The Effect of Substrate Temperature on The Structure and Morphologies of PbS Thin Films Deposited by Ultrasonic Spray Pyrolysis

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Abstract

In this work, we aimed to deposit PbS thin films at relatively low temperature and therefore thin films were deposited onto preheated glass substrates at 473 K and 523 K by ultrasonically spraying of equimolar aqueous solution of lead acetate and thiourea. The thickness of deposited thin films was determined by spectroscopic ellipsometry (SE) prior to investigate physical properties of deposited PbS films. In order to investigate structural and morphological properties of PbS thin films, x-ray diffraction (XRD) patterns and Atomic Force Microscopy (AFM) images were obtained. Crystal structure, mean crystallite size, lattice parameters, micro-strain of deposited thin films were evaluated by means of XRD patterns and it was seen that deposited PbS thin films were successfully obtained in polycrystalline form with cubic crystal structure. Also lattice parameter of a was calculated as 5.866 Å and 5.870 Å for thin films deposited at 473 K and 523 K, respectively. Additionally, the surface roughness of PbS thin films was determined via AFM images as 5.8 nm and 9.9 nm in non-contact mode. The obtained results confirm that deposition of PbS thin films can be successfully achieved at relatively low temperature.

Keywords: Ultrasonic Spray Pyrolysis, PbS Thin Films, Structural Properties, Morphological Properties

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1. Introduction

Because of their adjustable physical properties, semiconductor materials attract great interest in scientific and technological applications. One of the most attractive semiconducting material is lead sulfide (PbS) which is a member of IV-VI metal chalcogenides. PbS has quite small direct band gap (0.41 eV at 300 K) in bulk form [1]. However, for the nanosized form, optical absorption edge shifts from infrared to visible region due to strong quantum confinement effect because of its larger Bohr radius (~18 nm) [2]. In general, undoped PbS have p-type electrical conductivity [3]. Considering all these mentioned unique properties, PbS have wide range of application fields including infrared detectors [4], gas sensors [5] diode lasers [6] thin film solar cells [7] etc.

PbS thin films can be deposited by adopting various techniques such as DC sputtering [8], RF sputtering [9], vacuum evaporation [10] chemical bath deposition (CBD) [3], spray pyrolysis [11] etc. In this work, spray pyrolysis equipped with ultrasonic nozzle was used to deposit thin film due to its simplicity and practicality. This technique is based on spraying aqueous solutions of chemical salts prepared at certain concentrations and volumes onto pre-heated substrates at certain flow rates and durations in accordance with the thin films desired to be deposited. Thin film deposition process with spray pyrolysis technique consists of three basic steps in order of atomization of solution, transport of atomized droplets and decomposition [12, 13]. Physical properties of thin films deposited by using this technique tightly depends on precursor compositions and solution molarity, used solvent and chemical salts, distance between nozzle and substrate, solution flow rate, substrate temperature, spray duration, type and pressure of carrier gas [14].

2. Methods

2.1. Preparation of Precursor Solution

For the deposition of PbS thin films, 100 ml of precursor aqueous solutions which contain 0.05 M lead acetate [$Pb(CH_3CO_2)_2.3H_2O$] and 0.05 M thiourea [CH_4N_2S] were prepared using deionize water (DI) as solvent. All precursor solution was not subject to any further aging process and freshly prepared before each deposition.

2.2. Deposition of PbS Thin Films

Prior to deposition, cleaning of glass substrates realized as given in [15] Ultrasonic spray pyrolysis technique was used to deposit PbS thin films. Details about deposition technique was given in [16]. In present study, a total of 100 ml precursor solution was sprayed onto the glass substrates for 20 min with a flow rate of 5 ml/min. For the atomization of solution, ultrasonic atomizer nozzle that works at 100 kHz frequency was used. The distance between the nozzle and the substrate was maintained at 35 cm and compressed air with a pressure of 1 atm was used as carrier gas. To investigate the effect of substrate temperature on the physical properties of PbS thin films, all the above-mentioned parameters were kept constant except the substrate temperature which was adjusted as 473 K and 523 K and controlled within ±5ºC by using an iron-constantan thermocouple.

2.1. Characterization Techniques

First of all, thickness value of PbS thin films was determined by using PHE 102 Spectroscopic Ellipsometry and found to be 551 nm and 487 nm for thin films deposited at 473 K and 523 K, respectively. The structural investigations of the films were carried out by using X-ray diffractometer (PANalytical Empyrean), having CuKα radiation (λ= 1.5405 Å). For the morphological evaluations, The AFM images were obtained by using Park System XE 70 Atomic Force Microscope.

