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Structural and Physical Properties of the PbS Films Obtained by Chemical Bath Deposition at Different Deposition Temperature

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Abstract

In the present study, structural and physical properties of the PbS thin films produced using chemical bath deposition method were investigated. Deposition temperature was varied between 25 °C and 50 °C throughout the deposition period. The pH value of electrolyte solution and the deposition time of the films were 10.5 and 25 min, respectively. Characterizations of the PbS thin films were performed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods. XRD results showed that all PbS thin films had a cubic structure irrespective of deposition temperature. Morphological characterizations of the films indicated that not only the number but also the size of pinholes, formed on the film surfaces, were significantly affected by the deposition temperature. Consequently, the film obtained at 25℃ exhibited a surface morphology with less and smaller pinholes, compared to others deposited at higher deposition temperatures.

Keywords: Chemical bath deposition, Thin film, Lead nitrate, Thiourea, Pinhole

1. INTRODUCTION

Recently, interest in nanoscale lead sulphide (PbS) has increased in solar photovoltaics due to their extraordinary exciting physical properties and potential applications [1]. PbS is an important dual IV-VI semiconductor material [2] with a direct narrow optical energy gap (0,41 eV at 300 K) and a relatively large excitation Bohr radius (18 nm). Thus, by controlling the crystallite size, it provides strong quantum and electron confinement that varying the band gap value. PbS thin films have become a comprehensive research topic due to their wide applications such as gas sensors, infrared radiation detectors, optoelectronics, solar cells, diode lasers, etc. [3]. There is dry and wet method to produce PbS. Vacuum evaporation; hot wall epitaxy and molecular beam epitaxy are among the most successful "dry" methods for PbS synthesis. Frequently used "wet" methods, spray pyrolysis, electrochemical deposition and chemical bath deposition [4]. Among these methods, CBD is relatively less expensive, easy to use and can cover large surfaces. Some metal doppings to PbS films were investigated to varied in the electrical properties of the film materials. The dopping to the PbS thin film precipitate is intended to increase the electrical conductivity or resistivity [5].

The reactions for the formation of PbS are given by [6] as follows:

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

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

$$[Pb(OH)_4]^{2-} \rightarrow Pb^{2+} + 4OH^- \quad (3)$$

$$CS(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + HS^- \quad (4)$$

$$HS^- + OH^- \rightarrow H_2O + S^{2-} \quad (5)$$

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$$Pb^{2+} + S^{2-} \rightarrow PbS \quad (6)$$

2. MATERIALS AND METHODS

PbS thin films were deposited on the chemically cleaned substrate. Glass substrates were cleaned using nitric acid and isopropyl alcohol. After this process, the glass substrates were washed with distilled water. To prepare the PbS thin films, aqueous solutions of 0.0090 M $Pb(NO_3)_2$ (lead nitrate) and 0.051 M $CS(NH_2)_2$ (thiourea) were mixed together by rotating at 600 rpm. The pH value of the prepared bath solution was adjusted to 10.5 by adding dropwise of NH_3. The volumes of bath solutions were choosen as to be 90 mL. The glass substrates are immersed vertically in the bath solution. The bath temperatures were varied between 25 °C and 50 °C. Deposition duration was choosen as to be 25 minutes. Deposition parameters are shown in Table 1. After the deposition, the glass is covered with PbS on both sides of the substrates. After the deposition, the substrates were washed with distilled water and dried in the air. However, the other side of surface was cleaned with 10% dilute hydrochloric acid.

PANalytical Empyrean XRD (X-ray diffractometer) was used to analyze the structural properties of the produced PbS thin films. Thicknesses of PbS thin films were calculated by gravimetric method. Zeiss SUPRA 40VP SEM (scanning electron microscope) was used to analyze the surface morphology of the PbS thin films.

Table 1. Deposition parameters

Experiments	$Pb(NO_3)_2$ (M)	$CS(NH_2)_2$ (M)	Deposition Timedk	Solution Volume mL	Deposition Temperature ^{0}C	pH
D1	0,0090	0,051	25	90	25	10,5
D2	0,0090	0,051	25	90	30	10,5
D3	0,0090	0,051	25	90	35	10,5
D4	0,0090	0,051	25	90	40	10,5
D5	0,0090	0,051	25	90	45	10,5
D6	0,0090	0,051	25	90	50	10,5

2.1. The X-ray Analysis of the PbS films

The properties of the films examined by XRD technique such as crystal structure, crystalite size, preferential orientation, strain and stress acting on the unit surface have been determined.

