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Synthesis and Structural Properties of Nanocrystalline $(Pb_{1-x}Bi_x)S$ Thin Films

Rajesh Kumar, Prashant Kumar Sahu, R. Das and Samit Tiwari
Department of Applied Physics, Bhilai Institute of Technology, Durg-491001 (C.G.) India

Abstract

Nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films were successfully deposited on suitably cleaned glass substrate at constant room temperature, using the chemical bath deposition technique. After deposition the films were also annealed at 400^0C for 1 hour in air. The crystal structures of the films were determined by X-ray diffraction studies. The films are adherent to the substrate and well crystallized according to cubic structure with the preferential orientation (200). The crystallite size of the pure PbS thin films at optimized deposition time 30 min was found to be 40.4 nm, which increased with Bi content in pure nanocrystalline PbS thin films. The surface roughness of the films was measured by AFM studies. Experiments showed that the growth parameters, doping and annealing influenced the crystal structure of the films.

Key word: A. Thin films, B. Chemical synthesis C. Atomic force microscopy, D. X-ray diffraction

Corresponding author. Tel: +91 788 2323997; Fax: +91 788 2210163
Email address: rajeshlalwani12003@yahoo.co.in

1. Introduction

Lead sulphide (PbS) is an important semiconductor material with a narrow band gap of 0.4 eV at 300 K and a relatively large excitation Bohr radius of 18 nm [1-2]. This material has also been used in many fields such as infrared photography, diode laser, humidity and temperature sensors, and decorative and solar control coatings among other applications [3-5]. Novel materials are needed for thin film solar cells apart from the most extensively studied material CdTe and $CuInSe_2$. PbS thin films has excellent solar control characteristics [6]. Nanocrystalline PbS materials are novel materials, and their properties are different and often superior to those of conventional coarse- grained materials. The absorption edge has been found to be blue shifted as particle size reduced [7]. Also polycrystalline PbS thin films show good photoconductive properties [8]. These properties have been correlated with the synthesis method, thickness, composition and structure [9]. For these reasons, many research groups have shown a great interest in the development and study of this material by various deposition processes.

Among the several thin film deposition techniques [10-11], chemical bath deposition (CBD) [12] is the convenient and frequently used deposition technique to grow good quality thin films. On account of the various applications of these films, an attempt has been made to deposit nanocrystalline $(Pb_{1-x}Bi_x)S$ thin film using the CBD method and to investigate the structural properties of these films.

2. Experimental details

$(Pb_{1-x}Bi_x)S$ thin films were deposited on properly cleaned glass substrates by chemical bath deposition (CBD) technique. The substrates of commercial quality microscopic glass slide of dimensions 24mm x 75mm were previously degreased in nitric acid for 48 hours, and then cleaned in ultrasonic cleaner with tripled distilled water. The previously cleaned substrates were introduced vertically in a chemical bath containing an aqueous solution consisting of: 0.06M lead nitrate, 0.24M thiourea, 0.6 M Sodium hydroxide and a reducing agent 0.1M hydroxylamine hydrochloride and 2.06×10^{-4} M Bismuth Nitrate (All AR grade 99.9% pure). The solution was prepared in triple distilled water and pH value of the mixture was 12.56. All the depositions were made at constant room temperature. After deposition the films were annealed in air at 400^0C in furnace for 1hr. The film thicknesses were determined by gravimetric method.

The characterization of the films for crystal structure was done with D8 Advance X-Ray diffractometer with CuK_α irradiation (λ= 1.54060 Å) and operated at 40 kV and 100 mA and the two dimensional images of the surface samples were obtained by atomic force microscopy (AFM) with a Nano scoped E model contact mode instrument at UGC-DAE Consortium for Scientific Research, Indore.

3. Results and Discussion

3.1 XRD Studies

The X-ray diffractograms of nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films (x = 0.05, 0.10, 0.15, 0.20) and annealed $(Pb_{1x}Bi_x)S$ thin films (x = 0.10, 0.20) are shown in Fig. 1. The assignments of the different peaks were made by comparison with JCPDS cards No. PbS; 78-1901, and BiS; 83-0425. The crystallography of the films is good and characterized by five principal peaks at 2 theta values of approximately 26, 30, 43, 51 and 53 degree

corresponding to $(111)_c$, $(200)_c$, $(220)_c$,$(311)_c$, and $(222)_c$ orientations. The peaks of BiS confirms the formation of mixed base. The intensity pattern of these films is very much similar to each other, but the peak intensities are decreased for higher Bi doping concentration. After annealing, the increament in the peak intensities is also observed. The narrow peaks show that the material has good crystallinity preferentially oriented along the (200) direction which is the maximum intensity in all compositions.

