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MORPHOLOGICAL AND STRUCTURAL PROPERTIES OF IRON COPPER SULPHIDE (CuS) AND IRON LEAD SULPHIDE (PbS) THIN FILMS SYNTHESISED BY SILAR METHOD

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Abstract

The influence of iron on lead sulphide(PbS) and Copper Sulphide (CuS) thin films deposited on glass substrates via successive ionic layer adsorption (SILAR) Technique using lead nitrate, Cupric chloride dehydrate, thiourea, Iron (II) Chloride dehydrate(Fe Cl $_2$. 2H $_2$ O), ethanol and ammonia in alkaline medium annealed between 300K 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 films of cubic crystalline PbS thin films, cubic and face-centred crystalline PbSFe thin films, cubic CuS thin film, hexagonal Cu $_2$ S thin films and cubic and hexagonal crystalline natured CuSFe thin films with the preferential (111),(002)(004) (311) orientations.

Keywords: structural properties; iron copper sulphide and iron lead sulphide thin films; SILAR

1. INTRODUCTION

It is the energy crisis in the world that gave 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]. 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 [2] Solar energy, an energy obtained from the sun, is the world's most abundant and cheapest source of energy available from Nature [3]. 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 [4]. 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) and Copper Sulphide (Cu $_2$ S) are groups IV-VI and I-VI compounds of semiconducting materials respectively [5] 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[6 - 8] .

The present study describes successive ionic layer adsorption and reaction method for the synthesis and deposition of PbS, $(PbS)_x(Fe)_{1-x}$, CuS and (CuS)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.[9]

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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 and CuS 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 between 8.5 and 11.5. The iron ions were got from iron(II) chloride dehydrate. The copper ions were got from cupric acetate. It was equally deposited in alkaline environment too.

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 35seconds , where lead ions were adsorbed on the surface of the substrate.

(i) 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.

(ii) 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,

(iii) Finally, the substrate was rinsed again with deionised water to remove unadsorbed and loose material from the substrate surface.

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

(v) The glass substrate was first immersed in lead nitrate solution for 35 seconds , where lead ions were adsorbed on the surface of the substrate.

(vi) 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.

(vii) 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,

(viii) Finally, the substrate was rinsed again with deionised water to remove unadsorbed and loose material from the substrate surface,

(ix) The substrate was immersed in iron(II) Chloride dehydrate solution to adsorb iron ions on the pre-adsorbed lead sulphide layer,

(x) 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 below)

Table 1: Deposition scheme for the growth of $PbS_x Fe_{(1-x)}$ thin films

Preparative Parameter	Cationic precursors		Anionic precursor
	Lead nitrate	$FeCl_2.2H_2O$	$SC(NH_2)_2$
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

Films	Composition parameter(x)	Number of SILAR cycles PbS	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	283
$PbS_{0.2}Fe_{08}$	0.20	60	30	299
$PbS_{.10}Fe_{0.9}$	0.10	45	45	230

The thickness of the composite $(PbS)_x(Fe)_{(1-x)}$ thin film was measured by weight difference method. The density of PbS was taken as 4.9g/cm ^{3} and iron as 5.2g/cm ^{3}.

The densities of the composite $(PbS)_x(Fe)_{(1-x)}$ thin films were estimated by considering compositional parameter 'x'. The weights of the deposited films were determined by using an electronic microbalance. In the present investigation thickness of $(PbS)_x(Fe)_{(1-x)}$ films measured using sensitive microbalance is listed in table 2 above. Thickness,t(nm), of the thin films were calculated using the equation:

$$t = \frac{\lambda 1 \lambda 2}{2[\lambda 1 n 2 - \lambda 2 n 1]} \quad (1)$$

where n1 and n2 are the refactive indices while λ_1, λ_2The 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 were performed using scanning electron microscopy analysis and energy dispersive spectrometry (EDS) analysis at the Department of Industrial Chemistry, The Technical University, Ibadan Nigeria.

