Experimental Demonstration of the Structure of Silar Synthesised Iron Lead Sulphide (PbS) Thin Films for Poultry Farms in Agbaja Unuhu-Ebonyi State-Nigeria

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DOI: <http://doi.org/10.38177/ajast.2021.5114>

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Article Received: 27 December 2020

Article Accepted: 14 March 2021

Article Published: 31 March 2021

ABSTRACT

The effect of iron-doping on lead sulphide (PbS) thin films deposited on glass substrates via successive ionic layer adsorption (SILAR) Technique using lead Nitrate, $Pb(NO_3)_2$, thiourea, Iron (II) Chloride dehydrate ($FeCl_2 \cdot 2H_2O$), ethanol and ammonia by in alkaline medium annealed between 283K and 500K was investigated. The X-ray diffraction (XRD) Analysis and Scanning electron microscopy (SEM) were done to determine the structure and morphology respectively for use in poultry farms in Akpabuyo-Cross River State. The XRD showed PbS thin films being cubic and face-centred crystalline nanoparticles.

Keywords: Experimental study, Iron-doping, Lead sulphide, Structural and morphological studies.

1.0 Introduction

Energy crisis in the world has given rise to the thin film growth research as a way to cushion problems associated with it. The continuous increase in population and industrialisation in almost every country in the world, has been very responsible for the ever growing or increasing energy demand. In Nigeria, less than 40% of the country is connected to the national electric grid and less than 60% of the energy demand by this group is generated and distributed (1-4). The advantage of energy is facilitation of the provision of those things which are necessary for the welfare of human existence: health, heat, food, light, clothing, shelter and transport, etc. Energy availability improves the standard of living (5-14). Solar energy, an energy obtained from the sun, is the world's most abundant and cheapest source of energy available from Nature (15). It is free and automatically renewable every day. In the world over, emphasis has shifted from the use of hydro and fossil-powered electricity generation to renewable energy such as solar source through nanotechnology involving growing of thin films from the abundant transition metals, resulting in getting ones with excellent properties that will be useful in solving the problem of energy crisis (16-19). In the present study, lead sulphide and copper sulphide are studied to ascertain the structural and morphological properties when doped with iron. These new assumed properties will help determine their best areas of applicability. Lead sulphide (PbS) is groups IV-VI compounds of semiconducting materials (20-24) that have drawn attention of many researchers because of its properties that have been applied widely in optoelectronic devices, photoconductors, sensors, infra-red detector devices solar cells, solar control and solar absorber coatings (25). The present study describes successive ionic layer adsorption and reaction method for the synthesis and deposition of PbS, $(PbS)_x(Fe)_{1-x}$, ternary thin films and the influence of iron added to the halide thin films structurally and morphologically. Variety of materials such as insulators, semiconductors, metals and temperature sensitive materials like polyester can be used as a substrate since the deposition is carried out at or near to room temperature. As it is a low temperature process, it avoids oxidation and corrosion of the substrate. In spite of this SILAR having a number of advantages as compared to other methods; it does not require vacuum at any stage,

doping of any element can be achieved easily, film thickness can be easily controlled by adjusting the number of deposition cycles, operating at room temperature, no restrictions on substrate material, dimensions or its surface profile etc. The prime requisite for obtaining good quality thin film is the optimization of various preparative parameters viz. concentration of precursors, nature of complexing agent, pH of the precursor solutions and adsorption, reaction and rinsing time durations etc., (27).

2.0 Experimental Procedure

The layer-by-layer growth of the material is achieved by dipping the substrate alternately into separately placed cationic and anionic precursors. After every cationic and anionic immersion the substrate is rinsed in deionised water to remove the un-adsorbed ions from the surface. The synthesis and deposition of PbS involved four steps while that of PbSFe thin films involved six steps. After pre-treatment of the substrates, the syntheses were done using .05M lead nitrate and thiourea solution. Ammonia was used to control the pH. It was done between pH between 8.5 and 11.5. The iron ions were got from iron (II) chloride dehydrate.

For a SILAR growth of PbS thin film, only four steps are involved, namely:

- ✕ The glass substrate was first immersed in lead nitrate solution for 35 seconds, where lead ions were adsorbed on the surface of the substrate.
- ✕ The second step involves the rinsing of the substrate for 35 seconds in deionised water to remove loose and unadsorbed lead ions from the surface.
- ✕ The substrate was then immersed in thiourea solution for 35seconds, where the sulphur ions react with the pre-adsorbed lead ions on the substrate surface to form lead sulphide layer.
- ✕ Finally, the substrate was rinsed again with deionised water to remove unadsorbed and loose material from the substrate surface.