XRD analyzes of PbS thin films produced in D1, D2, D3, D4, D5 and D6 are given in Figure 2.1. The peaks of 25.9 °; 30 °; 43 °; 50.9 °; 53.4 °; 62.5 ° and 68.9 ° belong to the (111), (002), (022), (113), (222) and (133) planes of PbS respectively. These peaks were examined and found to be in conformity with the ASTM number (98-060-0243). In XRD analyzes, it was determined that all films were in cubic structure. In addition, the film obtained in D6 has a higher XRD peak intensity than the others. The calculated film thicknesses for the produced PbS thin films were measured using gravimetric analysis and tabulated.

The TC (Texture coefficient) is used to determine the preferential orientation of the PbS thin films. It is not mentioned that if there are two or more TC bigger than 1 [7-10]. The value of the texture coefficient of the films obtained in this study is calculated using equation (7) for any (hkl) reflection plane and they are given in Table 2.

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

The crystalite sizes of the films obtained in this study were calculated by the Scherrer formula which is given in Eq. (8) and the crystallite sizes are also given in Table 3.

$$D = \frac{0{,}9\lambda}{B(radyan)cos(\theta_B)} \quad (8)$$

Where D is the crytallite size, λ the wavelength of the x-ray used in the diffraction, the width at half maxima of the considered peak B, and θ_B the peak angle Bragg reflection angle [11]. The lattice constant for the cubic rock salt structure is calculated by using the Equation (9).

$$a = d\sqrt{(h^2 + k^2 + l^2)} \quad (9)$$

where h, k and l are Miller indices, and d is the distance between planes [12].

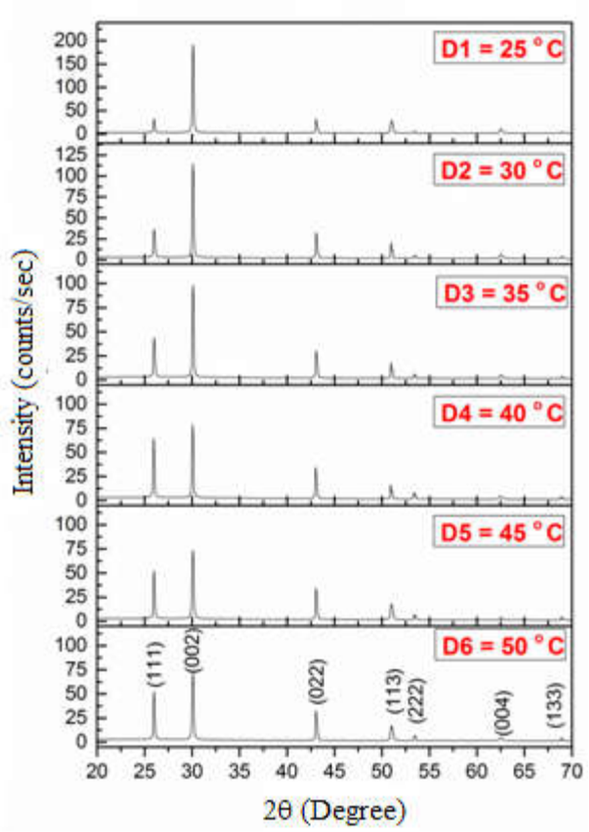

Figure 2.1XRD analysis of PbS thin films produced in D1, D2, D3, D4, D5 and D6

Furthermore, average stress and micro strain for all planes were calculated using Equation (10) and Equation (11), respectively, and they are given in Table 3.

$$S = \varepsilon Y/(2\sigma) \quad (10)$$

$$\varepsilon = (a_0 - a)/a_0 \quad (11)$$

where, a_0 the lattice parameter of the bulk sample a is the corrected value of the lattice parameter of a thin film samples, σ is the poisson ratio of bulk crystal and Y is Young's modulus. The value of Y for PbS is 70.2GPa and σ value is taken as 0.28. Using Nelson-Riley graphs, the corrected values were calculated and it is given in Figure 2.2

