BŞEÜ Fen Bilimleri Dergisi
8(2), 1017-1023, 2021

BSEU Journal of Science
https://doi.org/10.35193/bseufbd.996335

BİLECİK ŞEYH EDEBALİ ÜNİVERSİTESİ

e-ISSN: 2458-7575 (https://dergipark.org.tr/tr/pub/bseufbd)

Araştırma Makalesi-Research Article

Pinhole-Free PbS Thin Films Obtained by Chemical Bath Deposition Method

Kimyasal Banyo Biriktirme Yöntemiyle Elde Edilen İğne Deliksiz PbS İnce Filmler

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Geliş / Received: 16/09/2021 ***Revize / Revised: 02/11/2021*** ***Kabul / Accepted: 09/11/2021***

ABSTRACT

In this study, the (Lead Sulfide) PbS thin films with one, two, and three layers were fabricated by employing the chemical bath deposition method. Layer by layer production of PbS thin films was realized for the first time as seen in the literature review. For investigating the crystal structures, the X-ray diffraction (XRD) analysis was used. The structural analyses indicated that the crystallite size was decreased from about 40 nm to 8-10 nm depending on the number of layers. The surface micrographs of the films were obtained using scanning electron microscopy (SEM). When the PbS film was obtained in one layer, some cracks, pinholes, and voids were observed on the sample surface. However, no cracks, voids, or pinhole formation were found on the film surface when the films were coated in two and three layers.

Keywords- PbS, Characterization, Materials, Thin Film, CBD

ÖZ

Bu çalışmada, kimyasal banyo biriktirme yöntemi kullanılarak tek, iki ve üç katmanlı (Kurşun Sülfür) PbS ince filmler üretilmiştir. Literatür taramasında görüldüğü gibi, PbS ince filmlerin katman katman üretimi ilk kez gerçekleştirilmiştir. Kristal yapılarını araştırmak için X-ışını difraktometre (XRD) analizi kullanıldı. Yapısal analizler kristalit boyutunun tabaka sayısına bağlı olarak yaklaşık 40 nm'den 8-10 nm'ye düştüğünü göstermiştir. Filmlerin yüzey görüntüleri taramalı elektron mikroskobu (SEM) cihazı ile incelenmiştir. PbS filmi tek kat olarak elde edildiğinde numune yüzeyinde bazı çatlaklar, iğne delikleri ve boşluklar gözlenmiştir. Ancak filmler iki ve üç kat kaplandığında film yüzeyinde herhangi bir çatlak, boşluk veya iğne deliği oluşumu görülmedi.

Anahtar Kelimeler- PbS, Karakterizasyon, Malzeme, İnce Film, KBB

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BSEU Journal of Science
https://doi.org/10.35193/bseufbd.996335

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I. INTRODUCTION

Lead sulfide (PbS) is a very useful semiconductor material for various technological applications including absorber layers in thin-film solar cells [1,2], heterojunction photo voltaic cells [3,4], thermoelectric devices [5,6], infrared radiation detectors, [7,8] and chemical sensors [9]. Among the IV-VI semiconductors, PbS is an important direct narrow-gap semi-conductor material with a band gap energy of 0.4 eV and it has a cubic lattice with a unit cell face centre cube[10]. PbS thin films have been deposited by several methods, such as thermal evaporation [11], galvanic method [12], electro deposition [13], pulsed laser deposition [14], spray pyrolysis [15], successive ionic layer adsorption and reaction (SILAR) [16–18], atomic layer deposition [19], sol–gel [20], chemical vapour deposition (CVD), [21] and chemical bath deposition (CBD) [22].The chemical bath deposition technique is quite simple compared to other techniques. It can be applied at low temperatures. It has a low process cost, and it can be easily applied to large surfaces [23]. The PbS precipitation process is as follows [24]:

$$Pb\,(NO_3)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaNO_3$$

$$(OH)_2 + 2NaOH \rightarrow Na_2\,[Pb(OH)_4]$$

$$[(OH)4\,]^{2-} \rightarrow Pb^{2+} + 4OH^- \quad (1)$$

Furthermore, the hydrolysis of thiourea (TU) $(NH_2)_2$, in the solution releases S^{2-} ions as below:

$$(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \rightarrow H_2O + S^{2-} \quad (2)$$