B. Copper Sulphide and Copper Sulphide Iron thin films.

The substrates were pre-treated as in the case above. For the SILAR deposition of $(CuS)_{(1-x)}$ thin films, 0.05 M cupric chloride dihydrate solutions were taken as cationic precursor and 0.05 M thiourea as anionic precursor. The pH of the anionic and cationic precursors was adjusted to 12 and 8 by ammonia addition. Substrate was immersed in the cupric acetate solution for 35 s to adsorb Cu^{2+} ions. (a) The un-adsorbed Cu^{2+} ions were removed from the substrate by rinsing it in deionised water for 35 s. (b) The substrate was then again immersed in thioacetamide solution for 35 s, where S^{2-} ions reacted with Cu^{2+} to form a layer of CuS. After repeating a sufficient number of cycles. It was removed and dried in an oven to avoid dust and oxidation. . For the SILAR deposition of $(CuS)_{(1-x)}$ Fe (1-x) thin films, the pre-treated glass substrates were immersed into 0.05 M cupric chloride solutions taken as cationic precursor, then rinsed in deionised water for 35 seconds before immersing into 0.05 M thiourea , taken as anionic precursor for 35 seconds before rinsing in deionised water. This was repeated for several cycles before the substrate was immersed in iron(II) nitrate dehydrate solution to adsorb iron ions on the pre-adsorbed copper sulphide layer.

The unadsorbed iron ions were removed from the substrate by rinsing in deionised water for 35seconds. It is worthy to note that the substrate was again immersed in thioactetamide solution where S^{2-} ions react with Cu^{2+} to form a layer of CuS. After repeating a sufficient number of cycles, $(Fe)_{1-x}(CuS)_{(x)}$ composite thin films were deposited. The number of deposition cycles for CuS and Fe was adjusted to obtain various compositions of $(Fe)_{1-x}(CuS)_x$.

Table 3: Deposition scheme for the growth of $CuS_x Fe_{(1-x)}$ thin films

Preparative Parameter	**Cationic precursors**		**Anionic precursor**
	$CuCL_2.2H_2O$	**$Fe(III)NO_2.2H_2O$**	**$SC(NH_2)_2$**
Concentration(M)	0.05	0.05	0.05
pH	12	9	12
Immersion time (seconds)	35	35	35
Rinsing time (seconds)	35	35	35

3. Results and discussion:

3.1 Structural Characterisation:

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 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 below. The crystallite size of the deposited material was calculated using Debye- Scherer's formula (equation 2)

$$D = K\lambda / B\cos\theta, \quad (2)$$

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. The Bragg's law is the principle on which the X-ray diffraction analysis operates. The law is given as:

$$n\lambda = 2\, d \sin\theta \quad (3)$$

where n is the constant($0.7 < n < 0.9$) , λ is the X-ray wavelength used (0.1542 nm), and θ is the Bragg's angle in degrees. See tables 4 and 5 below.

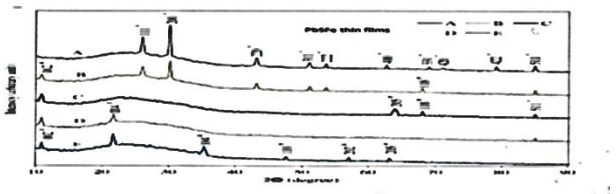

Figure 1. XRD of $(PbS)_x(Fe)_{(1-x)}$ composite thin films: (A) PbS, (B) $(PbS)_{0.80}(Fe)_{0.20}$, (C) $(PbS)_{0.5}(Fe)_{0.5}$, (D) $(PbS)_{0.20}(Fe)_{0.80}$ and (E) $(PbS)_{0.10}(Fe)_{0.90}$.

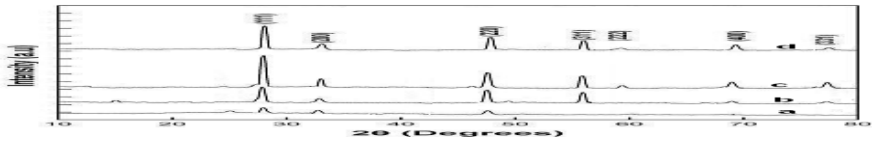

Figure 2 :XRD of $(CuS)_x(Fe)_{(1-x)}$ composite thin films: (a) $(CuS)_{0.50}(Fe)_{0.50}$ (b) $(CuS)_{0.20}(Fe)_{0.80,}$ (c) $(CuS)_{0.1}(Fe)_{0.9,}$ (D) CuS