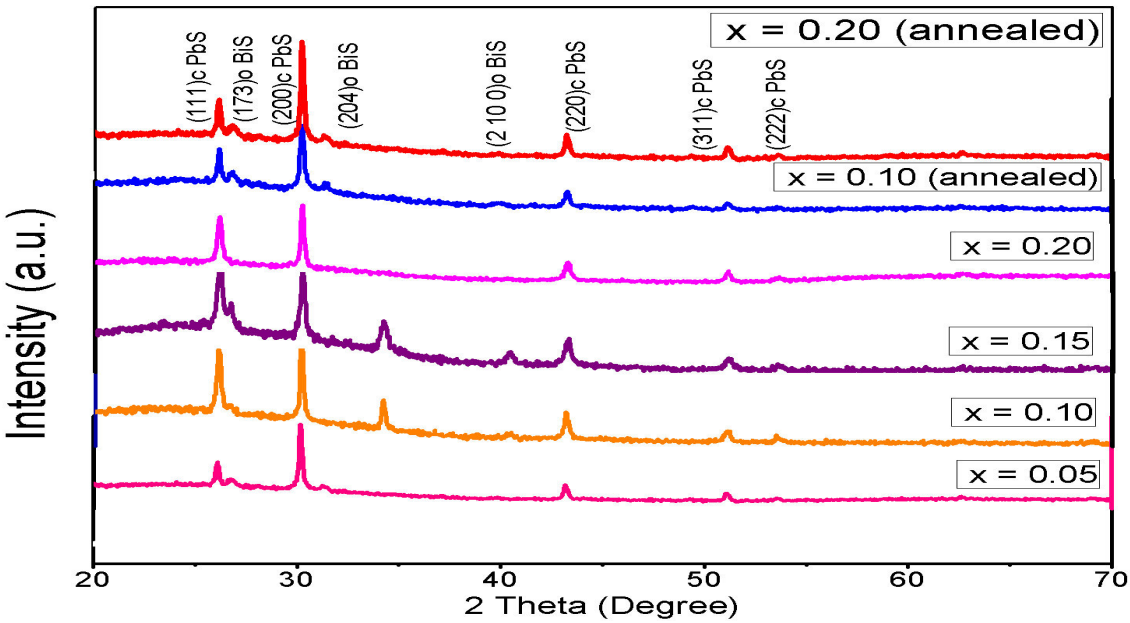

Fig. 1: X-ray diffraction spectra of different nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films deposited at room temperature for 30 min.

Table 1 displays the values of interplanar spacing and lattice constant of different nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films. The values of interplanar spacing d and lattice constant a were calculated by reported formulas [13]. These values are in good agreement with the standard values given for the cubic phase (galena). The lattice constant value is very much similar to the bulk PbS, indicating that the films grow on the glass substrate without stresses at the interface.

The maximum intensity peak is $(200)_c$ plane of PbS in all these films but the intensity and the FWHM of this peak vary with incorporation of doping concentration of Bi. The crystallite size of the films was estimated for the preferential peak $(200)_c$ by Scherrer's formula [14] and are shown in Table 2. The crystallite size of nanocrystalline PbS thin film was found 40.4 nm [15], which increases with increasing Bi doping concentration in nanocrystalline PbS thin films. After annealing at 400^0C, the crystallite size of the films is found to be further decreased. The change in crystallite size and boundary with Bi composition must be due to built-in strain and dislocations which depend on preparation process.

The strain (ε) developed in the thin films can be calculated from the relation [16]. The strain values of as-deposited and annealed films are given in Table 2. It is observed that, the strain of as-deposited films decreases with increasing doping concentration of Bi. This type of change in the strain may be due to the predominant recrystallization process in the films and due to the movement of interstitial Pb and Bi atoms from inside the crystallites to its crystallite boundary which dissipate and lead to a reduction in the concentration of lattice imperfections.

Dislocation density can be calculated by Williamson and Smallman's relation [17]. The calculated values of the dislocation density for different $(Pb_{1-x}Bi_x)S$ thin films are represented in Table 2. It is found that, dislocation density decreases with increasing doping concentration of Bi in pure PbS thin films. The decrease in dislocation density suggests that films become more crystalline.