When the Pb^{2+} and S^{2-} ions exceed the solubility limit in solution, the insoluble solid PbS precipitate as below:

$$Pb^{2+} + S^{2-} \rightarrow PbS \quad (3)$$

According to the literature, when the PbS was obtained by chemical bath deposition, there occurred an important problem, such as cracks and pinholes [25,26]. These problems were eliminated in this study, in which the PbS films were produce done, two, and three times in arow. It was discovered that when the film was produced as two layers, the film surface was very compact and smooth.

II. EXPERIMENTAL DETAILS

Polycrystalline PbS thin films were produced by the chemical bath deposition (CBD) method onto glass substrates. In the experiment, thin films of PbS were obtained as one, two, and three layers. Before the depositions, the glass substrate surface and the bath container were washed with 10% HCl acid in order to remove the impurities and residuals. After that, they were rinsed with deionized water. Referring to the literature [27]; 0.0085 M Pb $(NO_3)_2$ and 0.1460 M NaOH were put in in 100ml deionized water, after then 0.510 M $SC(NH_2)_2$ thiourea added into the solution and mixed at 20 ℃. The pH of the final solutions was measured as 11.5. The chemical reaction of the solution started in a short time, in about 30 seconds. The depositions were ended after 40 minutes. After precipitation, the samples were rinsed with deionized water.

The crystal structure of the PbS films was investigated by employing an X-ray diffractometer, which is a PANALYTICAL-EMPYREAN X-ray diffractometer, for 2θ in range 20°-70°. As a radiation source, we used Cu-Kα radiation with a scan rate of 2 °/min. The surface morphologies of the samples were analyzed by a Zeiss Supra 40VP SEM.

III. RESULTS

A. Structural analysis

XRD analysis was carried out on PbS films and typical diffraction patterns of PbS thin films prepared by chemical bath deposition technique on glass substrates were analyzed with different thickness values. The XRD patterns are presented in Figure 1.

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e-ISSN: 2458-7575 (https://dergipark.org.tr/tr/pub/bseufbd)

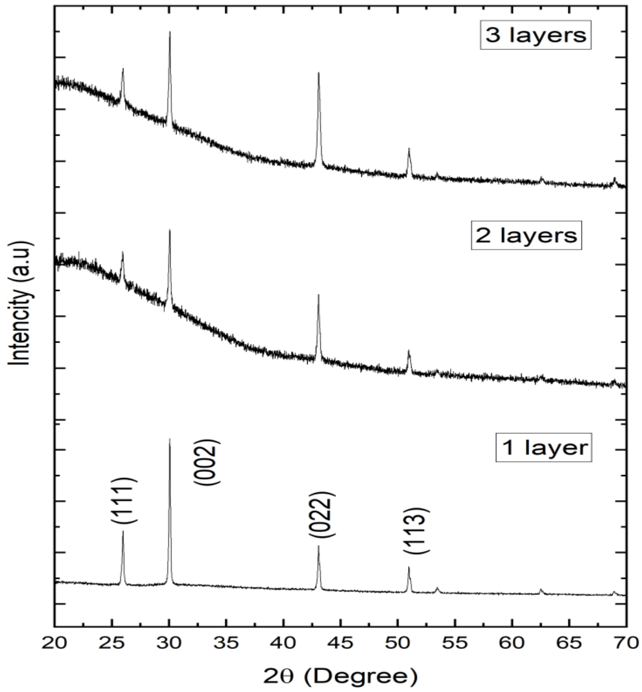

Figure 1. XRD Samples of the PbS films

The film thicknesses were calculated by the well-known gravimetric method. The film thicknesses were calculated as 620 nm, 950 nm, and 1200 nm for one layer, two layers, and three layers, respectively.

