak density increased significantly when thiourea was inserted at intervals of three, six and nine minutes. A scanning electron microscope (SEM) was utilized in analyzing the morphological properties of the films. When SEM images were examined, it was observed that when thiourea was inserted at different time intervals, there were no pinholes.

Keywords: Chemical bath deposition, PbS, Thiourea, Thin films

PbS İNCE FİLMLERİN KİMYASAL BANYO YÖNTEMİ İLE BİRİKTİRİLMESİ

Özet

Bu çalışmada, PbS ince filmler 35°C banyo sıcaklığında kimyasal banyo biriktirme (CBD) yöntemi kullanılarak üretilmiştir. Deney sırasında, 0.0085 M Pb $(NO_3)_2$ ve 0.1460 M NaOH, 100 ml deiyonize suda çözündürüldü ve 0.510 M tiyoüre eklendi. Ligand kaynağı olarak kullanılan tiyoüre, çözeltiye geleneksel üretim yöntemlerinden farklı olarak 10 parça halinde sıfır, bir nokta beş, üç, altı ve dokuz dakika aralıklarla ilave edildi. İlk numune üretilirken, tiyoüre çözeltiye tek seferde eklenmiş ve elde edilen numune diğer numunelerle karşılaştırılmıştır. Elde edilen filmlerin yapısal özellikleri XRD desenleri kullanılarak belirlenmiştir. XRD desenleri, tiyoüre üç, altı ve dokuz dakikalık aralıklarla ilave edildiğinde pik şiddetinin önemli ölçüde arttığını göstermektedir. Filmlerin morfolojik özellikleri taramalı elektron mikroskobu (SEM) ile analiz edilmiştir. SEM görüntüleri incelendiğinde tiyoüre çözeltiye farklı zaman aralıklarında ilave edildiğinde elde edilen numunede deliklerin olmadığı görülmüştür.

Anahtar Kelimeler: Kimyasal banyo biriktirme, PbS, Tiyoüre, İnce filmler.

Cite

Önal, M. and Altıokka, B. (2020). "Chemical Bath Deposition of PbS Thin Films", Mugla Journal of Science and Technology, 6(2), 94-98.

1. Introduction

Many different methods such as electro deposition, chemical bath deposition (CBD), ultrasound deposition, vacuum evaporation, spray pyrolysis, ultrasound deposition, and pulsed laser deposition are used to produce PbS thin films [1], [2].The chemical bath deposition method is an easy, efficient and inexpensive method that is widely used to produce thin-film with many different materials [3]. The CBD method can be used for the production of PbS thin films with high-quality since parameters such as stirring speed, deposition temperature, deposition time and solution pH can be easily controlled [4].

Synthesis, characterization of nanocrystalline semiconductors and the production of possible devices are of great interest. II-VI and IV-VI semiconductor groups are mostly used due to their potential in various optoelectronic devices [5]. Among the IV-VI compounds, PbS is one of the materials of considerable interest due to its wide variety of applications such as thin films solar cells, light-emitting diodes, optical switches, infrared detectors, display circuits [6], [7]. This semiconductor with a strong quantum size in nanocrystalline form has a narrow band gap of 0.41 eV. Its direct band gap can be varied in a range of (0.41–2.3 eV). PbS has a large excitation Bohr radius such as 18 nm. Band gap of PbS can be determined to the visible region by the formation of nanocrystals [7]. PbS has been gown in cubic phase, which is a mineral of lead sulfide with a chemical composition of PbS[8].

The reaction process of the lead sulfur films formation in the chemical bath deposition is as follows [9];

$$Pb(NO_3)_2 + 2NaO \rightarrow Pb(OH)_2 + 2NaNO_3 \quad (1)$$

$$Pb(OH)_2 + 4NaOH \rightarrow Na_4Pb(OH)_6 \quad (2)$$

$$Na_4Pb(OH)_6 \rightarrow 4Na^+ + HPbO^{-2} + 3OH + H_2O \quad (3)$$

$$SC(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + SH^- \quad (4)$$

$$HPbO^{-2} + SH^- \rightarrow PbS + 2OH^- \quad (5)$$

When the literature is examined, it is seen that PbS thin films are produced in very wide bath temperature ranges such as 20 °C [10], 25°C[11] 30°C[12], 40°C, 55, 65, 70 and 80°C[13], 80°C[14] and 90°C [15].

In the current study, the temperature of the solutions was 35 °C, which was a temperature in this range. In addition, in the study, unlike the practices in the literature, thiourea was subdivided into 10 parts and inserted to the solution at intervals of zero, one point five, three, six and nine minutes. Therefore, the problems of pinholes and cracks in the films produced by the traditional method were eliminated.