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Table 4. Comparison of observed XRD data of thin films with the JCPDS card (PbS: 18–162115**).**

Film	Observed values		Standard value		*h k l*	Phase
	2θ (°)	*d* (A^0)	2θ (°)	*d* (A^0)		
PbS	10.098	3.42223	10.032	3.43	1 1 1	PbS
	30.1183	2.96726	30.148	2.962	2 0 0	
	43.1379	2.09710	43.17	2.093	2 2 0	
	51.109	1.78723	51.099	1.785	3 1 1	
	53.5155	1.71234	53.574	1.71	2 2 2	
	62.6934	1.48195	62.683	1.49	4 0 0	
	69.178	1.35805	69.056	1.359	3 3 1	
	71.0566	1.32667	71.117	1.325	4 2 0	
	79.0952	1.21078	79.146	1.208	4 2 2	
	84.8416	1.14192	85.0156	1.16	5 1 1	
$PbS_{0.80\ Fe\ 0.20}$	11.924	8.1365	1.866	8.135	0 0 2	Fe
	25.9988	3.45341	26.034	3.424	1 1 1	PbS
	30.0278	2.9776	30.148	2.960	2 0 0	PbS
	43.1276	2.08929	43.165	2.093	2 2 0	PbS
	51.093	1.7814	51.097	1.786	3 1 1	PbS
	53.418	1.7125	53.575	1.714	2 2 2	PbS
	67.973	1.3788	68.042	1.3769	1 1 8	Fe
	85.846	1.1483	95.017	1.1423	5 1 1	Fe
$PbS_{0.5}Fe_{0.5}$	10.9072	8.16616	10.866	8.136	0 0 2	Fe
	64.0563	1.45376	63.944	1.453	2 0 5	Fe
	68.1835	1.3755	68.042	1.376	1 1 8	Fe
	85.1396	1.1457	85.015	1.146	5 1 1	$PbS_{0.10}Fe_{0.90}$
$PbS_{0.20}Fe_{0.80}$	10.836	8.1534	10.866	8.135	0 0 2	$PbS_{0.10}Fe_{0.90}$
	21.6314	3.99874	21.617	4.0676	0 0 4	$PbS_{0.10}Fe_{0.90}$
	85.846	1.14897	85.015	1.146	5 1 1	PbS
$PbS_{0.10}Fe_{0.90}$	11.092	8.19824	10.866	8.136	0 0 2	$PbS_{0.10}Fe_{0.90}$
	21.7535	4.08553	21.617	4.067	0 0 4	
	35.2242	2.53723	35.233	2.543	1 0 4	
	47.5747	1.91135	47.636	1.912	1 1 0	
	57.0542	1.61385	57.005	1.6142	2 0 2	
	53.3501	1.46695	53.112	1.4719	2 0 5	

Table 5. Thickness, grain size, strain and dislocation density of $(PbS)_x$ ($Fe)_{(1-x)}$ thin films.

Fi	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 Studies

The morphological characterisation of CuS, CuSFe, PbS and PbSFe thin films were done using the scanning electron microscopy analysis(SEM) and Energy Dispersive spectrometry analysis .

3.2.1 Scanning electron microscopy(SEM) analysis

The SEM Micrographs of the doped and undoped PbS and CuS thin films are show in Figures 3 and 4 below:

(A) (B)

Figure 3. SEM images of $(PbS)_x(Fe)_{(1-x)}$ composite thin films: (A) $PbS)_{0.20}$($Fe)_{0.80}$, at 10 µm(HFW=125 µm) (G) $(PbS)_{0.8}(Fe)_{0.2}$. at 10 µm(HFW=124 µm)

SEM of doped CuS thin film SILAR (deposited at 90cycles) is shown below in Figure 6 below.