Table 2. XRD intensities of the obtained PbS thin films, calculated constructions coefficient values of the obtained PbS thin films and calculated film thicknesses of the obtained PbS thin films using gravimetric analysis

EXPERIMENT	2θ	INTENSITY (COUNT/SECONDS)	I/I_0	TC	*(hkl)*	FILM THICKNESS (nm)
D1	**25,908**	**52567,39**	**73,5**	**1,88**	**(111)**	**510**
	30,062	**71462,92**	**100**	**2,56**	**(002)**	
	43,053	**32439,97**	**53,96**	**1,38**	**(022)**	
	50,997	16389,33	25,08	0,64	(113)	
	53,430	7088,885	9,91	0,25	(222)	
	62,511	4914,722	5,17	0,13	(004)	
	68,901	4306,281	5,88	0,15	(133)	
D2	**25,977**	**52318,55**	**70,91**	**1,83**	**(111)**	**568**
	30,058	**73564,56**	**100**	**2,57**	**(002)**	
	43,048	**34572,57**	**54,32**	**1,40**	**(022)**	
	50,991	17232,60	24,76	0,64	(113)	
	53,427	7579,82	10,53	0,27	(222)	
	62,505	4363,98	5,53	0,14	(004)	
	68,895	4235,38	5,82	0,15	(133)	
D3	**25,969**	**59329,36**	**78,39**	**2,02**	**(111)**	**620**
	30,061	**75202,36**	**100**	**2,58**	**(002)**	
	43,043	**34592,34**	**47,86**	**1,24**	**(022)**	
	50,961	16235,01	23,64	0,61	(113)	
	53,412	7263,76	11,07	0,29	(222)	
	62,515	5107,37	5,21	0,13	(004)	
	68,884	3006,55	4,99	0,13	(133)	
D4	**25,994**	**42867,76**	**38,47**	**1,32**	**(111)**	**692**
	30,075	**97401,34**	**100**	**3,42**	**(002)**	
	43,067	**30476,23**	**32,36**	**1,11**	**(022)**	
	50,973	18028,77	20,46	0,70	(113)	
	53,432	6318,23	5,69	0,19	(222)	
	62,510	5569,29	4,47	0,15	(004)	

	68,900	3841,97	3,19	0,11	(133)	
D5	**25,989**	**36445,56**	**27,04**	**1,00**	**(111)**	**755**
	30,073	**114354,1**	**100**	**3,71**	**(002)**	
	43,068	**32737,47**	**29,8**	**1,11**	**(022)**	
	50,973	20435,37	20,08	0,75	(113)	
	53,441	5643,00	4,03	0,15	(222)	
	62,514	6922,47	4,81	0,18	(004)	
	68,913	4062,92	2,76	0,10	(133)	
D6	25,987	32453,65	14,54	0,66	(111)	**864**
	30,075	**190282,6**	**100**	**4,51**	**(002)**	
	43,062	31844,11	17,36	0,78	(022)	
	51,005	26374,83	14,47	0,65	(113)	
	53,430	5551,34	2,35	0,11	(222)	
	62,515	10681,27	4,86	0,22	(004)	
	68,907	4035,55	1,64	0,07	(133)	

The calculated lattice parameters of the produced films are plotted versus $\boldsymbol{F(\theta)}$and given in Equation (12)

$$F(\theta) = (cos^2\theta/2) * (\frac{1}{sin^2\theta} + \frac{1}{\theta}) \quad (12)$$

$$(cos^2\theta/2) * (\frac{1}{sin^2\theta} + \frac{1}{\theta}) = 0 \quad (13)$$

Equation (13)which is the linear line cut off point, provides the presence of the corrected lattice constant and is given in Table 3 [13]. The dislocation density of the produced films can be derived from the crystalite size as given in Equation (14) and is given in Table 3 [3].