A SILAR growth cycle for $PbS_x Fe_{(1-x)}$ thin films has six steps, namely:

- ✕ The glass substrate was first immersed in lead nitrate solution for 35 seconds, where lead ions were adsorbed on the surface of the substrate.
- ✕ The second step involves the rinsing of the substrate for 35 seconds in deionised water to remove loose and unadsorbed lead ions from the surface.
- ✕ The substrate was then immersed in thiourea solution for 35seconds, where the sulphur ions react with the pre-adsorbed lead ions on the substrate surface to form lead sulphide layer.
- ✕ Finally, the substrate was rinsed again with deionised water to remove unadsorbed and loose material from the substrate surface.
- ✕ The substrate was immersed in iron(II) Chloride dehydrate solution to adsorb iron ions on the pre-adsorbed lead sulphide layer.
- ✕ The unadsorbed iron ions were removed from the substrate by rinsing in deionised water for 35seconds.

After repeating for sufficient number of cycles (90 cycles), $\text{PbS}_x \text{Fe}_{(1-x)}$ composite thin films were deposited. The number of deposition cycles for PbS and Fe were adjusted to obtain various compositions of $\text{PbS}_x \text{Fe}_{(1-x)}$ thin films (see table 1 below):

Table 1. Deposition scheme for the growth of $\text{PbS}_x \text{Fe}_{(1-x)}$ thin films

S. No.		Preparative Parameter	Cationic precursors	Anionic precursor
		$\text{Pb}(\text{NO}_3)_2$	$\text{FeCl}_{2.2}\text{H}_2\text{O}$	$\text{C}_2 \text{H}_5 \text{NS}$
1.	Concentration (M)	0.05	0.05	0.05
2.	pH	11.5	8.5	11.5
3.	Immersion time (seconds)	35	35	35
4.	Rinsing time (seconds)	35	35	35

Table 2. $\text{PbS}_x \text{Fe}_{(1-x)}$ thin films composition

S. No.	Films	Composition parameter (x)	Number of SILAR cycles		Thickness (nm)
			PbS	Fe	
1.	PbS	1.00	90	00	397
2.	$\text{PbS}_{0.80}\text{Fe}_{0.20}$	0.80	80	10	393
3.	$\text{PbS}_{0.50}\text{Fe}_{0.50}$	0.50	70	20	283
4.	$\text{PbS}_{0.2}\text{Fe}_{0.8}$	0.20	60	30	299
5.	$\text{PbS}_{.10}\text{Fe}_{0.9}$	0.10	45	45	230

3.0 Results and Discussions

The thickness of the composite $(\text{PbS})_x(\text{Fe})_{(1-x)}$ thin film was calculated using transmittance values. The Allah *et al.* equation (2007) used as given:

$$\frac{\gamma_1 \gamma_2}{2[\gamma_1 n_1 - \gamma_2 n_2]} \quad (1)$$

Where, γ_1 and γ_2 are the corresponding wavelengths and n_1 and n_2 are the refractive indices. The inter planar distance, d , is obtained using the Bragg's equation, namely:

$$d = \frac{n\gamma}{2 \sin \theta} \quad (2)$$

Where, γ is the wavelength of the X-rays and θ is the Bragg's angle. The site for the research work was the crystal growth laboratory, Physics and Astronomy Department, University of Nigeria, Nsukka, Nigeria. The structural

properties of the $(\text{PbS})_x(\text{Fe})_{(1-x)}$ composite thin films were studied by X-ray diffractometer with $\text{CuK}\alpha$ radiation of wavelength 0.154 nm. The surface morphological investigations were performed using scanning electron microscopy analysis and energy dispersive spectrometry (EDS) analysis at the Department of Industrial Chemistry, The Technical University, Ibadan Nigeria.

3.1 Structural Characterisation

The structural characterizations of $(\text{PbS})_x(\text{Fe})_{(1-x)}$ thin films were carried out using X-ray diffraction (XRD) technique. The peaks of XRD patterns have been assigned from the x-ray diffraction files ref. numbers: INEL/EZEMA/18-162115 and INEL/EZEMA/18-171343 respectively. Using the PbSFe as case study, detailed analyses are given in Tables1 and 2 above. The crystallite size of the deposited material was calculated by using Debye- Scherer's formula (equation 3):

$$D = K\lambda / B\cos \theta \quad (3)$$

Where, D is the average crystallite size, k is the particle shape factor that varies with the method of taking the breadth and shape of crystallites , λ is the X-ray wavelength used (0.1542 nm), β is the angular line width of half-maximum intensity (FWHM) of diffraction peak, θ is the Bragg's angle in degrees.