Table 1
XRD data of nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films deposited at room temperature

x	hkl	Interplanar Spacing d (Å)		Lattice Constant a (Å)	
		Observed	Reported	Observed	Reported
0.05	$(200)_c$	2.9602	2.9681	5.9203	5.9362
0.10	$(200)_c$	2.9651	2.9681	5.9303	5.9362
0.15	$(200)_c$	2.967	2.9681	5.9339	5.9362
0.20	$(200)_c$	2.9623	2.9681	5.9245	5.9362
0.10 (Annealed)	$(200)_c$	2.968	2.9681	5.936	5.9362
0.20 (Annealed)	$(220)_c$	2.0981	2.0988	5.9344	5.9362

Table 2
Values of FWHM β, Crystallite size (D), Strain (ε), Dislocation density (δ) for different nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films

x	FWHM (β) (radian)	Crystallite Size (D) (nm)	Strain (ε) ($lin^{-2}m^{-4}$)	Dislocation Density (δ) x 10^{14}(lin/m^2)
0.05	0.003243	43.2	0.003008	5.35
0.10	0.003186	44.6	0.002944	5.03
0.15	0.003107	45.1	0.002889	4.91
0.20	0.003005	46.6	0.002788	4.60
0.10(Annealed)	0.003967	35.6	0.003725	7.89
0.20(Annealed)	0.003946	32.3	0.003686	9.58

3.2 AFM Studies

Fig. 2 represents the 2D and 3D images of nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films 0.20. The AFM images show that the small spherical grains are distributed to cover the surface of the substrate completely. The morphology of the thin films shows a very smooth surface. The grain sizes of thin films are measured from the two dimensional images. The grain size of nanocrystalline $(Pb_{1-x}Bi_x)S$ thin film is measured to be 55.1 nm for x = 0.20 respectively. The increase in the grain size in the AFM study matches well with the results obtained from XRD. The surface roughness profile was drawn by using the reported software [18]. The surface roughness is found to be 12.16 nm for x = 0.20. The increase of roughness suggests that the Bi content reduces the crystallinity of the films.

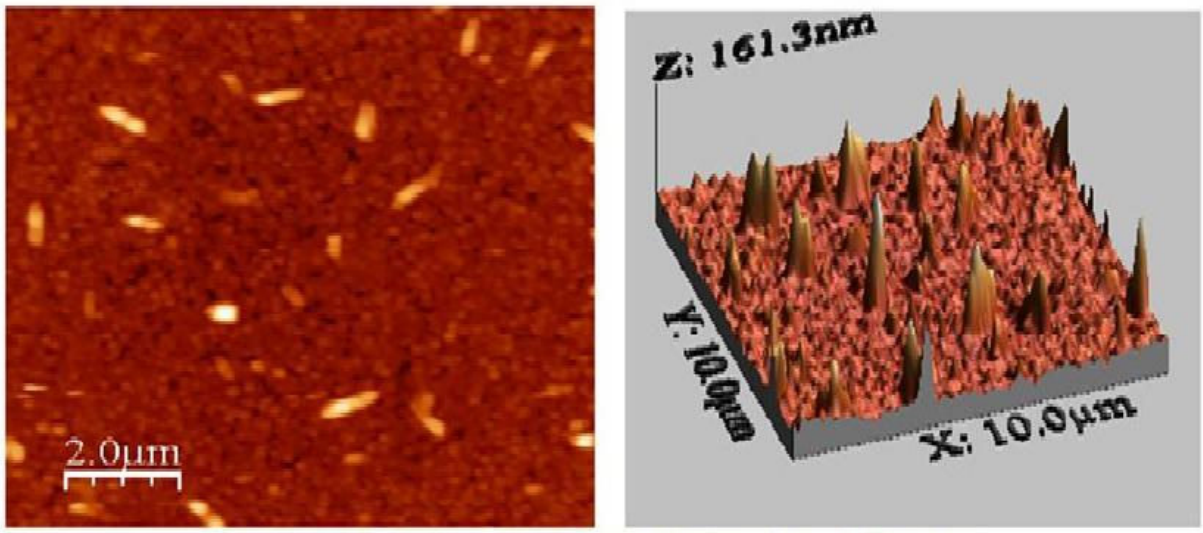

Fig. 2: 2D and 3D AFM images of nanocrystalline $(Pb_{1-x}Bi_x)S$ thin film with x = 0.20

4. Conclusions

In this study, nanocrystalline $(Pb_{1-x}Bi_x)S$ thin films were deposited by chemical bath deposition technique. The experimental characterization indicates that Bi doping and annealing play an important role in the structural properties of the films. The XRD results show that, the films are well crystalline and face centered cubic structure. The interplanar spacing, lattice constant, cystallite size, strain and dislocation density were found to change significantly with doping and annealing. The crystallite size of nanocrystalline PbS was calculated 40.4 nm, which increased with Bi concentration. Also FWHM, strain value and dislocation density decreased with increasing Bi concentration. The AFM studies suggest that rms roughness of the films increases with increasing doping. There is a good agreement between grain size calculated from AFM and crystallite size from XRD studies.

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