Structure of iron- doped lead sulphide (PbS) thin films made by SILAR technique for media room applications

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The effect of iron-doping on lead sulphide (PbS) thin films deposited on glass substrates via successive ionic layer adsorption (SILAR) Technique using lead acetate, $Pb(CH_3COO)_2$, thioacetamide (S_2H_5NS), Iron (II) Chloride dehydrate $(FeCl_2 . 2H_2O)$, ethanol and ammonia in alkaline medium annealed between 283K and 500K was investigated. The structural and morphological studies were performed by X-ray diffraction (XRD) Analysis and scanning electron microscopy (SEM) respectively. The XRD showed that PbS thin films were cubic and face-centred crystalline.

1. 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 industrialization 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 (16-17). 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(18) 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 (19).

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.(20)

2. 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 and CuSFe thin films involved six steps. After pre-treatment of the substrates, the synthesis were done using .05M lead acetate and thioacetamide solution. Ammonia was used to control the pH. It was done between pH of 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 acetate solution for 35seconds, 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 thioacetamide 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 acetate 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 thioacetamide 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), $PbS_x Fe_{(1-x)}$ composite thin films were deposited. The number of deposition cycles for PbS and Fe were adjusted to obtain various compositions of $PbS_x Fe_{(1-x)}$ thin films(see table 1)

Table 1. Deposition scheme for the growth of $PbS_x Fe_{(1-x)}$ thin films(Udeajah,2021, Udeajah and Onah,2021)).

Preparative Parameter	Cationic precursors $Pb(CH_3COO)_2$	$FeCl_2.2H_2O$	Anionic precursor $S_2 H_5 NS$
Concentration(M)	0.05	0.05	0.05
pH	11.5	8.5	11.5
Immersion time (seconds)	35	35	35
Rinsing time (seconds)	35	35	35

Table 2.PbS $_x$ Fe $_{(1-x)}$ thin films composition.(Udeajah,2020)

Films	Composition parameter(x)	Number of SILAR PbS	Cycles Fe	Thickness (nm)
PbS	1.00	90	00	397
$PbS_{0.80}Fe_{0.20}$	0.80	80	10	393
$PbS_{0.50}Fe_{0.50}$	0.50	70	20	299
$PbS_{0.2}Fe_{08}$	0.20	60	30	283
$PbS_{.10}Fe_{0.9}$	0.10	45	45	230

3. Results and discussion

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

$$\frac{\gamma 1 \gamma 2}{2[\gamma 1 n1 - \gamma 2 n2]} \tag{1}$$

where $\gamma 1$ and γ2 are the corresponding wavelengths and n1 and n2 are the refractive indices. The inter planar distance, d, is obtained using the Bragg's equation, namely:

$$d = \frac{n\gamma}{2\sin\theta} \tag{2}$$

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

3.1. Structural characterization

The structural characterizations of $(PbS)_x(Fe)_{(1-x)}$ and $(CuS)_x(Fe)_{(1-x)}$ thin films were carried out using X-ray diffraction (XRD) technique. The peaks of XRD patterns have been assignedfrom 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 below. The crystallite size of the deposited material was calculated by using Debye- Scherer's formula (equation 3)

$$D = K\lambda / B\cos\theta, \tag{3}$$

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 the diffraction peak, and θ is the Bragg's angle in degrees.
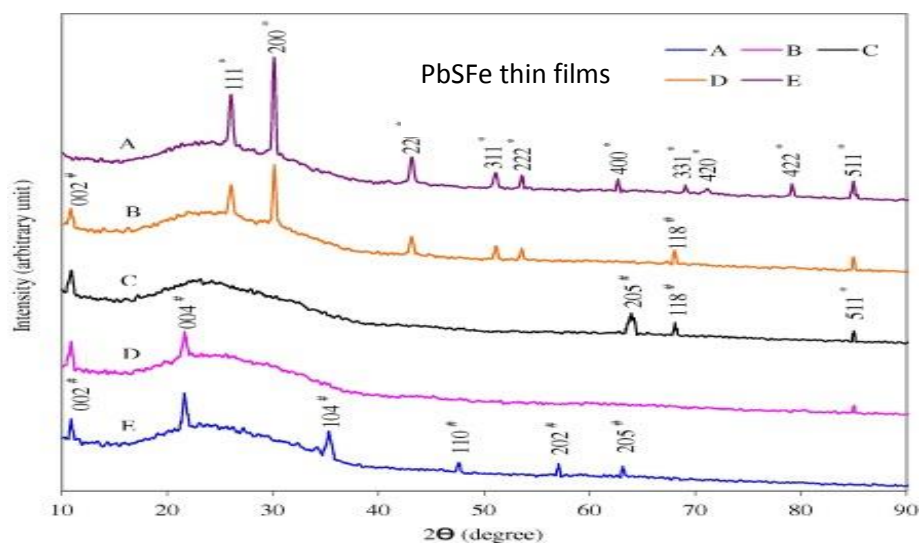
Fig.1. XRD of $(PbS)_x(Fe)_{(1-x)}$ composite thin films: (A) PbS, (B) $(PbS)_{0.80}(Fe)_{0.20}$, (C) $(PbS)_{0.5}(Fe)_{0.5}$, (D) $(PbS)_{0.20}(Fe)_{0.80}$ and (E) $(PbS)_{0.10}(Fe)_{0.90}$. (Udeajah and Onah,2021)