Figure 1. XRD of $(\text{PbS})_x(\text{Fe})_{(1-x)}$ composite thin films: (A) PbS, (B) $(\text{PbS})_{0.80}(\text{Fe})_{0.20}$, (C) $(\text{PbS})_{0.5}(\text{Fe})_{0.5}$, (D) $(\text{PbS})_{0.20}(\text{Fe})_{0.80}$ and (E) $(\text{PbS})_{0.10}(\text{Fe})_{0.90}$

Table 3. Thickness, grain size, strain and dislocation density of $(\text{PbS})_x(\text{Fe})_{(1-x)}$ thin films

	Film composition	Thickness (nm)	Grain Size (nm)	Dislocation density ($\delta \times 10^{10}$ lines/cm ²)	Strain ($\epsilon \times 10^{-4}$)
A	PbS	375	34	10.91	10.17
B	$(\text{PbS})_{0.80}(\text{Fe})_{0.20}$	301	26	14.26	14.30
C	$(\text{PbS})_{0.5}(\text{Fe})_{0.5}$	290	25	15.99	14.77
D	$(\text{PbS})_{0.20}(\text{Fe})_{0.80}$	285	18	16.87	14.90
E	$(\text{PbS})_{0.10}(\text{Fe})_{0.90}$	280	16	32.47	21.03

Figure 2. SEM images of $(\text{PbS})_x(\text{Fe})_{(1-x)}$ composite thin films: (A) $\text{PbS}_{0.20}(\text{Fe})_{0.80}$, at 10 μm (HFW=125 μm) (G) $(\text{PbS})_{0.8}(\text{Fe})_{0.2}$ at 10 μm (HFW=124 μm)

3.2. Energy Dispersive Spectrometry (EDS) Analysis

This is show in Figure 3.

Figure 3. EDS of $(\text{PbS})_x(\text{Fe})_{(1-x)}$ composite thin films

Lead sulphide thin film has ten diffraction peaks (111)(200 (220) (311) (222)(400) (331)(420)(422)(511), which corresponds to 2θ angles ranging from 10.098-85.846. The XRD of doped PbS annealed at about 650K has been included. These had thirteen and seven peaks ranging from angles 2θ ranging from 10.429-85.9645 and 18.012-80.012 respectively. The cubic lattice is distinct in pure PbS thin films. The PbSFe thin films annealed at temperature less than 500K were crystals that were cubic and face-centred. However, at $x = 0.5$ i.e. for $(\text{PbS})_{0.5}(\text{Fe})_{0.5}$, strong orientations disappear showing the non-formation of crystals due to the sp-d orientation. The crystallite sizes of the deposited materials were calculated using Debye-Scherrer's formula.

Thickness for PbS , $(\text{PbS})_{0.8}(\text{Fe})_{0.2}$, $(\text{PbS})_{0.5}(\text{Fe})_{0.5}$, $(\text{PbS})_{0.2}(\text{Fe})_{0.8}$, $(\text{PbS})_{0.1}(\text{Fe})_{0.9}$ were 375nm, 301nm, 290nm, 285nm and 280nm while their grain sizes were 34, 26, 25, 18,16.

From literature, the lead Sulphide thin films have been reported as having thermal stability as observed in this study. The samples (doped and undoped) were annealed between temperatures of 293K and 493K and from the XRD, the intensity ratio some diffractions changed but no additional peaks were observed up to 475K; this showed that the PbS nanofilm was not oxidized. The change in the diffraction reflection intensities was attributed to the fact that the phase transition to cubic structure takes place in the PbS film at 375K (26). The presence of oxygen atoms

as shown by the EDS studies showed that the proportion of iron to lead sulphide and iron to copper sulphide were not in equal proportion and also oxidation must have taken place because of their large surface area (26). The optical studies carried out showed that it had high absorbance and low transmittance. These properties were advantageous in a poultry farm at Agbaja Unuhu, Abakaliki in Ebonyi state, Nigeria to warm chicken as the walls and roof of the place were glazed with the material. Based on this finding, the lead sulphide thin films (doped and undoped) can be used in devices as fire alarm sensors, flame sensors and heat source detection systems.

4.0 Conclusions

A simple, cheap and convenient SILAR method was employed to deposit good quality $(\text{PbS})_x(\text{Fe})_{1-x}$ composite thin films. The deposited films were uniform and adherent to the substrate. Their structural and morphological properties of those composite thin films were studied. The EDS Studies showed that in $(\text{PbS})_x(\text{Fe})_{1-x}$ composite thin films, the compositional ratio of iron was 21.8 wt%. The XRD and morphological studies revealed that $\text{PbS}_x(\text{Fe})_{(1-x)}$ thin films were nanocrystalline in nature depending on film composition. The average crystallite size was found to vary for the PbSFe thin films from 34 to 16 depending on film composition. The variation in thickness, strain and dislocation densities was also composition dependent. Similar observation has been reported by Wang et al., (2009) and Udejah (2020) (21-29). The samples annealed at different temperatures (383K-500K) never showed any prominent peaks structurally and morphologically as confirmed by studies done by He *et al.*, (2008). From literature, considerable changes can be seen for temperatures up to 700⁰K (30). These properties can be well used in solar energy conversion devices and media room sterilisation.

Acknowledgment

The authors are grateful to Nanoscience Research Group, University of Nigeria, Nsukka.

Declarations

Source of Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing Interests Statement

The authors declare no competing financial, professional and personal interests.

Consent to participate

Not Applicable

Consent for publication

We declare that we consented for the publication of this research work.

Availability of data and material

Authors are willing to share data and material according to the relevant needs.

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