$$\delta = \frac{1}{(D)^2} \quad (14)$$

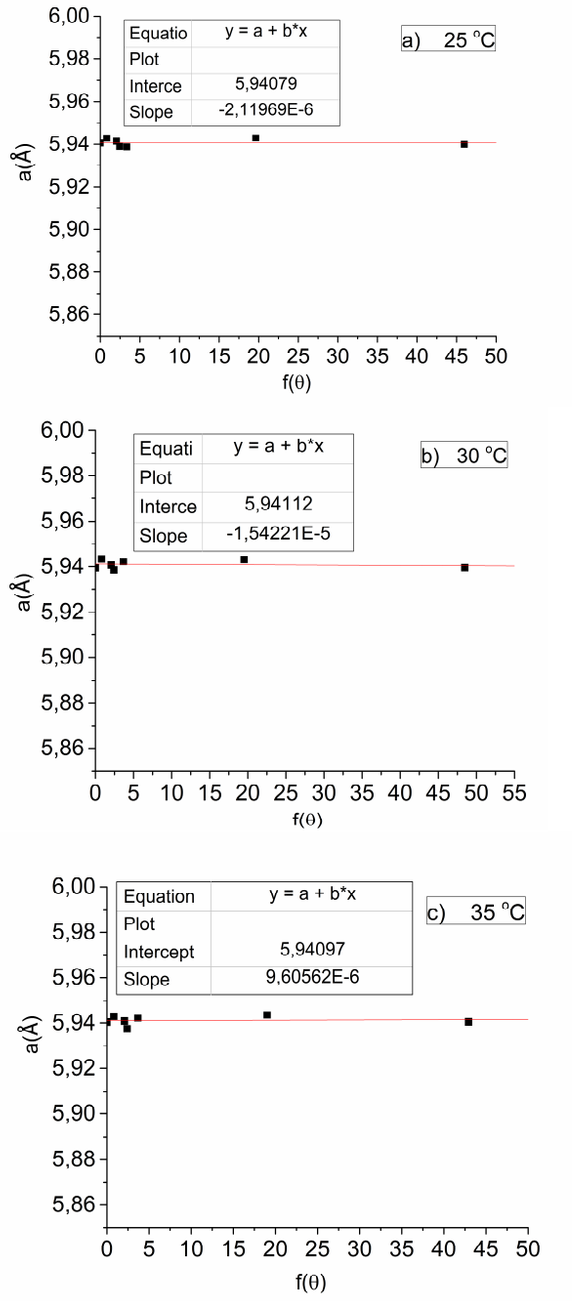

Figure 2.2 Nelson-Riley graphs of PbS thinfilms a) D1, b) D2 and c) D3

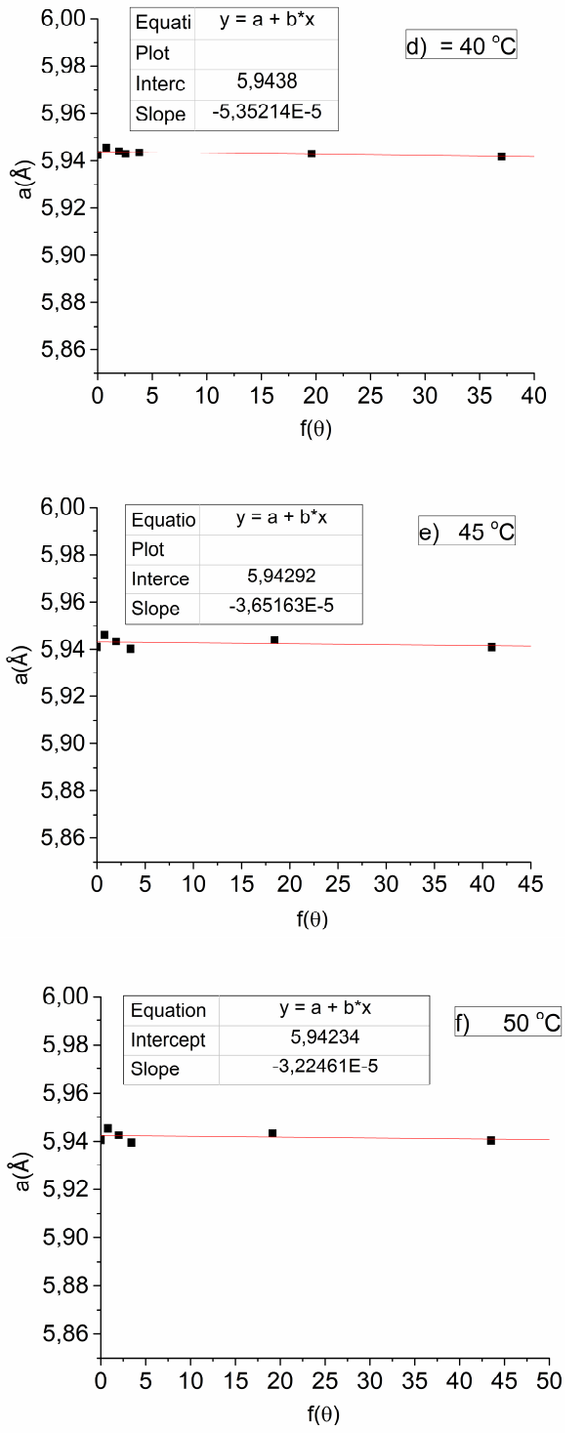

Figure 2.2 Nelson-Riley graphs of PbS thin films d) D4, e) D5 and f) D6

Table 3. The particle sizes, dislocation densities, confirmed weave parameters, micro tensile values and average stress values of the produced PbS thin films obtained from D1, D2 to D3, D4 and D5

EXPERIMENT	2θ	CRYSTALITE SIZE (nm)	LATICE PARAMETER a (VERIFIED) (Å)	MİKRO STRAİN *10-4	DISLOCATION DENSITY (lines/m²)*10¹⁴	AVERAGE STRESS (10⁷N/m²)
D1	25,908	63,00	5,94038	7,38	2,52	9,25
	30,062	52,97	5,94538	15,80	3,56	19,8
	43,053	66,00	5,94261	11,14	2,30	14,0
	50,997	42,50	5,93954	5,97	5,54	7,48
	53,430	68,74	5,94055	7,67	2,12	9,62
	62,511	29,92	5,94336	12,40	11,2	15,5
	68,901	93,09	5,94035	7,33	1,15	9,19
D2	25,977	63,01	5,9410	8,49	2,52	10,6
	30,058	52,97	5,9461	17,01	2,47	21,3
	43,048	66,00	5,9432	12,18	1,47	15,3
	50,991	42,50	5,9402	7,03	5,53	8,82
	53,427	85,94	5,9409	8,25	1,35	10,3