2. Experimental Procedure

PbS thin films were obtained by using chemical bath deposition method. Before starting the deposition process, the glass substrates and the bath container were washed with acetone and rinsed with distilled water. 0.1460 M NaOH (sodium hydroxide), 0.510 M $CS(NH_2)_2$ (thiourea) and 0.0085 M $Pb(NO_3)_2$ (lead nitrat), and were dissolved in 100 ml of pure water. However, 0.510 M thiourea, except for the first sample, was subdivided into 10 equal parts and inserted to the solution at one point five, three, six and nine minute intervals. Thus, the depositions were ended 25, 38.5, 52, 79 and 106 minutes according to the delay time of 0, 1.5, 3, 6 and 9 minutes respectively. The bath temperature was kept at 35 °C degrees for all experiments. The solutions were mixed at 600 rpm with a magnetic stirrer.

Table 1. Experimental conditions

Experiments	$Pb(NO_3)_2$ (M)	NaOH (M)	$CS(NH_2)_2$ (M)	Delay time intervals (minutes)	Stirring (rpm)
DT0	0.0085	0.146	0.051	0.0	600
DT1.5	0.0085	0.146	0.051	1.5	600
DT3	0.0085	0.146	0.051	3.0	600
DT6	0.0085	0.146	0.051	6.0	600
DT9	0.0085	0.146	0.051	9.0	600

When PbS film deposited on glass substrates was completed, each sample was washed with pressurized water and allowed to dry at room temperature. Before starting all these procedures, the bath container and the glass substrate were washed with acetone and ww 5% hydrochloric acid solution and then rinsed with deionized water.

In the study, lead nitrate was source of Pb^{2+} and thiourea S^{2-} ion. In addition to being used as sodium hydroxide complex agent, it provided PH control.

The samples were named as to be PbS0, PbS1.5, PbS3, PbS6 and PbS9, according to delay time of zero, one point five, three, six and nine respectively. To calculate the film thicknesses, gravimetric method was used. Experimental parameters are given in Table 1. A Zeiss SUPRA 40VP SEM (scanning electron microscope) was employed in order to analyze the surface morphology of the PbS thin films. A PANalytical Empyrean XRD (X-ray diffractometer) was employed in order to analyze the structural properties of the PbS thin films.

3. Result and Discussion

3.1. Structural investigation of PbS films

Film thicknesses, calculated using gravimetric method, were found to be average 700 nm. The structural parameters of PbS thin films are presented in Table 3. It is seen from the X-ray diffractometer patterns given in Fig.1 that all films formed in cubic structure.

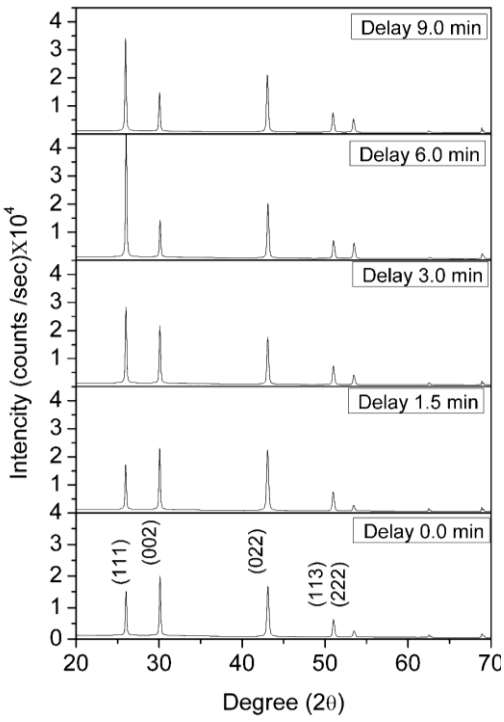

Figure 1. XRD patterns of PbSthinfilms

To use the ASTM card 98-003-8293, the standards of X-ray diffraction data was verified by using with (2θ) the peak positions of the XRD patterns of the films. The diffraction peaks were seen at diffraction angles 2θ of 25.987°, 30.095°, and 43.081°, subtend to the (111), (002), and (022) planes of the cubic PbS form. For the cubic phase structure the ' a 'lattice constant is determined by the relationship [16]

$$a = d(h^2 + k^2 + l^2)^{1/2} \quad (6)$$

In the equation, d is the planar distance values while h, k and l are Miller indices. The calculated lattice constant values are seen to be almost the same as the ASTM card 5,934 Å values given in the crystallographic parameters of the galena ASTM card.

In the calculation of the preferred orientation of the films, the texture coefficient was used, and is given in Eq. 7[17]

$$TC = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{N}\sum N(\frac{I_{(hkl)}}{I_{0(hkl)}})} \quad (7)$$

In this formula: I (hkl) is the measured relative intensity of a plane (hkl), Io (hkl) is the standard intensity of (hkl) plane and N is the number of diffraction peaks, Texture coefficient values calculated using this formula are given in Table .2. The values in Table .2 show that the preferred orientation has changed from plane (002) to plane (111) depending on the delay time intervals of the addition of thiourea.