3. Results and Discussion

3.1. Structural Studies

X-ray diffraction patterns which are used to investigated structural properties of PbS thin films were given in Figure 1. As it can be seen from Figure 1, all XRD patterns for PbS thin films deposited at 473 K and 523 K have a set of diffraction peaks which are indexed to fcc cubic structure of PbS by comparing Joint Committee on Powder Diffraction Standards (JCPDS Card No: 65-0346) data file. Existing more than one peaks on XRD patterns indicates that PbS thin films are in polycrystalline form. The peaks located at 2θ ~26.3°, 30.4°, 43.5°, 51.4°,53.8°, 62.9° are indexed as (111), (200), (220), (311), (222) and (400) crystal planes.

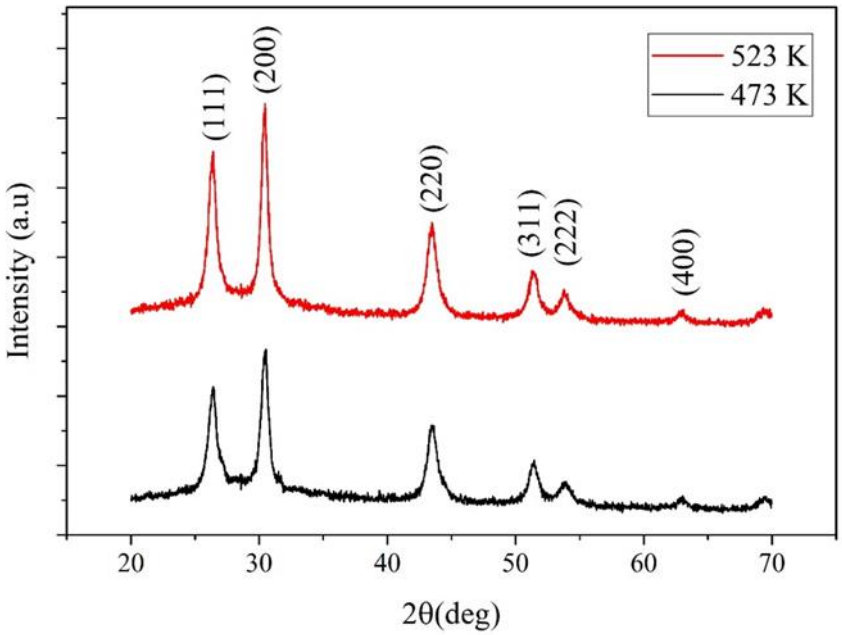

Figure 1. XRD patterns of PbS thin films deposited at 473 K and 523 K.

The position of diffraction angles, full wide half maxima (FWHM) of peaks, interplanar spacing (d) were extracted from XRD patterns and tabulated in Table 1. As it can be seen from Table 1, FWHM values belonging to three predominant peaks which exist on XRD patterns slightly decreases when substrate temperature increases from 473 K to 523 K. This may indicate the mean crystallite size of polycrystalline PbS thin films increases with the deposition temperature. The mean crystallite size of PbS thin films was calculated by applying Debye-Scherr's equation [17] on the highest diffraction peak (200) and listed in Table 1.

$$D = {}^{0.94\lambda}/_{\beta cos\theta} \quad (1)$$

where λ is the wavelength of the x-ray used, which is 0.15406 nm, θ is the Bragg angle and β is the FWHM (in radians). The mean crystallite size of the PbS thin films was found to be 12 nm and 13 nm for PbS films deposited at 473 K and 523 K, respectively. Not only instrumental broadening and crystallite size contribute broadening of diffraction peaks but also micro strain which exist through thin films makes contribution. Therefore, we may estimate micro-strain (ε) formed in thin films by using following equation for highest diffraction peak (200) [18],

$$\varepsilon = {}^{\beta cot\theta}/_{4} \quad (2)$$

Based on above equation, micro-strain values belonging to thin films were calculated as 1.12×10^{-2} and 1.04×10^{-2}.

Table 1. Thickness (t), diffraction angle (2θ), FWHM (β), interplanar spacing (d), crystallite size (D) and micro-strain (ε) values of deposited PbS thin films.

Substrate Temp. (K)	t (nm)	2θ (°)	β (°)	d (Å)	a (Å)	D (nm)		ε (×10^{-2})	
						Scherrer	W-H (nm)	Eq. (2)	W-H
473	551	26.38	0.854	3.376	5.847	10	13	1.59	0.169
		30.45	0.699	2.933	5.866	12		1.12	
		43.52	1.065	2.078	5.877	8		1.16	
523	487	26.35	0.780	3.380	5.853	11	17	1.45	0.370
		30.43	0.646	2.935	5.870	13		1.04	
		43.48	0.995	2.080	5.882	9		1.09	

Williamson-Hall (W-H) method is another approach to find out more realistic crystallite size and micro-strain. Total broadening in diffraction peak is the sum of broadening due to crystallite size (βC) and broadening due to strain (βS) [19, 20].

$$\beta = \beta_C + \beta_S \quad (3)$$

By assuming that the particle size and strain contributions to broadening are independent to each other and the strain is uniform in all directions, then the total broadening of diffraction peak can be expressed as

$$\beta\cos\theta = {}^{\lambda}/_{D} + 4\varepsilon\sin\theta \quad (4)$$

Therefore, by constructing plot of β cosθ vs. 4 sinθ given in Figure 2, crystallite size (D) and micro-strain (ε) can be extracted from y-intercept and the slope of the linear fit, respectively [19, 20, 21].