	62,505	89,79	5,9439	13,27	4,96	16,6
	68,895	93,09	5,9408	8,14	1,15	10,2
D3	25,969	63,01	5,9429	11,67	2,52	14,6
	30,061	63,57	5,9455	16,11	2,47	20,2
	43,043	66,00	5,9439	13,47	2,30	16,9
	50,961	85,04	5,9434	12,56	1,38	15,7
	53,412	85,93	5,9424	10,88	1,35	13,6
	62,515	44,88	5,943	11,79	4,97	14,8
	68,884	93,08	5,9417	9,606	1,15	12,0
D4	25,994	52,50	5,9374	2,36	3,63	2,96
	30,075	63,58	5,9429	11,56	2,47	14,5
	43,067	66,01	5,9408	8,04	2,30	10,1
	50,973	85,04	5,9422	10,44	1,38	13,1
	53,432	85,94	5,9403	7,32	1,35	9,18
	62,510	44,88	5,9434	12,53	4,97	15,7

	68,900	93,09	5,9404	7,48	1,15	9,37
D5	25,989	52,50	5,938	4,19	3,63	5,26
	30,073	63,58	5,943	12,3	2,47	15,4
	43,068	66,01	5,941	7,85	2,30	9,84
	50,973	85,04	5,942	10,4	1,38	13,1
	53,441	68,74	5,939	5,75	2,12	7,20
	62,514	35,91	5,943	11,93	7,75	15,0
	68,913	74,46	5,939	5,86	1,80	7,35
D6	25,987	63,01	5,9389	4,90	2,52	6,14
	30,075	63,58	5,9428	11,6	2,47	14,5
	43,062	66,01	5,9413	9,09	2,30	11,4
	51,005	42,50	5,9387	4,57	5,54	5,73
	53,430	85,94	5,9405	7,67	1,35	9,62
	62,515	35,91	5,943	11,8	7,75	14,8
	68,907	74,46	5,9399	6,60	1,80	8,27