The XRD schema is presented in Figure1. According to Figure1, the good crystallization is seen in the one-layer film. Two and three-layers film patterns showed relatively low crystallization. All peaks were related to the galena type cubic crystals according to the 98-060-0243 ASTM card no.

For calculating crystallite, the Debye-Scherer equation which is given in Equation (4) was used;

$$\mathrm{cs} = \frac{0.089*180*\lambda}{314*\beta*\cos\theta_C}\,\mathrm{nm} \tag{4}$$

where β is full width half maximum (FWHM), λ is the wavelength of X-ray radiation (1.54056 Å) and 2θC is the peak centre (28).

Table 1 presents the crystallite sizes of the samples. According to Table.1, the amazing results are noticed. When the thin films were produced as two and three layers, the crystallite sizes decreased about 5 times. Quantization effects are observed when the crystallite size of a semiconductor is near to or less than the bulk Bohr exciton radius [29,30]. Generally, when the crystallite size of PbS quantum dots decreases to 5–18 nm, it is seen [31].

Table 1. The thicknesses and crystallite sizes of the PbS films

Experimental	Thickness	Average crystallite size
One Layer	620 nm	40.99nm
Two Layers	950nm	8.15nm
Three Layers	1200nm	10.20nm

B. SEM images of the PbS films

The 10000 times magnified surface images are given in Figure 2. There can be seen plenty of cracks and pinholes on the surface of the one-layer PbS film. However, when the films were produced as two or three layers, the surface became compact and smooth.

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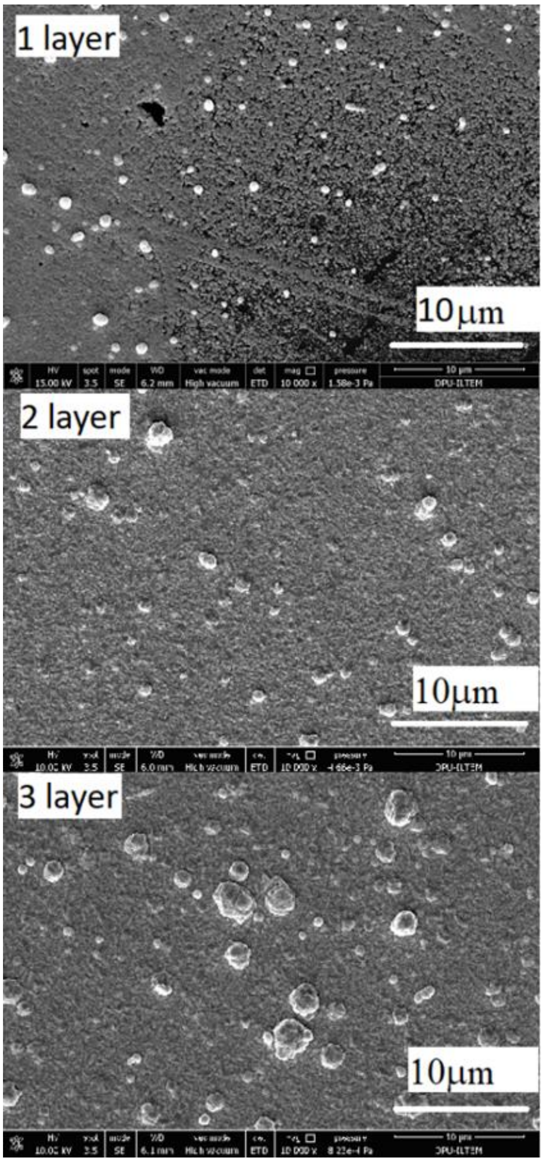

Figure 2. 10000 times magnified surface images of PbS films

In Figure 3, the surface images magnified 40000 times are given. According to these images, when the film was obtained as one layer, there were voids on the surface. On the other hand, when the films were obtained as two and three layers, the surfaces were quite compact and pinhole-free.