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

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

3.2 Morphological characterisation using Scanning electron microscopy(SEM)

The SEM images below showed the morphology of the deposited thin films. The thin films readily covered the glass substrate. No agglomerations were visibly seen in the SILAR Deposited thin films, ; Possibly the doping of lead sulphide and iron was in the correct molar ratio of 1:4   and vice versa (Fig.2).
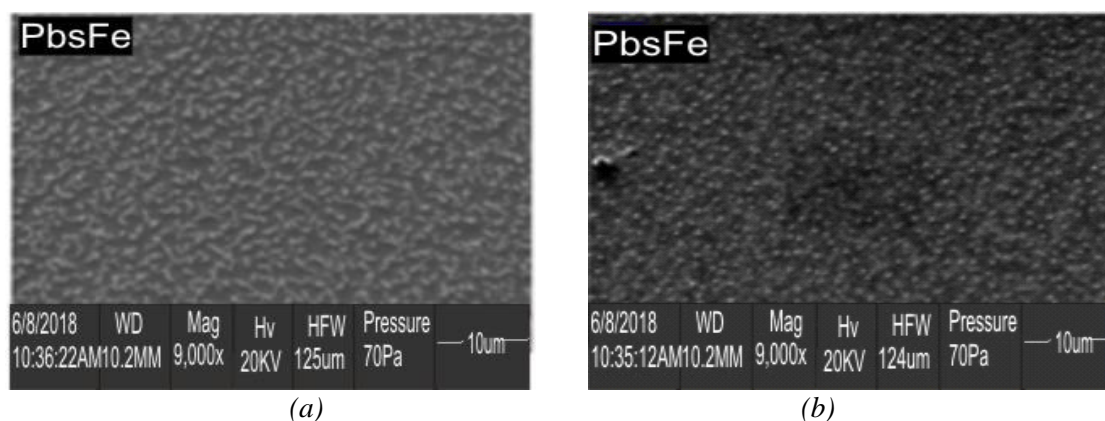

(a)   *(b)*

Fig.2. SEM images of $(PbS)_x(Fe)_{(1-x)}$ composite thin films: (A) $PbS)_{0.20}(Fe)_{0.80}$, at 10 μm(HFW=125 μm) (b) $(PbS)_{0.8}(Fe)_{0.2}$, at 10 μm(HFW=124 μm).(Udeajah, 2021)

3.2.2. Energy Dispersive Spectrometry (EDS) Analysis

The elemental composition of the doped thin films were done using the energy dispersive spectrometry(EDS) shown in Fig.3. Lead(Pb) was 25.6w%, Sulphur(S) was 18.2wt%, iron was 21.8wt%, oxygen (O) was 15.4wt%. This showed that there was oxidation process in the course of the SILAR Deposition of PbSFe thin films unlike in the deposition of PbS thin films.
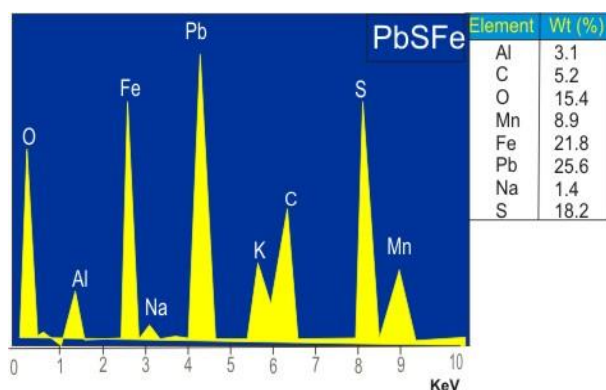

Fig.3. EDS of $(PbS)_x(Fe)_{(1-x)}$ composite thin films.{Udeajah,2021}

Structurally, Lead sulphide thin film has ten diffraction peaks (111)(200 (220) (311) (222)(400) (331)(420)(422)(511), which corresponds to 2θ angles ranging from10.098-85.846. The XRD of doped PbS annealed at about 650K has been included. The cubic lattice are 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 $(PbS)_{0.5}(Fe)_{0.5,}$ strong orientations disappeared showing the non-formation of crystals due to the sp-d orientation. The crystallite sizes of the deposited materials were calculated using Debye-Scherer's formula.

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

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 of293K 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 385K (21). The presence of oxygen atoms as shown by the EDS studies showed that the proportion of iron to lead sulphide and iron were not in equal proportion and also oxidation must have taken place because of their large surface area(22).

Based on this finding, the lead sulphide(PbS) thin films (undoped) and Lead Sulphide iron (PbSFe) thin films were polycrystalline as they had sharp peaks but if their peaks were broad, they could have been considered nanofilms. while lead Sulphide iron thin films were polycrystalline ..

4. Conclusions

A simple, cheap and convenient SILAR method was be employed to deposit good quality(PbS)$_x$ (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 (PbS)$_x$ (Fe)$_{1-x}$ composite thin films, the compositional ratio of iron was 21.8wt%. The XRD and morphological studies revealed that PbS$_x$(Fe)$_{(1-x)}$ thin films were polycrystalline 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 were also composition dependent. Similar observation has been reported by Wang et al (2009), Udeajah (2020) and Udeajah and Onah(2021) .(23-29). 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 to700 ^{0}K(30-31). These properties can be well used in solar energy conversion devices and media room sterilisation.

Acknowledgments

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