2.2. SEM Analysis of the PbS Thin Films

The surface morphologies of the obtained PbS thin films were examined by using JEOL SM-5600LV electron microscope. The SEM images of the PbS thin films with 100 and 30.000 magnificationsare shown in Figure 2.3. As clearly seen from Fig. 2.3, there are pinholes on the surfaces of the films regardless of deposition temperature. Furthermore, the deposition temperature significantly influenced the number and the size of pinholes observed on the film surfaces. As the deposition temperature increased, the pinholes in the SEM images were observed to be larger and larger. Furthermore, the number of pinholes also increased with increasing deposition temperature.

As seen from Figure 2.3a, the granules were observed to be polymorphic form.

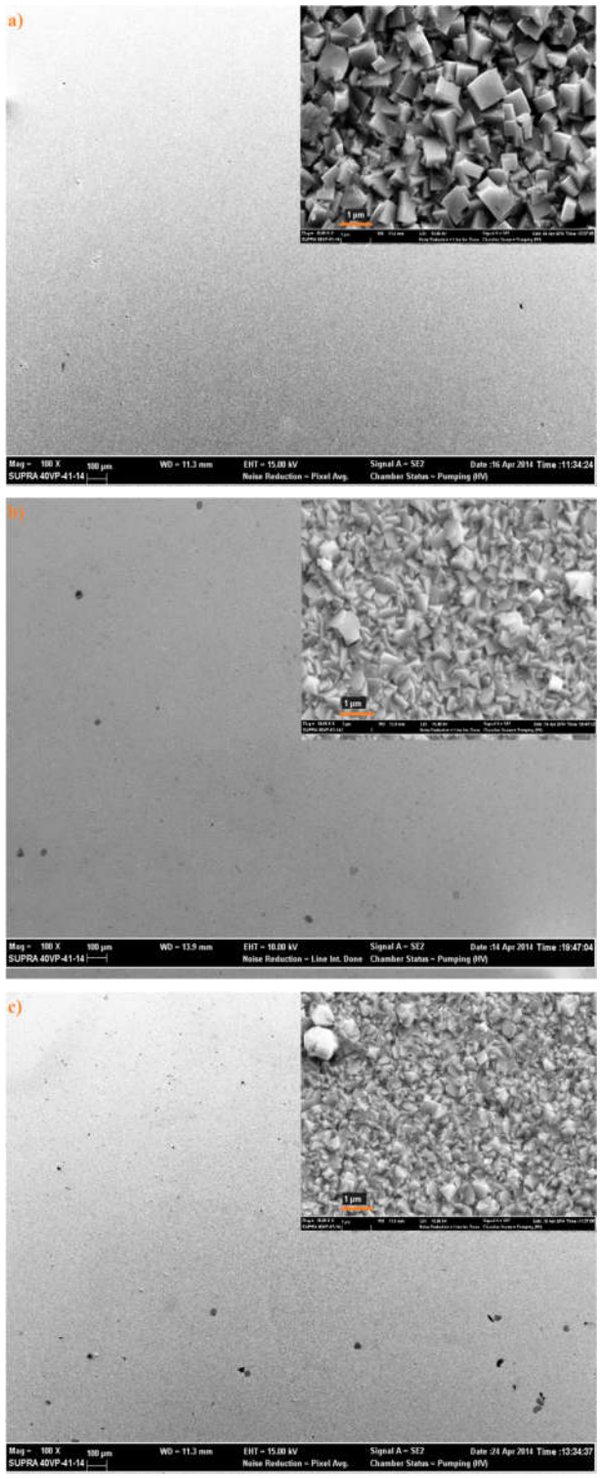

Figure 2.3. 100 times and 30000 times magnified SEM images of PbS thin films obtained from **a)**D1 **b)** D2 **c)**D3