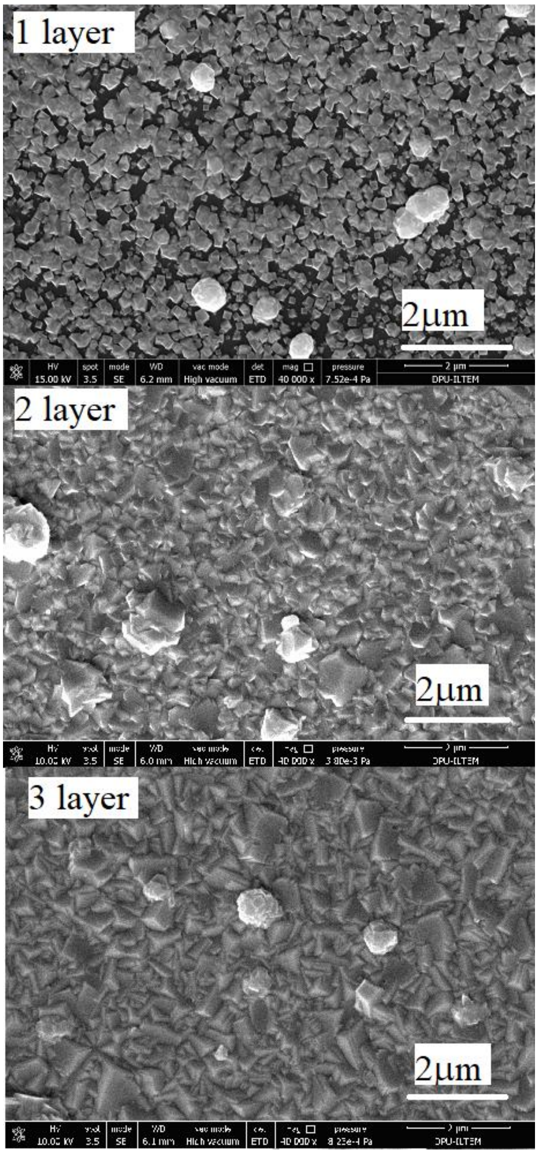

Figure 3. 40000 times magnified surface images of PbS films

C. The visual properties of the PbS films

The visual photos of the PbS thin films are given in Figure 4. According to the photos, the film obtained as one layer is relatively dark. On the other hand, the other samples are relatively weak. It was concluded that the differences in the colour could be due to crystallite sizes.

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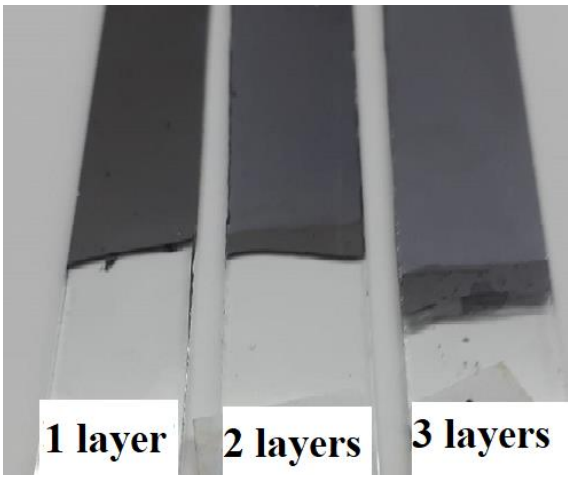

Figure 4. The surface photographs of the PbS films

IV. DISCUSSION

In this study, thin films of PbS were grown on glass substrates by using the CBD method. The PbS films were deposited as one, two, and three layers. The two and three layers of PbS films were obtained for the first time. The structural analysis was realized by using XRD pattern. All films were formed in galena type cubic structure. According to the patterns, the crystallite size was decreased from 40 nm to 8-10 nm. The morphologic characteristics were investigated by SEM images. According to the both 10000-times and 40000-times magnified SEM images, when film was obtained one layer, there were plenty of cracks and voids on surface. The problem of cracks and holes was solved by producing films in two and three layers on top of each other.

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