Figure 4. SEM Micrograph of CuSFe (A) micrograph at 15µm (B) micrograph at 20µm

3.2.2 Energy Dispersive Spectrometry (EDS) Analysis : These are show in Figures 7 and 8 below.

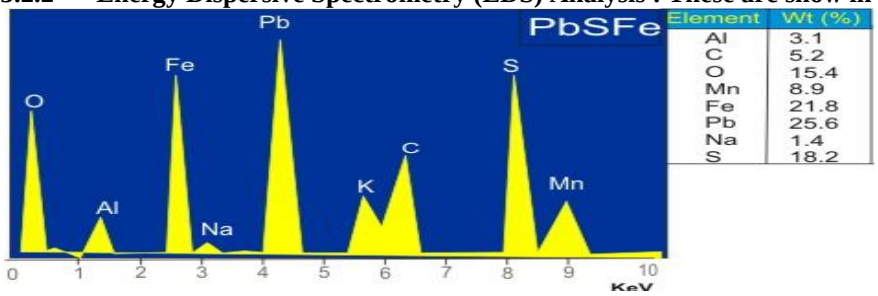

Figure 5. EDS of $(PbS)_x(Fe)_{(1-x)}$ composite thin films:

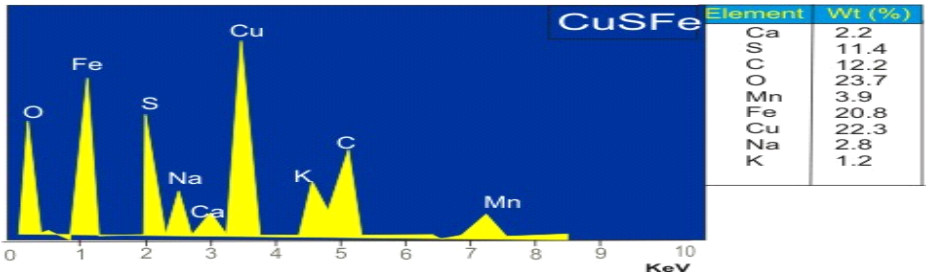

Figure 6. EDS of $(CuS)_x(Fe)_{(1-x)}$ composite thin films:

The X-ray diffraction patterns of CuSFe and $(PbS)_x(Fe)_{1-x}$ composite films were shown in Fig.1 and 2 above. 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.

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 and CuS 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 (0 0 2) and (0 0 4) orientations due to hexagonal lattice are prominent in CuSFe and (1 1 1) and (2 0 0) orientations due to cubic lattice are distinct in pure PbS and CuS thin films[10-14]. The PbSFe thin films annealed at temperature less than 500K were crystals that was cubic and face-centred. However, at $x = 0.5$ i.e. for $(PbS)_{0.5}(Fe)_{0.5,}$ and $(CuS)_{0.5}(Fe)_{0.5}$ 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-Scherer's formula[15-23].

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 [24]. Their dislocation density(∂) calculated were 10.91,14.26, 15.99, 16.87 and 32.47 respectively. The strain were calculated as 10.77, 14.30,14.77,14.90 and 21.03 respectively while thickness for CuS, $(CuS)_{0.8}(Fe)_{0.2}$, $(CuS)_{0.5}(Fe)_{0.5,}$ $(CuS)_{0.2}(Fe)_{0.8,}$ $(CuS)_{0.1}(Fe)_{0.9}$,. were 386, 300, 298,287,273 while their grain sizes were 35, 33, 30, 27, 17. The variation in the strain and dislocation density may influence the 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 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[24].

The presence of oxygen atoms as shown by the EDS studies showed that the proportion ofiron 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[25].

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 Conclusion

A simple, cheap and convenient SILAR method was be employed to deposit good quality CuSFe and $(PbS)_x (Fe)_{1-x}$ 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 composition of iron was 21.8wt% while in $(CuS)_x (Fe)_{1-x}$ composite thin films, iron composition was 20.8wt%.. The XRD and morphological studies revealed that CuSFe and $PbS_x(Fe)_{(1-x)}$ thin films were nanocrystalline in nature depending on film composition. The average crystallite size was found to vary for the CuSFe thin films between 35 and 17 nm and for PbSFe thin films 34 and16 depending on film composition. The variation in thickness, strain and dislocation densities were also composition dependent. Similar observation has been reported by [25]. The samples annealed at different temperatures (383K-500K) never showed any prominent peaks structurally and morphologically as confirmed by studies done by [25]. From literature, considerable changes can be seen for temperatures up to 700 ^{0}K [25]. These properties can be well used in solar energy conversion devices and optoelectronics.

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