Table 2. Texture coefficient of PbS thin films

Experiment	DT0	DT1.5	DT3	DT6	DT9
T.C.(111)	0.779	0.730	1.16	1.585	1.769
T.C.(002)	1.010	0.944	0.83	0.446	0.533
T.C.(022)	1.210	1.325	1,01	0.967	1.138

While the peak intensity is approximately the same when the delay time is 0 and 1.5 minutes, there is a noticeable increase in peak intensity when the delay time increases to 6 and 9 minutes. Although the calculated film thicknesses were the same, the high peak intensity in PbS6 and PbS9 was such an indication that crystallization was good. It has known from previous studies that crystallization was better when the reaction rate was reduced [10]. Debye Scherrer formula was used for the calculation of the average crystallite size of the thin films and this formula is given in the Eq.8.

$$cs = \frac{0.089*180*\lambda}{314*\beta*\cos\theta_C} \text{nm} \quad (8)$$

where β was the full width of half maximum, $2\theta_C$ was the peak center, λ was the wavelength of X-ray radiation (1.54056 Å), β and $2\theta_C$ were calculated by fitting the XRD peak profile [18].The calculated crystallite sizes are given in Table 3. Table 3 shows that the crystallite size of the film was 39,776 nm when thiourea was added into the solution at one time. On the other hand, when thiourea was inserted at various delay times, the crystallite size was increased up to 47.046 nm. The previous study in the literature indicated that the crystallite size depends on the reaction rate [10].

Table 3. Structurel parameters of the PbS thin films

Experiment	Crystallite Size average (nm)	Latticeparameter a (corrected) (Å)	Micro strain $*10^{-3}$	DislocationDensity (lines/m^2)$*10^{14}$
DT0	39,776	5.937	2.41	6.314
			(7(7)	
DT1.5	41,315	5.944	2.41	5.858
DT3	47,046	5.939	2.27	4.518
DT6	46,647	5.935	2.26	4.595
DT9	41,443	5.948	2.27	5.808

The crystallite size was used for calculating dislocation density given in Eq.9 [19]

$$\delta = \frac{1}{(cs)^2} \quad (9)$$

When thiourea was inserted to the solution at once, Dislocation density was found to be highest. This result showed that the crystallite size was reduced depending on the time of the addition of thiourea.

3.2 SEM analysis of the PbS films

SEM images magnified 30,000 times to examine the surface morphology of the obtained PbS thin films are given in Fig. 2. It was understood that the thin films obtained had a very good adhesion on the glass substrate, the surface morphology was smooth and they were of high quality. The only exception was that there were local pin holes on the film surface when thiourea was inserted to the solution without time delay. When the thiourea addition time intervals were increased from 1.5 minutes to 9 minutes, particle size increased, there voids and pinholes were not seen on the film surfaces. This study showed that the addition of thiourea to the solution at different time intervals changes the reaction rate, and this change has a positive effect on better crystallization and compact structure.

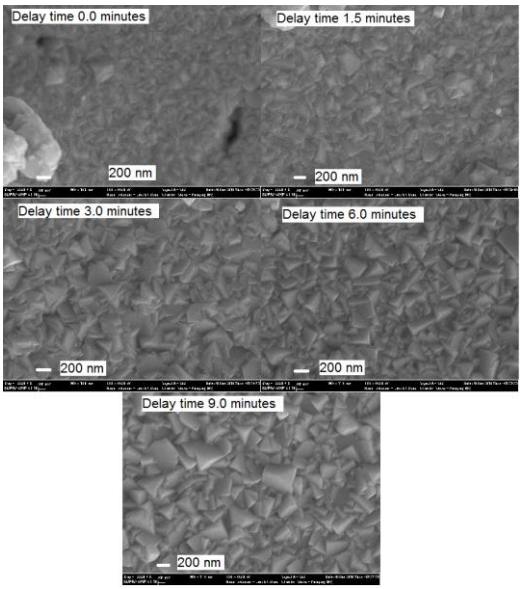

Figure 2. SEM images of PbS thin films at 30000 times magnification.

4. Conclusions

In this study, PbS thin films were fabricated by using the CBD method. When producing thin films, thiourea was inserted to the final solution at specific time intervals. Between delay time of zero and nine, XRD analysis showed that addition time of thiourea changed the crystal orientation, which causes the crystallite size to change. The variation of the crystallite size causes the bandgap change.

When thiourea was inserted to the final solution at one time, it was seen that there were holes on the film surface. On the other hand, when thiourea was inserted at certain time intervals, there were no pinholes and voids on the surface and surfaces of these films were quite compact.

This study showed that pinhole-free thin films can be produced depending on the delay time of thiourea addition.

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