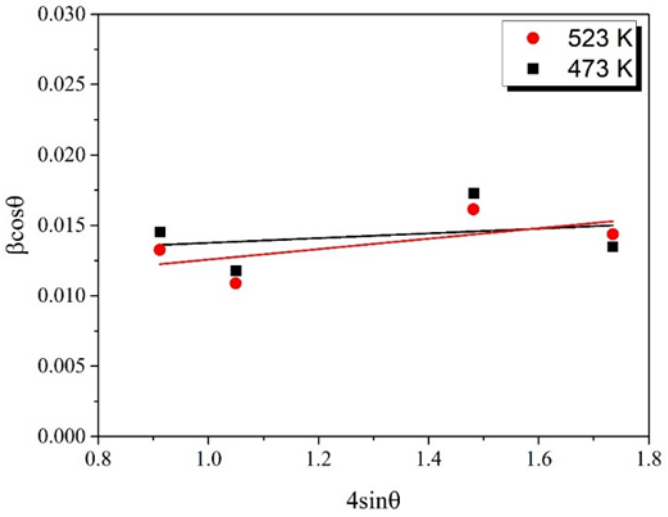

Figure 2. Williamson-Hall plots of PbS thin films deposited at 473 K and 523 K.

As it can be seen from the Table 1, the mean crystallite size values were extracted from W-H plots as 13 nm and 17 nm for PbS thin films deposited at 473 K and 523 K, respectively. However, these results are slightly different from the calculated by Debye-Scherrer equation due the difference in averaging the particle size distribution [21].

3.2. Morphological Studies

The surface morphology of deposited PbS thin films was examined by means of captured AFM images which are given in the Figure 3. The AFM images show that all the thin films were successfully deposited with the absence of voids and holes through the surface and thin films have almost homogeneous surface. They also reflect the dark and bright regions which represent hollow and hill formation were observed through the surface of all deposited films [22]. The R_{pv} values which represent the distance between highest hill and lowest hollow increased from 60 nm to 86 nm with the increase in substrate temperature. In addition to this, average roughness of thin films (Rave) increased from 6 nm to 10 nm.

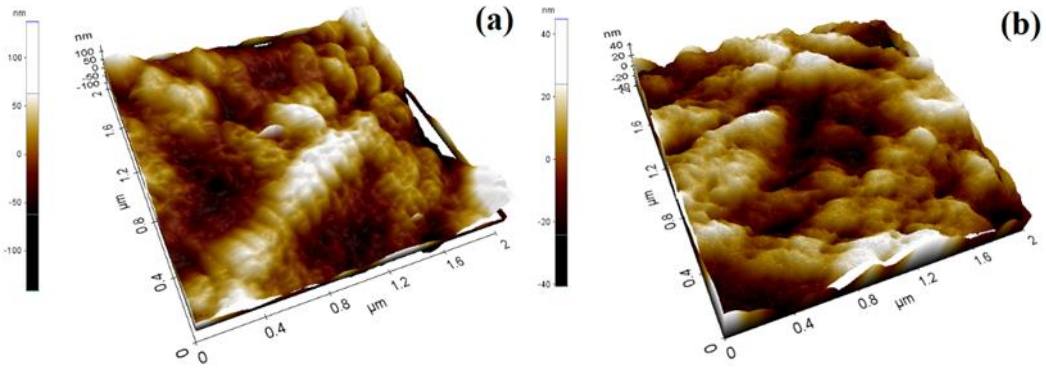

Figure 3. AFM images of PbS thin films (a) deposited at 473 K and (b) 523 K

This kind of variation indicates that the surface morphologies of deposited thin films deteriorated with the increase in substrate temperature and it may be related with the sulphur losses with the substrate temperature. This needs to be proven by the elemental analysis such as EDS or XPS.

4. Conclusion

In the present study, we successfully deposited PbS thin film at 473 K and 523 K by ultrasonic spray pyrolysis to investigate the effect of substrate on the structure and morphology of PbS. XRD patterns revealed that both two thin films deposited at 473 K and 523 K have fcc cubic structure and increase in substrate temperature led to slightly enhance in crystalline. The Debye-Scherrer and Williamson-Hall approaches were used to determine mean crystalline size of thin films and found to be between 12 nm- 17 nm. Additionally, it was seen that calculated lattice parameters are slightly less than the value (a=5.938 Å) in JCPDS card of PbS. AFM images unveil that the surface of PbS thin films were adversely effected from the increase in substrate temperature.

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