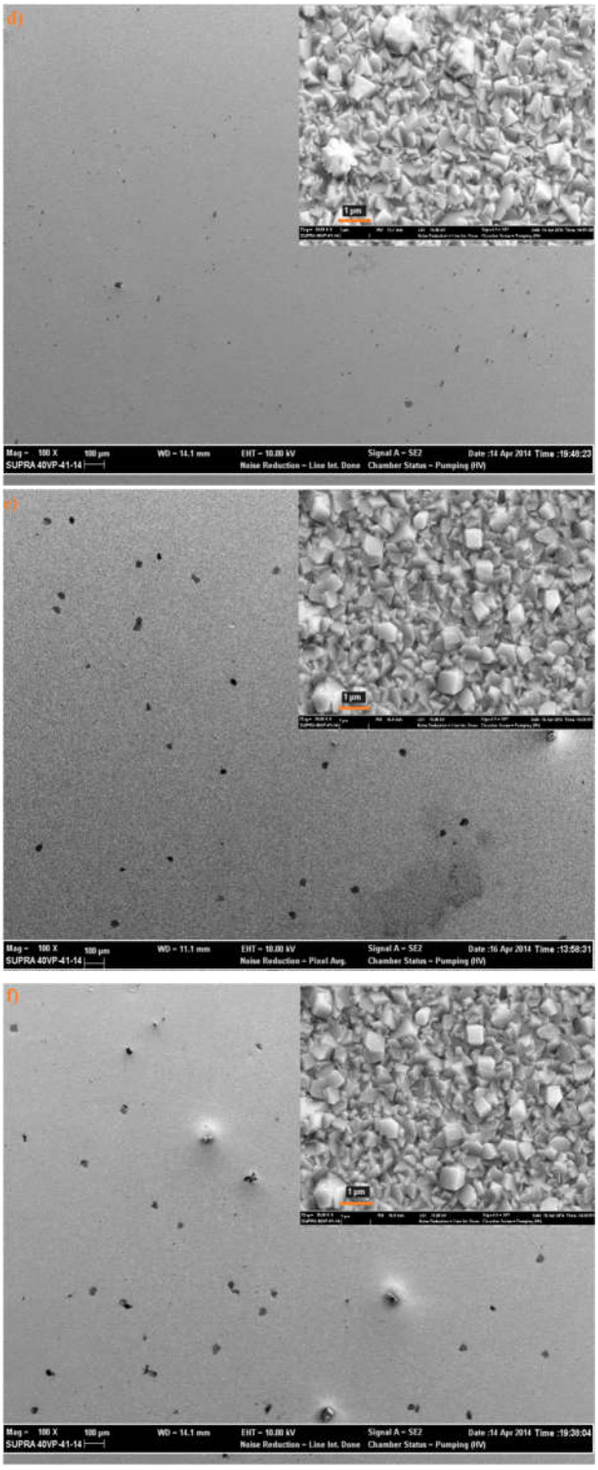

Figure 2.3. 100 times and 30000 times magnified SEM images of PbS thin films obtained from **d)**D4 **e)** D5**f)** D6

3. CONCLUSION

In this study, PbS thin films were produced on glass substrates by chemical bath deposition technique. $Pb(NO_3)_2$ and $CS(NH_2)_2$ aqueous solutions were used to produce the films. The amount of $CS(NH_2)_2$ and the amount of $Pb(NO_3)_2$ were kept constant. The structural properties of all the PbS films were determined by XRD analysis.

According to XRD results, it is understood that all films formed in cubic PbS structure. It has been found that the PbS thin films have three texture coefficient values larger than 1 belonging to different planes. However, it is understood that the film produced in D6 has a preferential orientation of (002) plane. In addition to that, this film has higher peak intensities compared to other films. It is thought that the preferred orientation for other films is random.

The dislocation densities, the microstrain, and mean stress values were also estimated from the XRD analyses. According to findings, it is found that the dislocation density of the film obtained in D1 is greater than that of the other films. The SEM analyses suggest that not only the number but also the size of pinholes formed on the film surfaces increase with increasing deposition temperature.

This study showed that when bath temperature was kept at 25°C, the XRD peak intensity was measured high although film thickness of this film was measured low. Furthermore, there are no voids, cracs and pinhole on the surface of this film.

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